06 Chemical kinetics

Syllabus

6.1 Introduction

Q.1 Can you recall?

i. What is the influence of particle size of reacting solid on rate of a chemical reaction?

Ans : Smaller particle size results in an increase in the rate of reaction because the surface area of the reactant has been increased.

ii. Why is finely divided nickel used in hydrogenation of oil?

Ans: A high catalytic activity, coupled with the fact that hydrogen is absorbed within the pores of the catalyst during activation, makes Raney nickel a useful catalyst for many hydrogenation reactions.

iii. What is effect of change of temperature on the rate of a chemical reaction?

Ans: In increase in temperature causes a rise in the energy levels of the molecules involved in the reaction, so the rate of the reaction increases. Similarly, the rate of reaction will decrease with a decrease in temperature.

Q.2 Define chemical kinetics.

Ans: Chemical kinetics is a branch of chemistry which deals with the rate of chemical reactions and the factors those affect them.

Q.3 Give the applications of chemical kinetics?

Ans:

i. It help us to predict how rapidly the reaction approaches equilibrium.

ii. Also helps us to know the rates of reactions for different reasons.

iii. It gives information on the mechanism of chemical reactions.

6.2 Rate of reactions

Q.4 Write a short note on rate of a reaction.

Ans: The rate reaction describes how rapidly the reactants are consumed or the products are formed.

Q.5 What is Average rate of a reaction and how it is calculated?

Ans:

i. The average rate of reaction can be described by knowing change in concentration of reactant or product divided by time interval over which the change occurs.

Thus,

$$\text{Average rate} = \frac{\text{change in concentration of a species}}{\text{change in time}}$$

$$= \frac{\Delta c}{\Delta t}$$

Consider the reaction $A \rightarrow B$ in which A is consumed and B is produced.

$$\text{average rate of consumption of A} = -\frac{\Delta[A]}{\Delta t}$$

$$\text{average rate of formation of B} = +\frac{\Delta[B]}{\Delta t}$$

Therefore, average rate of reaction $= -\frac{\Delta[A]}{\Delta t}$

$= +\frac{\Delta[B]}{\Delta t}$

ii. The rate of reaction represents a decrease in concentration of the reactant per unit time or increase in concentration of product per unit time.

iii. The dimensions of rate are concentration divided by time, that is, mol $dm^{-3}sec^{-1}$.

★Q.6 How is instantaneous rate of a reaction determined?

Ans:

i. To determine the instantaneous rate of a reaction the progress of a reaction is followed by measuring the concentrations of reactant or product for different time intervals.

ii. The changes in concentration are relatively fast in the beginning which later become slow.

iii. The concentration of a reactant or a product plotted against time.

iv. A tangent drawn to the curve at time t_1 gives the rate of the reaction.

v. The slope thus obtained gives the instantaneous rate of the reaction at time t_1.

vi. The instantaneous dc/dt, is represented by replacing Δ by derivative dc/dt in the expression of average rate.

vii. In chemical kinetics we are concerned with instantaneous rates.

For the reaction, $A \rightarrow B$

Rate of consumption of A at any time

$t = \frac{d[A]}{dt}$

Rate of formation of B at any time $t = \frac{d[B]}{\Delta t}$

Rate of reaction at time $t = \frac{d[A]}{dt} = \frac{d[A]}{dt}$

Q.7 Determine the rate of a reaction in terms of change in concentration of each constituent for a reaction. $A + 3B \rightarrow 2C$

Ans:

i. $A + 3B \rightarrow 2C$

When one mole of A is consumed three moles of B are consumed and two moles of C are formed.

ii. The stoichiometric coefficients of the three species are different.

iii Thus the rate of consumption of A.

iv Likewise the rate of formation of C is twice the rate of consumption of A.

v $-\frac{d[B]}{dt} = -3\frac{d[A]}{dt}$ and $\frac{d[C]}{dt} = -2\frac{d[A]}{dt}$

With this

$$-\frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt}$$

or rate of reaction

$$= \frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt} = \frac{1}{2}\frac{d[C]}{dt}$$

In general, For

$aA + bB \rightarrow cC + dD,$

$$\text{rate} = -\frac{1}{2}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt}$$

$$= \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

+Q.8 Write the expression for $2N_2O(g) \rightarrow 4NO_2(g) + O_2(g)$?

Ans: Rate of a reaction

$$= \frac{-1}{2}\frac{d[N_2O]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

+Q.9 For the reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ in liquid bromine, N_2O disappears at a rate of 0.02 moles dm^{-3} sec^{-1}. At what rate NO_2 and O_2 are formed? What would be the rate of reaction?

Ans:

Given : $\frac{d[N_2O_5]}{dt} = 0.02$

$$\frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

Rate of reaction

$$= -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{2} - \frac{d[N_2O_5]}{dt}$$

Rate of formation of $O_2 = \frac{d[O_2]}{dt}$

$$= \frac{1}{2} \times 0.02$$

$$= \frac{1}{2} - \frac{d[N_2O_5]}{dt} = \frac{1}{2} \times 0.02 \text{ moles dm}^{-3}\text{ sec}^{-1}$$

= 0.01 moles dm^{-3} sec^{-1}

Rate of formation of $NO_2 = \frac{d[NO_5]}{dt}$

$$= \frac{4}{2} - \frac{d[N_2O_5]}{dt}$$

=2 × moles dm^3 sec^{-1}
0.04 moles dm^3 sec^{-1}

Q.10 For the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$. What is the relationship among

$$\frac{d[N_2]}{dt}, \frac{d[H_2]}{dt} \text{ and } \frac{d[NH_3]}{dt} \text{ ?}$$

Ans: The relationship among

$$\frac{d[N_2]}{dt}, \frac{d[H_2]}{dt} \text{ and } \frac{d[NH_3]}{dt}$$

is $-\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

+11. Try this
For the reaction,

$$3I^-_{(aq)} + S_2O_8^{2-}{}_{(aq)} \rightarrow I^-_{3(aq)} + 2SO_4^{2-}{}_{(aq)}$$

Calculate the rate of formation of I_3^- the rates of consumption of I^- and $S_2O_8^{2-}$ and the overall rate of reaction if the rate of formation of SO_4^{2-} is 0.022 moles dm^{-3} sec^{-1}.

Ans : Given Rate of formation of $SO_4^{2-} = 0.022$ moles dm^{-3} sec^{-1}
To find

i. Rate of formation of I_3^-

ii. Rate of formation of $S_2O_8^{2-}$

iii. Overall rate of a reaction
Calculation : for the reaction

$$3I^-_{(aq)} + S_2O_8^{-2}{}_{(aq)} \rightarrow I^-_{3(aq)} + 2SO_4^{2-}{}_{(aq)}$$

Overall rate of a reaction

$$\frac{-1}{3}\frac{d[I^-]}{dt} = \frac{d[S_2O_8^{2-}]}{dt} = \frac{d[I_3^-]}{dt} = \frac{1}{2}\frac{d[SO_4^{2-}]}{dt}$$

Rate of formation of $I_3^- = \frac{d[I_3^-]}{dt}$

Rate of consumption of $I^- = \frac{d[I]}{dt}$

Rate of consumption of $S_2O_8^{2-} = \frac{d[S_2O_8^{2-}]}{dt}$

Rate of consumption of

$$I^- = \frac{d[I^-]}{dt} = \frac{3}{2}\frac{d[SO_2^-]}{dt}$$

$$= \frac{3}{2} \times 0.022 \text{ mole dm}^{-3}\text{s}^{-1}$$

= 0. 033 mole dm^{-3} s^{-1}

Rate of consumption of $S_2O_8^{2-} = \frac{d[S_2O_8^{2-}]}{dt}$

$$= \frac{1}{2} \times \frac{d[SO_2^{2-}]}{dt} = \frac{1}{2} \times 0.022$$

= 0. 011 mole dm^{-3} s^{-1}

Rate of formation of $I_3^- = \frac{d[I_3^-]}{dt} = \frac{1}{2}\frac{d[SO_4^{2-}]}{dt}$

$$= \frac{1}{2} \times 0.022$$

= 0. 011 mole dm^{-3} s^{-1}

∴ Overall rate of a reaction $= \frac{1}{2}\frac{d[SO_4^{2-}]}{dt}$

6.3 Rate of reaction and reactant concentration

Q.13 What is rate law?

Ans : The rate of a reaction at a given temperature for a given time instant depends on the concentration of reactant this relation between the rate and concentration relation is known as rate law.

Q.14 Explain rate law with the help of a reaction.

Ans : Consider the general reaction,

$$aA + bB \longrightarrow cC + dD \qquad ......(i)$$

The rate of reaction at a given time is proportional to its molar concentration at that time raised to simple powers.

Rate of reaction $\alpha[A]^x\ [B]^y$

rate = $k\ [A]^x[B]^y$ ......(ii)

where k the proportionality constant is called the rate constant, which is independent of concentration and varies with temperature.

For unit concentrations of A and B, k is equal to the rate of reaction.

Equation (ii) is called differential rate law.

Note :

The powers x and y of the concentration terms A and B in the rate law not necessarily equal to stoichiometric coefficients (a and b) appearing in Eq. (i).

Thus x and y may be simple whole numbers, zero or fraction. Realize that x and y are experimentally determined.

The rate law in Eq. (ii) is determined experimentally and expresses the rate of a chemical reaction in terms of molar concentrations of the reactants and not predicted from the stoichiometry of the reactants.

Q.15 How the concentration change affects rate of the reaction.

Ans : Consider the general reaction

$$aA + bB \longrightarrow cC + dD$$

$\therefore$ Rate of reaction $\alpha[A]^x\ [B]^y$

rate = $k\ [A]^x[B]^y$

For x = y = 1, rate = k[A][B] gives

The equation implies that the rate of a reaction depends linearly on concentrations of A and B. If either of concentration of A or B is doubled, the rate would be doubled.

For x = 2 and y = 1. The rate = k[A][B] leads to rate = $k[A]^2[B]$. If concentration of A is doubled keeping that of B constant, the rate of reaction will increase by a factor of 4.

If x = 0, the rate is independent of concentration of A.

If x < 0 the rate decreases as [A] increases.

Q.16 Write the rate law, for the below reaction if the rate of reaction is proportional to concentration of the reactant.

i. $2H_2O_{2\,(g)} \longrightarrow 2H_2O_{(l)} + O_{2(g)}$

Ans: $2H_2O_{2\,(g)} \longrightarrow 2H_2O_{(l)} + O_{2(g)}$

If the rate of the reaction is proportional to concentration of H_2O_2. The rate law is given by

rate = $k[H_2O_2]$

★ Q.17 For the reaction

i. $CH_3Br_{(aq)} + OH^-_{(aq)} \longrightarrow CH_3OH^-_{(aq)} + Br^-_{(aq)}$

rate = k $[CH_3Br][OH^-]$

i. How does reaction rate change if $[OH^-]$ is decreased by a factor of 5?

ii. What is change in rate of it concentration of both reactants are doubled?

Ans: For me reaction

$$CH_3Br_{(aq)} + OH^-_{(aq)} \longrightarrow CH_3OH^-_{(aq)} + Br^-_{(aq)}$$

Rate = $k[CH_3Br][OH^-]$

i. If $[OH^-]$ is increased by the factor of 5, the rate of me reaction will increase by a factor at 5 $[CH_3Br]$ is kept constant.

ii. If $[CH_3Br]$ and $[OH^-]$ is doubled , rate of the reaction will increase by a factor of 4.

Try this

+Q.18. For the reaction,

$NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)}$ the rate of reaction is experimentally found to be proportional to the square of the concentration of NO_2 and independent that of CO. Write the rate law.

Ans : The rate of the reaction will be expressed as

Rate = $k[NO_2][CO]^o$

= $k[NO_2]$

Type 1

Numerical based on Rate law

+1. Write the rate law for the reaction, $A + B \longrightarrow P$ from the following Given :

	[A] moles dm^{-3} sec^{-1} (Initial)	[B] moles dm^{-3} sec^{-1} (Initial)	Initial rate/ moles dm^{-3} sec^{-1}
i.	0.4	0.02	4.0×10^{-5}
ii.	0.6	0.2	6.0×10^{-5}
iii.	0.8	0.4	3.2×10^{-4}

Solution :

a. From above data (i) and (ii), when [A] increases by a factor 1.5 keeping [B] as constant, the rate increases by a factor 1.5. It means rate α [A] and x = 1

b. From observations (i) and (iii), it can be seen that when concentrations of A and B are doubled, the rate increases by a factor 8. Due to doubling of [A] the rate is doubled (because x = 1) that is rate increases by a factor 2.

This implies that doubling [B], the rate increases by a factor 4. or rate a $[B]^2$ and y = 2. Therefore, rate = $k[A][B]^2$

Alternatively

The rate law gives rate = $k\,[A]^x[B]^y$

a. From above observations (i) and (ii)

i. $4 \times 10^{-5} = (0.4)^x(0.2)^y$

ii. $6 \times 10^{-5} = (0.6)^x(0.2)^y$

Dividing (ii) by (i), we have

$$\frac{6\times10^{-5}}{4\times10^{-5}} = 1.5 = \frac{(0.6)^x\,\cancel{(0.2)}^y}{(0.4)^x\,\cancel{(0.2)}^y} = \left(\frac{0.6}{0.4}\right)^x$$

$= (1.5)^x$

Hence x = 1

b. From observations (i) and (iii) separately in the rate law gives

iii. $4 \times 10^{-5} = (0.4) \times (0.2)^y$ since x = 1

iv. $3.2 \times 10^{-4} = 0.8 \times (0.4)^y$

Dividing (iv) by (iii) we write

$$\frac{3.2\times10^{-4}}{4\times10^{-5}} = \frac{0.8\ (0.4)^y}{0.4\ (0.2)^y}$$

or $8 = 2\times\left(\frac{0.6}{0.2}\right)^y$ or $4 = 2^2 = 2^y$

Therefore y = 2.

The rate law is then rate = $k[A][B]^2$

★2. For the reaction $2A+B \longrightarrow$ Products find the rate law from the following data.

[A] / M	[B] / M	Rate / MS^{-1}
0.3	0.05	0.15
0.6	0.05	0.30
0.6	0.2	1.20

Solution :

From th above table

$0.15 = (0.03)^x\,(0.05)^y$ ....(i)

$0.30 = (0.6)^x\,(0.05)^y$ ....(ii)

Dividing eq (ii) by eq (i)

$0.30 = (0.6)^x\,(0.05)^y$

$0.15 = (0.3)^x\,(0.05)^y$

$(2)^1 = (2)^x\,(1)$

$\therefore$ x = 1

From the above table

$0.15 = (0.3)^x\,(0.05)^y$ ....(iii)

$1.20 = (0.6)^x\,(0.2)^y$ ....(iv)

Dividing eq (iv) by eq (v)

$1.20 = (0.6)^x\,(0.2)^y$

$0.15 = (0.3)^x\,(0.05)^y$

$$(8) = (2)^x\left(\frac{0.2}{0.05}\right)^y$$

since x = 1

$$(8) = (2)^1\left(\frac{0.2}{0.05}\right)^y$$

$$\frac{8}{2} = \left(\frac{0.2}{0.05}\right)^y$$

$$4 = \left(\frac{0.2}{0.05}\right)^y$$

$4 = (4)^y$

$\therefore$ y = 1

Ans : $\therefore$ The rate law is Rate = k [A][B]

+3. For the reaction,

$2NOBr_{(g)} \longrightarrow 2NO_{2(g)} + Br_{2(g)}$ the rate law is rate = $k[NOBr]^2$. If the rate of the reaction is 6.5×10^{-6} mol L^{-1} s^{-1} when the concentration of NOBr is 2×10^{-3} mol L^{-1}. What would be the rate constant for the reaction?

Solution :

rate = $k[NOBr]^2$ or $k = \frac{rate}{[NOBr]^2}$

$$= \frac{6.5\times10^{-6}\,mol\,L^{-1}s^{-1}}{(2\times10^{-3}\,mol\,L^{-1})^2}$$

$= 1.625$ mol^{-1} L^1 s^{-1}

+4. Use your brain power

The rate of the reaction for the reaction $2A+B \longrightarrow 2C+D$ is 6×10^{-4} mol dm^{-3} s^{-1} when [A] = [B] = 0.3 mol dm^{-3}. If the reaction is of first order in A and zeroth order in B what is the rate constant?

Solution :

Given : $2A + B \longrightarrow 2C + D$

$[A] = [B] = 0.3$ mol dm^{-3}

Rate = 6×10^{-4} mol dm^{-3} s^{-1}

order with respect to [A] = 1

order with respect to [B] = 0

To find : Rate constant

Calculation :

Rate law for the reaction

$2A + B \longrightarrow 2C + D$ is

Rate = k [A] [B]^o

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

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

$$= \frac{6 \times 10^{-4} \cancel{\text{mol}} \ \cancel{\text{dm}^{-3}} \ \text{s}^{-1}}{0.3 \cancel{\text{mol}} \ \cancel{\text{dm}^{-3}}}$$

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

Ans : The rate constant of the reaction is 2×10^{-3}s^{-1}.

+5. The rate of the reaction, $A + B \longrightarrow P$ is 3.6×10^{-2} mol dm^{-3} s^{-1} when [A] = 0.2 moles dm^{-3} and [B] = 0.1 moles dm^{-3}. Calculate the rate constant if the reaction is first order in A and second order in B

Solution :

The reaction is first order in A and second order in B. Hence, the rate law gives

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

or $k = \dfrac{\text{rate}}{[A][B]^2}$

rate = 3.6×10^{-2} mol/s, [A] = 0.2 mol dm^{-3} and [B] = 0.1 mol dm^{-3}

Substitution gives

$$k = \frac{3.6 \times 10^{-2} \text{s}^{-1}}{0.2 \text{mol dm}^{-3} \times (0.1 \text{mol dm}^{-3})^2}$$

$$= \frac{3.6 \times 10^{-2} \text{s}^{-1}}{0.2 \times 0.01 \text{mol}^2 \text{dm}^{-6} \text{sec}^{-1}}$$

= 18 mol^{-2} dm^{-6} sec^{-1}

+6. For the reaction,

$2NO_{(g)} + 2H_{2\,(g)} \longrightarrow N_{2(g)} + 2H_2O_{(g)}$ the rate law is rate = $k[NO]^2$ $[H_2]$. What is the order with respect to NO and H_2? What is the overall order of the reaction?

Solution :

In the rate law expression, the exponent of [NO] is 2 and that of $[H_2]$ is 1. Hence, reaction is second order in NO, first order in H_2 and the reaction is third order.

+7. Consider,

$A + B \longrightarrow P$ If the concentration of A is doubled with [B] being constant, the rate of the reaction doubles. If the concentration of A is tripled and that of B is doubled, the rate increases by a factor 6. What is order of the reaction with respect to each reactant ? Determine the overall order of the reaction.

Solution :

The rate law of the reaction :

rate = $k[A]^x[B]^y$ ....(i)

If [A] is doubled, the rate doubles.

Hence 2 × rate = k $[2A]^x[B]^y$

= k $2^x[A]^x[B]^y$ ....(ii)

6 × rate = k $[3A]^x[2B]^y$ ....(iii)

$$\frac{\text{(iii)}}{\text{(i)}} \text{gives} \frac{6 \times \cancel{\text{rate}}}{\cancel{\text{rate}}} = 3\frac{k[A]2^y[B]^y}{k[A][B]^y}$$

or $6 = 3 \times 2^y$ or $2 = 2^y$ and y =1

The reaction is first order in A and first order in B. The overall reaction is of the second order.

+8. Try this.......

The reaction

$CHCl_{3(g)} + Cl_{2\,(g)} \longrightarrow CCl_{4(g)} + HCl_{(g)}$ i s First order in $CHCl_3$ and 1/2 order in C_{12}. Write the rate law and overall order of the reaction.

Given - $CHCl_3$ = 1st order

$$C_{12} = \frac{1}{2} \text{order}$$

Rate = $[CHCl_3]^1[Cl_2]^{1/2}$

Problem for Practice

1. For a reaction A→B the rate of the reaction is 2×10^{-3} mol dm^{-3}s^{-1}, when the initial concentration is 0.05 mol dm^{-3} The rate of the same reaction is 1.6×10^{-2} mol dm^{-3} when the inital concentration is 0.1 mol dm^{-3}. The order of the reaction is.

Ans : The order of reaction is 3

2. For the decomposition of a compound AB at book the following data were obtained.

[AB] mol/dm^3	Rate of decomposition of AB in $mol/dm^{-3}\ s^{-1}$
0.20	2.75×10^{-8}
0.40	11.0×10^{-8}
0.60	24.75×10^{-8}

What is the order of the decomposition of AB?

Ans : The order of decomposition of AB is 2

3. Consider the decomposition of $N_2O_{5(g)}$ to form $NO_{2(g)}$ and $O_{2(g)}$. At a particular instant N_2O_5 disappears at a rate of 2.5×10^{-2} mol $dm^{-3}s^{-1}$. At what rate are NO_2 and O_2 formed?

Ans : i. Rate of formation of $NO_2 = 5 \times 10^{-2}$ mol dm^{-3} s^{-1}
ii. Rate of formation of $O_2 = 12.5 \times 10^{-2}$ mol dm^{-3} s^{-1}

4. In the reaction aA + bB → product. It concentration of A is doubled (keeping B constant) the intial rate becomes 4 times and if B is doubled (keeping A constant), the rate becomes double what is the rate law equation and order of reaction?

Ans : Rate law :
Rate = k $[A]^2[B]$
order of reaction = 1

5. The reaction given $2NO + O_2 \rightarrow 2NO_2$ follows the rate law = k $[NO]^2[O_2]$. What is the order of the reaction? If $k = 2.0 \times 10^{-6}$ $mol^{-2}L^2$ s^{-1}. What is the rate of the reaction when [NO] = 0.04 mol^{-1} and $[O_2] = 0.2$ mol L^{-1}.

Ans : Rate = 6.4×10^{-10} mol L^{-1} s^{-1}

Q.19 Explain the order of the reaction with the help of an example.

Ans :

For the reaction, $aA + bB \longrightarrow cC + dD$ is

If the rate of the reaction is given as

rate = k $[A]^x[B]^y$.

Then the sum x + y gives overall order of the reaction.

Thus overall order of the chemical reaction is given as the sum of powers of the concentration terms in the rate law expression.

For example :

i. For the reaction,

$$2H_2O_{2(g)} \longrightarrow 2H_2O(l) + O_{2(g)}$$

experimentally determined rate law is

rate = $k[H_2O_2]$.

The reaction is of first order.

ii. If the experimentally determined rate law for the reaction

$$H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)} \text{ is}$$

rate = $k[H_2][I_2]$.

The reaction is of first order in H_2 and I_2each and hence overall of second order

Q.20 Mention the key points about the order of reaction.

Ans : Key points about the order of reaction

a. The order of chemical reaction is experimentally determined.

b. The order can be integer or fractional. Look at the reaction,

$$CH_3CHO_{(g)} \longrightarrow CH_{4(g)} + CO_{(g)}$$

The rate law for the reaction was found to be rate = $k[CH_3CHO]^{3/2}$.

Here the order of the reaction is 3/2.

c. The order of the reaction, can be zero for :

$$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$$

The rate expression for this is : rate = $k[NO_2]^2$.

This shows that order of reaction with respect to NO_2 is 2 and with CO is zero or the rate is independent of concentration of CO.

The overall order of reaction is 2.

d. Only a few reactions of third order are known. Reactions with the orders higher than three are scanty.

6.4 Molecularity of elementary reactions

Q.21 Define the following terms and give an example.

i. Complex reaction

ii. Elementary reaction

Ans :

i. Complex reaction

Complex reaction are those which constitute a series of elementary reaction.

For example : $2NO_2Cl \rightarrow 2NO_{2(g)} + Cl_{2(g)}$

The reaction takes place in two simple steps.

$O_{3(g)} + O_{(g)}\ 2O_{2(g)}$

$2NO_{2(g)}\ 2NO_{(g)} + O_{2(g)}$

ii. Elementary reaction

Reaction that occur in a single step and cannot be broken further into simpler reactions. These are elementary reaction.

For example : $O_{3(g)} \rightarrow O_{2(g)} + O_{(g)}$

$C_2H_5I_{(g)} \rightarrow C_2H_{4(g)} + HI_{(g)}$

Q.22 Explain molecularity of reaction.

Ans : The molecularity refers to how many reactant molecules are involved in reactions. In the above reactions there is only one reactant molecule.

These are unimolecular reactions or their molecularity is one.

$$O_{3(g)} + O_{(g)} \longrightarrow 2O_{2(g)}$$

$$2NO_{2(g)} \longrightarrow 2NO_{(g)} + O_{2(g)}$$

The elementary reactions involving two reactant molecules are bimolecular reactions or they have molecularity as two.

The molecularity of an elementary reaction is the number of reactant molecules taking part in it

Q.23 State the molecularity rate law and order of reaction for each of the following elementary reactions.

i. $2NO \rightarrow 2NO_{2(g)} + O_{2(g)}$

ii. $C_2H_5I_{(g)} \rightarrow C_2H_{4(g)} + HI_{(g)}$

Ans :

i. $2NO \rightarrow 2NO_{2(g)} + O_{2(g)}$

The order of the reaction 2

and its molecularity is also 2

Expression of rate law : Rate = $k\,[NO_2]^2$

ii. $C_2H_5I_{(g)} \rightarrow C_2H_{4(g)} + HI_{(g)}$

The order of the reaction is 1

and its molecularity is also 1 (Unimolecular)

Expression of rate law : Rate = $k\,[C_2H_2I]$

Note : The order and molecularity of the reaction may or may not be the same

Q.24 What is the relationship between coefficients of reactants in balanced equation for an overall reaction and exponents in rate law. In what case the coefficients are the exponents?

Ans : Coefficients of reactants in a balanced chemical reaction may or may not be the same as the exponents in rate law for the same reaction. for elementary reaction, coefficients in balanced chemical equation are same as the exponents in rate law.

Q.25 Distinguish between order and molecularity

Ans:

	Order	Molecularity
i.	It is experimentally determined property.	It is theoretical entity.
ii.	It is the sum of powers of the concentration terms of reactants those appear in the rate equation.	It is the number of reactant molecules taking part in an elementary reaction.
iii.	It may be an integer, fraction or zero.	It is integer

★ **Q.26 What is the rate determining step.**

Ans : A number of chemical reactions are complex. They take place as a series of elementary steps. One of these steps is slower than others. The slowest step is the rate determining step.

Q.27 Write a short note on rate determining step.

Ans : *Refer Q.26*

The slowest step determines the rate of overall reaction.

Consider, $2NO_2Cl_{(g)} \rightarrow 2NO_{2(g)} + Cl_{2(g)}$.

The reaction takes place in two steps:

i. $NO_2Cl_{(g)} \xrightarrow{k_1} NO_{2\,(g)} + Cl_{(g)}$ (slow)

ii. $NO_2Cl_{(g)} + Cl_{(g)} \xrightarrow{k_2} NO_{2\,(g)} + Cl_{2\,(g)}$ (fast)

Overall $2NO_2Cl_{(g)} \xrightarrow{k_2} 2NO_{2(g)} + Cl_{2(g)}$

The first step being slower than the second it is the rate determining step.

The rate law is, rate = $k\,[NO_2Cl]$

This also represents the rate law of the overall reaction. The reaction thus is of the first order.

Q.28 Write a short note on reaction intermediate.

Ans :

i. The species which are formed in one step and consumed in other step are called reaction intermediate.

ii. The concentration of reaction intermediate does not appear on rate law.

iii. Consider the reaction

$$2NO_2Cl_{(g)} \longrightarrow 2NO_{2(g)} + Cl_{2(g)}$$

The reaction takes place in two steps.

i. $NO_2Cl_{(g)} \xrightarrow{k_1} NO_{2\,(g)} + Cl_{(g)}$ (slow)

ii. $NO_2Cl_{(g)} + Cl \xrightarrow{k_2} NO_{2\,(g)} + Cl_{2\,(g)}$ (fast)

Overall $2NO_2Cl_{(g)} \longrightarrow 2NO_{2(g)} + Cl_{2(g)}$

iv. In the above reaction the specie Cl is formed in the first step and consumed in the second. Hence it is a reaction intermediate.

+Q.29 A reaction occurs in the following steps

i. $NO_{2(g)} + F_{2(g)} \rightarrow NO_2F_{(g)} + F_{(g)}$ (slow)

ii. $F_{(g)} + NO_{2(g)} \rightarrow NO_2F_{(g)}$ (fast)

a. Write the equation of overall reaction.

b. Write down rate law.

c. Identify the reaction intermediate.

Solution :

a. The addition of two steps gives the overall reaction as

$2NO_{2(g)} + F_{2(g)} \rightarrow 2NO_2F_{(g)}$

b. Step (i) is slow. The rate law of the reaction is predicted from its stoichiometry. Thus, rate = $k[NO_2]\ [F_2]$

c. F is produced in step (i) and consumed in step (ii) or F is the reaction intermediate.

+Q.30 Try this

A complex reaction takes place in two steps:

i. $NO_{(g)} + O_{3(g)} \rightarrow NO_{3(g)} + O_{(g)}$

ii. $NO_{3(g)} + O_{(g)} \rightarrow NO_{2(g)} + O_{2(g)}$

The predicted rate law is

rate = $k[NO][O_3]$.

Identify the rate determining step. Write the overall reaction. Which is the reaction intermediate? Why

Ans :

i. According to rate law.

Rate = k [NO] $[O_3]$

The first step is the rate dertermining step since it involves NO and Cl_2 as the reactant.

i. $NO_2Cl_{(g)} \xrightarrow{k_1} NO_{2\,(g)} + Cl_{(g)}$ (slow)

ii. $NO_2Cl_{(g)} + Cl \xrightarrow{k_2} NO_{2\,(g)} + Cl_{2\,(g)}$ (fast)

Overall $2NO_2Cl_{(g)} \longrightarrow 2NO_{2(g)} + Cl_{2(g)}$

iii. $NO_{3(g)}$ and $O_{(g)}$ is prepared in the first step and get consumed in the next

Hence NO_3 and O are reaction intermediated

★ Q.31 A reaction takes place in two steps.

i. $NO_{(g)} + Cl_{2(g)} \rightarrow NOCl_{2(g)}$

ii. $NOCl_{2(g)} + Cl_{2(g)} \rightarrow NOCl_{2(g)}$

a. Write the overall reaction

b. Identify reaction intermediate

c. What is the molecularity of each step?

Ans: $2NO_{(g)} + Cl_{2(g)} \rightarrow 2NOCl_{(g)}$

where [A] is the concentration of reactant at time t. Rearranging Eq. (ii)

$$\frac{d[A]}{[A]} = -k\,dt \qquad ....(iii)$$

Let $[A]_0$ be the initial concentration of the reactant A at time t = 0. Suppose $[A]_t$ is the concentration of A at time = t.

The equation (iii) is integrated between limits

$[A] = [A]_0$ at t = 0 and $[A] = [A]_t$ at t = t

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{dt} = -k\int_0^t dt$$

On integration,

$$\left[\ln[A]\right]_{[A]_0}^{[A]_t} = -k(t)_0^t$$

Substitution of limits gives

$\ln [A]_t - \ln [A]_0 = -k$ t

$$\text{or } \ln\frac{[A]_1}{[A]_0} = -k\,t \qquad ....(iv)$$

ii. Since $NOCl_2$ is formed in the first step and got consumed in the next therefore it is the reaction intermediate.

iii. Since two reactant in involved in each of the steps, therefore the molecularity of each step is 2.

6.5 Integrated rate law

Q.32 What is integrated rate law.

Ans : Differential rate of a reaction describes now rate of a reaction depends on the concentration of reactants in terms of derivatives.

The differential rate laws are converted into integrated rate laws which tells us the concentrations of the reactants for different times.

Q.33 Derive the integrated rate law of first order reaction.

Ans : Consider first order reaction,

$A \to$ product ....(i)

The differential rate law is given by

$$\text{rate} = -\frac{d[A]}{dt} = k[A] \quad ....(ii)$$

i. The overall reaction is

or $k = \frac{1}{t} \text{In} \frac{[A]_0}{[A]_t}$

Converting ln to $\log_{10}$, we write

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_1} \quad ....(v)$$

Eq. (v) gives the integrated rate law for the first order reactions.

Q.34 Derieve the equations for integrated rate law of first order reaction.

Ans :

The rate law can be written in the following forms

i. The equation $\text{In} \frac{[A]_1}{[A]_0} = -k\,t$

By taking antilog of both sides we get

$$\frac{[A]_t}{[A]_0} = e^{-kt} \text{ or } [A]_t = [A]_0 e^{-kt} \quad .....(i)$$

ii. Let 'a' mol dm^{-3} be the initial concentration of A at t = 0

Let x mol dm^{-3} be the concentration of A that decreases (reacts) during time t. The concentration of A that remains unreacted at time t would be (a –x) mol/dm^3

Substitution of $[A]_0$ and $[A]_t = (a - x)$

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)} \quad .....(ii)$$

Equations (i) and (ii) represent the integrated rate law of first order reactions.

Q.35 Give the units of the rate constant for the first order reaction.

Ans:

i. The integrated law is

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$

ii. Because $\log_{10} \frac{[A]_0}{[A]_t}$ is unit less quantity, the dimensions of k will be (time)$^{-1}$. The units of k will be s^{-1}, min^{-1}or (hour)$^{-1}$

Q.36 Define half life.

Ans: The half life of reaction is time required for the reactant concentration to fall to one half of its initial value.

Note: Radioactive processes follow the first order kinetics.

Q.37 Obtain the relationship between the rate constant and half life of a first order reaction.

Ans: The integrated rate law for the first order reaction is

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$

where $[A]_0$ is the initial concentration of reactant at t = 0. It falls to $[A]_t$ at time t after the start of the reaction. The time required for $[A]_0$ to become $[A]_{0/2}$ is denoted as $t_{1/2}$

or

$[A]_t = [A]_0/2$ at $t = t_{1/2}$

Putting this condition in the integrated rate law we write

$$k = \frac{2.303}{t_{1/2}} \log_{10} \frac{[A]_t}{[A]_0 / 2}$$

$$= \frac{2.303}{t_{1/2}} \log_{10} 2$$

$$= \frac{2.303}{t_{1/2}} \times 0.3010$$

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

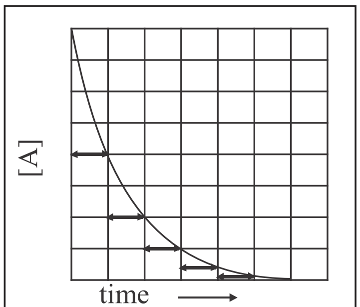
$$t = \frac{0.693}{k_{1/2}}$$

Q.38 Define half life.

Ans: half life of the first order reaction is independent of initial reactant concentration.

Q.39 Plot a graph of concentration vs time for a first order reaction.

Ans:



Half life period of first order reaction

★ Q.40 How will you represent first order reactions graphically?

Ans:

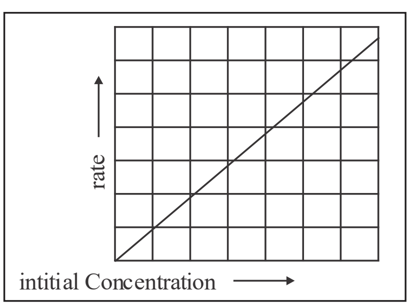
i. The differential rate law for the first order reaction A is

$$\text{rate} = -\frac{d[A]}{dt} = k[A]_t + 0$$

$$\updownarrow \quad \updownarrow \; \updownarrow \quad \updownarrow$$

$$y \quad m \; x \quad c$$

The equation is of the form y = mx + c. A plot of rate versus $[A]_t$ is a straight line passing through origin. The slope of straight line = k



Variation of rate with [A]

ii. From Eq. the integrated rate law is

$$k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$$

On rearrangement, the equation becomes

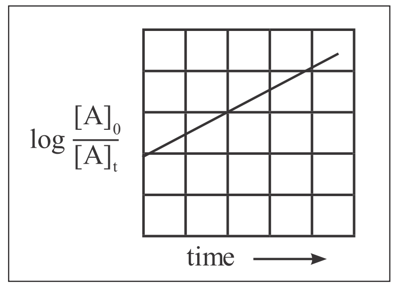
$$\frac{kt}{2.303}\log_{10}[A]_0 - \log_{10}[A]_t$$

Hence $\log_{10}[A]_t = -\frac{k}{2.303}t + \log_{10}[A]_0$

$$\updownarrow \quad \updownarrow \; \updownarrow \quad \updownarrow$$

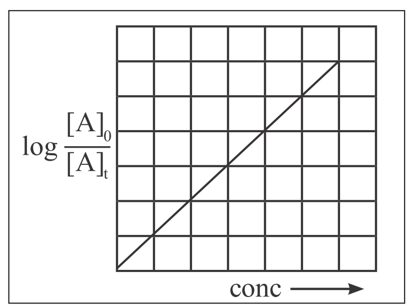
$$y \quad m \; x \quad c$$

The equation is of the straight line. A graph of $\log_{10}\frac{[A]_0}{[A]}$ versus t yields a straight line with slope -k/2.303 and y-axis intercept as $\log_{10}[A]_0$



iii. The equation has a straight line form y = mx .

Hence, the graph of $\log_{10}\frac{[A]_0}{[A]_t}$ versus t is straight line passing through origin



Q.41 Give some examples of first order reaction.

Ans:

Some examples of reactions of first order are:

i. $2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$,
rate = $k[H_2O_2]$

ii. $2N_2O(g) \rightarrow 4NO_2(g) + O_2(g)$.
rate = $k[N_2O_5]$

★ Q.42 Derive the integrated rate law for the first order reaction? $A_{(g)} \rightarrow B_{(g)} + C_{(g)}$ in terms of pressure.

Ans: Some examples of reactions,

$$A_{(g)} \rightarrow B_{(g)} + C_{(g)}$$

Let initial pressure of A be P_i that decreases by x within time t.

Pressure of reactant A at time t

$P_A = P_i - x$

The pressures of the products B and C at time t are

$P_B = P_C = x$

The total pressure at time t is then

$P = P_i - x + x + x = P_i + x$ ....(1)

Hence, $x = P - P_i$

Pressure of A at time t is obtained by substitution of x into Eq.(1) Thus

$P_A = P_i - (P - P_i) = P_i - P + P_i = 2P_i - P$

The integrated rate law turns out to be

$$k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$$

The concentration now expressed in terms of pressures.

Thus, $[A]_0 = P_i$ and $[A]_t = P_A = 2P_i - P$

Substitution gives in above

$$k = \frac{2.303}{t}\log_{10}\frac{P_i}{2P - P}$$

P is the total pressure of the reaction mixture at time *t*.

★ Q.43 What is zeroth order reaction? Derive its integrated rate law? What are the units of rate constant?

Ans: The rate of zero order reaction is independent of the reactant concentration.

Integrated rate law for zero order reactions:

For zero order reaction,

$$A \rightarrow P$$

the differential rate law is given by

$$k = \frac{[A]_0 - [A]_t}{t} = \frac{\text{mol}L^{-1}}{t} = \text{mol}\,\text{dm}^{-3}\text{t}^{-1}$$

Rearrangement of Eq. gives

$$d[A] = -k\,dt$$

Integration between the limits

$[A] = [A]_0$ at t = 0 and $[A] = [A]_t$ at t = t gives

$$\int_{[A]_0}^{[A]_t} d[A] = -k\int_0^t dt$$

or $[A]_t - [A]_0 = -kt$

Hence, $kt = [A]_0 - [A]_t$

Units of rate constant of zero order reactions

$$k = \frac{[A]_0 - [A]_t}{t} = \frac{\text{mol}L^{-1}}{t} = \text{mol}\,\text{dm}^{-3}\text{t}^{-1}$$

The units of rate constant of zero order reaction are the same as the rate.

Q.44 Derive the expression for half life of zero order reaction.

Ans:

Half life a zero order reactions:

The rate constant of zero order reaction is given by

$$k = \frac{[A]_0 - [A]_t}{t}$$

Using the conditions $t = t_{1/2}$, $[A]_t = [A]_{1/2}$, becomes

$$k = \frac{[A]_0 - [A]_{0/2}}{t_{1/2}} = \frac{[A]_0}{2t_{1/2}}$$

Hence, $t_{1/2} = \dfrac{[A]_0}{2k}$

The half life of zero order reactions is proportional to the initial concentration of reactant.

★ Q.45 Write the relationships between rate constant and half life of first order and zeroth order reactions.

Ans:

i. First order reaction : $t_{1/2} = \dfrac{0.693}{k}$

ii. Zero order reaction : $t_{1/2} = \dfrac{[A]_0}{2k}$

★ Q.46 How do half lives of the first order and zero order reactions change with initial concentration of reactants?

Ans:

i. Half life of the first order reaction is independent of initial concentration of the reactant.

ii. The half life of zero order reactions is proportional to the initial concentration of the reactant.

★ **Q.47 How will you represent zeroth order reaction graphically?**

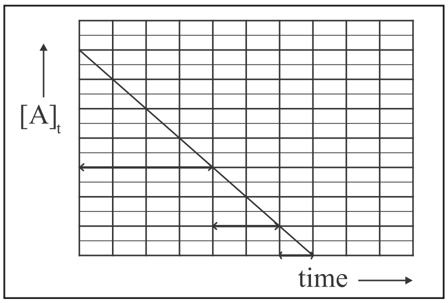
Ans:

Graphical representation of zero order reactions: The rate law is given as

$$\underset{y}{[A]_t} = \underset{mx}{kt} + \underset{c}{[A]_0}$$

Which is straight line given by y = mx + C.

A plot of $[A]_t$ versus t is a straight line.



$[A]_t$ vs t for zero order reaction

The slope of straight line is –k and its intercept on y–axis is $[A]_0$.

Q.48 Give two examples of zero order reaction.

Ans:

i. Decomposition of NH_3 on platinum metal

$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$

ii. The metals surface gets completely covered by a layer of NH_3 molecules.

iii. A number of NH_3 molecules attached on platinum surface is small compared to ammonia.

iv. A large number of the NH_3 molecules tend to remain as gas which do not react.

v. The molecules present on the metal surface only react.

vi. The rate of a reaction was thus independent of the total concentration of NH_3 and remains constant.

Q.49 Give two examples of zero order reaction.

Ans:

i. Decomposition of nitrous oxide in the presence of Pt catalyst.

$$2N_2O_{(g)} \xrightarrow{Pt} 2N_{2(g)} + O_{2(g)}$$

ii. The catalytic decomposition of PH_3 on hot tungsten at high pressure.

Q.50 Distinguish between zero order reaction and first order reaction.

Ans:

	Zero order reaction	First order reaction
i.	The reaction in which the rate is independent of concentration of the reactant is called zero order reaction.	Reaction in which the rate of the reaction is proportional to the single reactant concentration raised to a first power is called first power is called first order reaction.
ii.	Half life of a reaction depends on its initial concentration.	Half life a reaction is independent of its initial concentration.
iii.	Order of zero order reaction is O.	Order of first order reaction is 1.
iv.	Unit of 'k' for zero order reaction is mol dm^{-3} sec^{-1}	Unit of 'k' for first order reaction is sec^{-1}

Q.51 What are pseudo – first order reaction? Give one example and explain why it is pseudo – first order.

Ans:

i. Certain reactions which are expected to be of higher order follow the first order kinetics. Consider hydrolysis of methyl acetate.

$$CH_3COOCH_{3(aq)} + H_2O_{(l)} \rightarrow CH_3COOH_{(aq)} + CH_3OH_{(aq)}$$

The rate law is rate = k' $[CH_3COOH_3][H_2O]$

The reaction was expected to follow the second order kinetics, however, obeys the first order.

ii. The reason is that solvent water is present in such large excess that the change in its concentration is negligible compared to initial one or its concentration remains constant. Thus $[H_2O]$ = constant = k". The rate law becomes

rate = k' $[CH_3COOCH_3]$ k"

= k $[CH_3COOCH_3]$

where k = k'k"

The reaction is thus of first order.

+Q.52 The reaction $C_{12}H_{22}O_{11(aq)} + H_2O_{(l)}$ (excess)

$$\rightarrow \underset{\text{glucose}}{C_6H_{12}O_{6(aq)}} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Can it be of pseudo-first order type ?

Ans: The given reaction is a pseudo – first order reaction Because in hydrolysis of sugar, water is taken place in excess. Which means the change in its concentration will depend only on the initial concentration.

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

Type -2

Numericals based on half life of the reaction

Formula used

i. $k = \dfrac{0.693}{t_{1/2}}$

ii. $k = \dfrac{2.303}{t}\log_{10}\dfrac{[A]_0}{[A]_t}$

iii. $k = \dfrac{2.303}{t}\log_{10}\dfrac{P_i}{2P_i - P}$

+Q1. The half life of first order reaction is 990s. If the initial concentration of the reactant is 0.08 mol dm^{-3}, what concentration would remain after 35 minutes?

Solution :

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{990\,s} = 7\times10^{-4}\,s^{-1}$$

$$k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$$

$[A]_0$ = 0.08 mol dm^{-3}, t =35 min or 2100s, $[A]_t$ = ?

$$\log_{10}\frac{[A]_0}{[A]_t} = \frac{kt}{2.303} = \frac{7\times10^{-4}\times2100\,s}{2.303}$$

$$= 0.6383$$

$$\frac{[A]_0}{[A]_t} = \text{anti}\log 0.6383 = 4.35$$

$$\text{Hence, } [A]_t = \frac{[A]_0}{4.35} = \frac{0.08}{4.35}$$

= 0.0184 mol dm^{-3}

+Q2. In a first order reaction 60% of the reactant decomposes in 45 minutes. Calculate the half life reaction .

Solution :

$$k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$$

$[A]_0$ = 100, $[A]_t$ = 100 - 60 = 40, t = 45 min

Substituting of these in above

$$k = \frac{2.303}{t}\log_{10}\frac{100}{40}$$

$$= \frac{2.303}{45}\log_{10} 2.5$$

$$= \frac{2.303}{45}\times 0.3979 = 0.0204\,\text{min}^{-1}$$

$$= t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0204\,\text{min}^{-1}} = 34\text{ min}$$

+Q3. Following data were obtained during the First order decomposition of SO_2Cl_2 at the constant volume.

$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$

Times/s	Total pressure/bar
0	0.5
100	0.6

Calculate the rate constant of the reaction.

Solution :

$$k = \frac{2.303}{t}\log_{10}\frac{P_i}{2P_i - P}$$

P_i = 0.5 bar, P = 0.6 bar, t = 100 s

$$k = \frac{2.303}{100}\log_{10}\left(\frac{0.5\,\text{bar}}{2\times 0.5\text{ bar} - 0.6\text{ bar}}\right)$$

$$= \frac{2.303}{100}\log_{10}\left(\frac{0.5}{0.4}\right) = 2.23\times 10^{-3}\,s^{-1}$$

+Q4. The half life of a first order reaction is 0.5 min. Calculate time needed for the reactant to reduce to 20% and the amount decomposed in 55s.

Solution:

Given $t_{1/2}$ = 0.5 mins

$[A]_0$ = 100%

$[A]_t$ = 100% – 20% = 80%

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

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

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

$$k = \frac{0.693}{0.5}$$

k = 1.386 mins

Case I - Time required for the decomposition of 20% of the reactant.

$$k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$$

$$t = \frac{2.303}{1.386}\log_{10}\frac{[A]_0}{[A]_t}$$

$$= \frac{2.303}{1.386}\log\frac{100}{80}$$

$$= \frac{2.303}{1.386}\times\log(1.25)$$

$$= \frac{2.303}{1.386}\times(0.0969)$$

= Antilog [(log (2.303) – log (1.386) + log (0.0969)]

= Antilog [(0.3622 – 0.1417) +(–1.0136)]

=Antilog [(0.2205) – (1.0136)]

=Antilog [– 0.7931]

t = 0.1610 mins

Time required for the decomposition of 20% of reactant = 0.1610 mins

Case II - Amount of reactant decomposes in 55 seconds.

t = 55 sec

$$t = \frac{55}{60} = 0.916\text{ min}$$

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

$$1.386 = \frac{2.303}{0.916}\log\frac{[100]}{[A]_t}$$

$$\frac{1.36\times 0.916}{2.303} = \log\frac{[100]}{[A]_t}$$

$$\frac{1.386\times 0.916}{2.303} = \log\frac{[100]}{[A]_t}$$

$$\text{Antilog}\,[(\log(1.386) + \log(0.916) - \log(2.303)] = \log\frac{[100]}{[A]_t}$$

$$\text{Antilog}\,[(0.1417 - 0.0381) - (0.3622)] = \log\frac{[100]}{[A]_t}$$

$$\text{Antilog}\,[0.1036 - 0.3622] = \log\frac{[100]}{[A]_t}$$

$$\text{Antilog}\,[-0.2586] = \log\frac{[100]}{[A]_t}$$

Taking Antilog on both the side.

$$\text{Antilog}\,(0.5513) = \log\frac{[100]}{[A]_t}$$

$$3.5587 = \log\frac{[100]}{[A]_t}$$

$$[A]_t = \frac{100}{3.5587}$$

[A]t = 28.1%

Amount of reactant decomposed

= 100 – 28.18

= 71.82%

★ **Q5. In a first order reaction,the concentration of reactant decreases from 20 mmol dm^{-3} to 8 mmol dm^{-3} in 38 minutes. What is the half life of reaction ?**

Solution :

Given : $[A]_0 = 20$ mmol dm^{-3},

$[A]_t = 8$mmol dm^{-3}

t = 38 min

To find : Half life of reaction $t_{1/2}$

formulae : i. $k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$

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

Calculation : Substituting given value in

$$k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$$

$$k = \frac{2.303}{38}\log_{10}\frac{20}{8}$$

$$k = \frac{2.303}{38}\log_{10}(2.5)$$

$$k = \frac{2.303}{38}\times 0.3979 = 0.0241\ \text{min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0203\ \text{min}^{-1}} = 34\ \text{min}$$

★ **Q6. A first order reaction takes 40 minutes for 30% decomposition. Calculate its half life.**

Given : $[A]_0 = 100 - 30 = 70\%$, t = 40 min

To find : Half life reaction ($t_{1/2}$)

formula : $k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$

Calculation : Substituting of these in above

$$k = \frac{2.303}{t}\log_{10}\frac{100}{70}$$

$$= \frac{2.303}{40\ \text{min}}\log_{10}(1.429)$$

$$= \frac{2.303}{40}\times 0.1550$$

$$= \frac{2.303}{4\times 10}\times 0.1550$$

$= 0.5757\times 10^{-1}\times 0.1550$

$= 0.5757 \times 0.1550$

$=$ Antilog (log (0.05757) + log (0.1550))

= Antilog (– 1.2398 – 0.8096)

= Antilog (– 2.0494)

$k = 8.9248 \times 10^{-3}$ min^{-1}

$$t_{1/2} = \frac{0.693}{8.9248\times 10^{-3}}$$

$$= \frac{0.693}{8.9248}\times 10^{3}$$

$=$ Antilog (log (0.693) – log (8.9248))$\times 10^3$

= Antiolog (0.1592 – 0.9505) $\times 10^3$

= Antilog (– 1.1097) $\times 10^3$

$= 0.07767 \times 10^3$

$t_{1/2} = 77.67$ mins

Ans : The half life of reaction is 77.66 min.

★ **Q7. The half life of a first order reaction is 1.7 hours. How long will it take for 20% of the reactant to react ?**

Solution :

Given : Half life $t_{1/2} = 1.7$ hours,

$[A]_0 = 100\%$, $[A]_t = 100 - 20 = 80\%$

to find : Time for 20% of reactant to react = t

Formula :

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

ii. $k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$

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

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1.7} = \text{Anti}\log(\log(0.693) - \log(1.7))$$

= Antilog (– 0.1592 – 0.2304)

= Antilog (– 0.3896)

= 0.4076

$$k=\frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$$

$$=\frac{2.303}{0.4076}\log\frac{100}{80}$$

$$=\frac{2.303}{0.4076}\log(1.25)$$

$$=\frac{2.303}{0.4076}\times(0.0969)$$

$=$ Antilog [(log (2.303) + (0.0969)] –log (0.4076)]

$=$ Antilog = [(0.3622 – 1.0136) – (– 0.3897)]

$=$ Antilog [(– 0.3622 – 1.0136) – (– 0.3897)]

$=$ Antilog [(– 0.6514) + 0.3897]

$=$ Antilog (– 0.2617)

$=$ 0.5473 hrs

$=$ 0.5473 × 60

$=$ 32.838 mins

Ans : The time required for 20% of reaction to react is 32.9 min.

★ **Q8. Show that time required for 99.9% completion of a first order reaction is three times the time required for 90% completion.**

Solution :

For a first order reaction,

$$k=\frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$$

Time taken for 99.9% completion:

Let the time taken for 99.9% completion of the reaction be $t_{99.9\%}$.

Let initial concentration, $[A]_0$ = a

Then final concentration , $[A]_t$ = a - 99.9 % of a =

$$a-\left(\frac{99.9}{100}\times a\right)=0.001\,a$$

$$t_{99.9\%}=\frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}\ .... \text{(i)}$$

$$=\frac{2.303}{k}\log_{10}\frac{a}{0.001a}$$

$$=\frac{2.303}{k}\log_{10}1000$$

ii. Time taken for 90% completion :

Let the time taken for 90% completion of the reaction be $t_{90\%}$.

Let initial concentration, $[A]_0$ = a

The final concentration, $[A]_t$ = a - 90 % of a

$$[A]_t=a-\left(\frac{90}{100}\times a\right)=0.1\,a$$

$$t_{90\%}=\frac{2.303}{k}\log_{10}\frac{[A]_0}{[A]_t}=\frac{2.303}{k}\log_{10}\frac{a}{0.1a}$$

$$=\frac{2.303}{k}\log_{10}10\ ....\text{(ii)}$$

Dividing (1) by (2) ,we get

$$\frac{t_{99.9\%}}{t_{90\%}}=\frac{\frac{2.303}{k}\log_{10}1000}{\frac{2.303}{k}\log_{10}10}=\frac{\log_{10}1000}{\log_{10}10}$$

$$=\frac{\log_{10}10^3}{\log_{10}10^1}$$

$$\therefore\quad \frac{t_{99.9\%}}{t_{90\%}}=3=\frac{3\cancel{\log_{10}10}}{1\cancel{\log_{10}10}}=\frac{3}{1}$$

$$\therefore\quad t_{99.9\%}=3\,t_{90\%}$$

Ans : Therefore, for a first order reaction, the time required for 99.9% completion is 3 times of time required for 90% completion.

Problems for practice

1. In a first order reaction, the concentration of reactant decreases from 0.8 mol/dm$_3$ in 2 × 10^4 sec.

Ans : k = 2 × 10^4 s^{-1}

2. In a first order reaction 10% of reactant is consumed in 25 minutes. Calculate the half life of the reaction.

Ans : $t_{1/2}$ = 164.6 min

3. In a first order reaction, the concentration of reactant is reduced to 1/8 th of initial concentration in 75 min at 298 K. What is the half life of reaction in minutes ?

Ans : $t_{1/2}$ = 25 mins

4. At particular concentration, the half life of the reaction is 100 minutes. When the concentration of the reactant become double half life becomes 25 minutes then what will be the order of the reaction.

Ans : order of reaction = 3s

6.6 Collision Theory of bimolecular reaction

Q53. Explain briefly : Collision between reactant molecule.

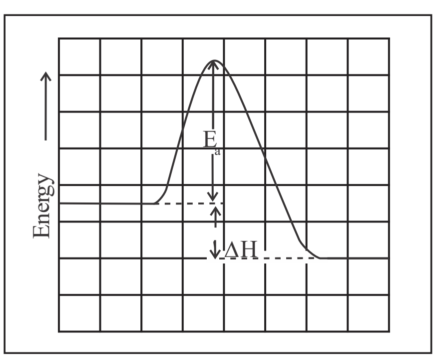
Ans : Chemical reactions occur as a result of collisions between the reactant species. It may be expected that the rate of the reaction is equal to the rate of collision. For the gas- phase reactions the number of collisions is far more and typically many powers of tens compared to the observed rate.

Q54. What is the activation energy of the reaction ?

Ans : For the reaction is occur the colliding reactant molecule must possess the minimum kinetic energy. This minimum kinetic energy is the activation energy.

Q55. What are requirements for the colliding reactant molecules to lead to products.

Ans: The reactants for colliding molecules to form the products are



Potential energy barrier

★ Q.56 Why all collisions between reactant molecules do not lead to a chemical reaction.

Ans: All collisions of reactant molecules do not lead to a chemical reaction because the colliding molecules needs to possess certain energy which is greater than the activation energy E and proper orientation.

Do you Know

For a gaseous reaction at 298 K, E_a = 75 kJ/mol. The fraction of successful collisions is given by $f = e^{-Ea/RT} = e^{-75000/8.314 \times 298}$ $= 7 \times 10^{-14}$ or only 7 collisions in 10^{14} collisions are sufficiently energetic to lead to the reaction.

Remember

All collisions of reactant molecules do not lead to a chemical reaction. The colliding molecules need to possess certain energy which is greater than the activation energy E_a and proper orientation.

6.7 Temperature dependence of reaction rates

Q.57 Write Arrhenius equation and explain the terms involved in it.

Ans:

i. The Arrhenius equation is : $k = Ae^{-Ea/RT}$

ii. Where k is the rate constant, E_a is the activation energy, R molar gas constant, T temperature in kelvin, and A is the pre–exponential factor.

Note:

i. The pre exponential factor A and the rate constant have same unit in case of the first order reactions.

ii. Beside A found to be relation to frequency of collisions.

Q.58 How will you determine activation energy.

i. graphically using Arrhenius equation

ii. from rate constants at two different temperature.

Ans:

i. Graphical representation of activation energy:

a. Taking logarithm of both sides of eqn we obtain

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

c. Converting natural base to base 10 we write

d. $\underset{y}{\log_{10} k} = -\underset{n}{\frac{E_a}{2.303R}}\underset{x}{\frac{1}{T}} + \underset{c}{\log_{10} A}$

e. This equation is of the form of straight line y = mx + c.

f. The Arrhenius plot of log10 k versus 1/T giving a straight line. A slope of the line is $-E_a/2.303R$ with its intercept being $\log_{10}A$.

g. From a slope of the line the activation energy can be determined.

ii. Determination of activation energy from rate constant of two different temperatures.

a. For two different temperatures T_1 and T_2

b. $\log_{10} k_1 = \log_{10} A - \frac{E_a}{2.303RT_1}$

c. $\log_{10} k_2 = \log_{10} A - \frac{E_a}{2.303RT_2}$

d. where k_1 and k_2 are the rate constants at temperatures T_1 and T_2 respectively.

e. $\log_{10} k_2 - \log_{10} k_1 = -\frac{E_a}{2.303R}\frac{1}{T_2} + \frac{E_a}{2.303R}\frac{1}{T_1}$

Subtracting Eq.7 from Eq.2

f. $\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

g. $= \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$

★ Q.59 Explain with the help of Arrhenius equation, how does the rate of reaction changes with

i. Temperature and

ii. activation energy.

Ans:

i. According to Arrhenius equation $k = e^{-Ea/RT}$, shows that with the rise in temperature, $\frac{E_a}{RT}$ decreases. This cause on increase in $-E_a/RT$ This increases k and the rate of reaction.

ii. The decrease in energy of activation (E_a), E_a/RT decreases, hence $-E_a/RT$ increases and rate of reaction.

★ Q 60. Explain graphically the effect of temperature on the rate of reaction.

Ans :

i. At a given temperature, the fraction of molecules with their kinetic energy equal to or greater that E_a may lead to the product.

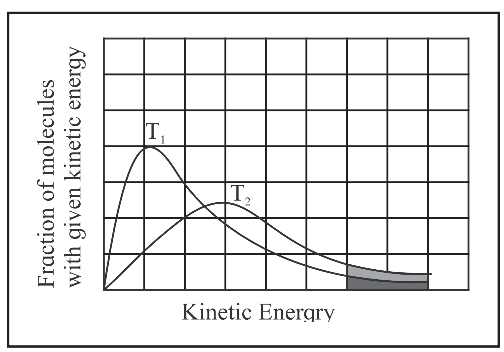
ii. With an increase of temperature the fraction of molecules having their energies (E_a) would increases. The rate of the reaction thus would increase.

iii. This is depicted by plotting a fraction of molecules with given kinetic energy versus kinetic energy for two different temperatures T_1 and T_2 (T_2 being > T_1).

iv. The shaded areas is proportional to total number of molecules. The total area is the same at T_1 and T_2.

v. The area (a + b) represents a fraction of molecules with kinetic energy exceeding E_a is larger at T_2 than at T_1 (since $T_2 > T_1$).

vi. This indicates that a fraction of molecules possessing energies larger than E_a increase with the temperature. The rate of reaction increases accordingly.



Comparison of fraction of molecule activated at T_1 and T_2

Type - 3

Numerical based on activation energy

Formula used

$$\log_{10}\frac{k_2}{k_1}=\frac{E_a}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \text{ or}$$

$$\log_{10}\frac{k_2}{k_1}=\frac{E_a}{2.303R}\left(\frac{T_2-T_1}{T_2T_1}\right)$$

1. The rate constants for a first order reaction are 0.6 s^{-1} at 313 K and 0.045 s^{-1} at 293 K. What is the activation energy ?

Solution :

$$\log_{10}\frac{k_2}{k_1}=\frac{E_a}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$k_1 = 0.045\ s^{-1}$, $k_2 = 0.6\ s^{-1}$, T_1 =293 k,
T_2 = 313 K, R =8.314 J K^{-1} mol^{-1}
Substituting

$$\log_{10}\frac{0.6}{0.045}=\frac{E_a}{2.303\times 8.314}\times\left[\frac{313-293}{293\times 313}\right]$$

$$\log_{10}13.33 = =\frac{E_a}{2.303\times 8.314}\times\frac{20}{293\times 313}$$

$$1.1248=\frac{E_a}{19.15}\times 2.18\times 10^{-4}$$

$E_a = 1.1248 \times 19.15$ J mol^{-1} / 2.18×10^{-4}
= 98810 J/ mol = 98.9 kJ/mol .

+2. A first order gas phase reaction has activation energy of 240 kJ mol^{-1} . If the pre-exponential factor is $1.6 \times 10^{13} s^{-1}$ What is the rate constant of the reaction at 600 K ?

solution : Arrhenius equation
$k = A\, e^{-Ea/RT}$ is written as

$$\log_{10}\frac{A}{k}=\frac{E_a}{2.303RT}$$

E_a = 240 kJ mol $^{-1}$ = 240×10^3 J mol^{-1},

T = 600 K, A = 1.6×10^{13} s^{-1}

$$\text{Hence } \log_{10}\frac{A}{k}=\frac{240\times 10^3\,\text{J mol}^{-1}}{2.303\times 8.314\,\text{J mol}^{-1}\,\text{K}^{-1}\times 600\,\text{K}}$$

$$= 20.89$$

$$\frac{A}{k} = \text{anti log } 20.89$$

$$= 7.78\times 10^{20} \text{ and } k = \frac{A}{7.78\times 10^{20}}$$

$$=\frac{1.6\times 10^{13}\text{s}^{-1}}{7.78\times 10^{20}} = 2.055\times 10^{-8}\,\text{s}^{-1}$$

+3. The half life of a first order reaction is 900 min at 820 K. Estimate its half life at 720 K if the activation energy is 250 kJ mol^{-1}.

solution :

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

Rate constants at two different temperatures, T_1 and T_2 are k_1 and k_2 respectively, and the corresponding half lives $(t_{1/2})_1$ and $(t_{1/2})_2$.

$$(t_{1/2})_1 = \frac{0.693}{k} \text{ and } (t_{1/2})_2 = \frac{0.693}{k}$$

$$\text{Hence, } \frac{(t_{1/2})_1}{(t_{1/2})_2}=\frac{k_2}{k_1}$$

$$\text{The equation, } \log_{10}\frac{k_2}{k_1}=\frac{E_a}{2.303RT}\times\left[\frac{T_2-T_1}{T_1T_2}\right]$$

$$\log_{10}\frac{(t_{1/2})_1}{(t_{1/2})_2}=\frac{E_a}{2.303RT}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

$E_a = 250$ kJ mol^{-1}, T_1 = 720 K,
T_2 = 820 K, $(t_{1/2})_2$ = 900 min

$$\text{Thus, } \log_{10}\frac{(t_{1/2})_1}{(t_{1/2})_2}=$$

$$\frac{250\times 10^3\,\text{J mol}^{-1}}{2.303\times 8.314\,\text{J K}^{-1}\text{mol}^{-1}}\left[\frac{820\text{K}-720\text{K}}{820\text{K}\times 720\text{K}}\right]$$

$$= 2.212$$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \text{antilog } 2.212 = 162.7$$

$(t_{1/2})_1 = (t_{1/2})_2 \times 162.7 = 900 \times 162.7$
$= 1.464 \times 10^5$ min

★ Q.4 What fraction of molecules in a gas at 300 K collide with an energy equal to activation energy of 50 kJ/mol?

solution:

Activation energy
(E_a) = 50 $kJmol^{-1}$ = 50×10^3J mol^{-1}
Temperature (T) = 300 K
Fraction of molecule (f) with energy equal to

E_a

$f = e^{-Ea/RT}$

Substituting the given value above

$$f = e^{\left[\frac{-50\times10^3\ \text{mol}^{-1}}{8.314\,\text{J K}^{-1}\times300\text{K}}\right]}$$

$$= -1\times\frac{-50\times10^3}{8.314\times300\times2.303}$$

$= -1 \times$ Antilog [(log50 + log10^3) – (log 8.314 + log 300 + log 2.303)]

– 1 × Antilog [(1.6989 + 3) – (0.9198 + 2.4771 + 0.3622)]

= – 1 × Antilog [4.6989 – 3.7591]

= –1 × Antilog (0.9398)

$\log_{10} f = -8.7056$

Taking Antilog on both the side we get

f = (Antilog (– 8.7056)

$f = 1.96 \times 10^{-9}$

$\therefore \quad f \approx 2.0\times10^{-9}$

Ans: Fraction of molecules having energy equal to activation energy is 2.0×10^{-9}.

★ Q.5 The rate constant of a reaction at 500ºC is 1.6 ×10M^{-1} s^{-1}. What is the frequency factor of the reaction if its activation energy is 56 kJ/mol?

Solution:

Rate constant *(k)* = $1.6 \times 10^3 M^{-1}s^{-1}$

$$= A\times e^{\left[\frac{-56\times10^3\ \text{mol}^{-1}}{8.314\text{JK}^{-1}\text{mol}^{-1}\times773\text{K}}\right]}$$

$$\frac{1.6\times10^3\,M^{-1}s^{-1}}{A} = e^{\left[\frac{-56000}{8.314\times773}\right]}$$

$$\log\left[\frac{1.6\times10^3\,M^{-1}s^{-1}}{A}\right] = \frac{-56000}{8.314\times773\times2.303}$$

$$= -1\times\frac{-56\times10^3}{8.314\times773\times2.303}$$

= – 1 × Antilog [(log56 + log 10^3) – (log 8.314 +log 773 + log 2.303)]

= –1 × Antilog [(1.7481 + 3) – (0.9198 + 2.8881+0.3622)]

= –1 × Antilog [4.7481 – 4.1701]

= – 1 ×Antilog (0.578)

$$\log\left[\frac{1.6\times10^3}{A}\right] = -3.7844$$

Taking antilog on both side we get

$$\frac{1.6\times10^3}{A}1.6428\times10^{-4}$$

$$A = \frac{1.6\times10^3}{1.6428\times10^{-4}}$$

$A = 9.7394 \times 10^6\ M^{-1}\ s^{-1}$

Ans: The frequency factor of reaction is $9.73\times 10^6 M^{-1}s^{-1}$.

★ Q.6 The rate constant for the first order reaction is given by log$_{10}$ k = 14.34 – 1.25 × 10^4 T. Calculate activation energy of the reaction.

Solution:

The given rate constant equation is

$\log_{10}k = 14.34 - 1.25 \times 10^4$ T .... (1)

Arrhenius equation is

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

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

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT} \quad .... (2)$$

Comparing (1) and (2),

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

$$\frac{E_a}{2.303\times8.314} = 1.25\times10^4$$

$Ea = 1.25 \times 10^4 \times 2.303 \times 8.314$

Antilog [log 1.25 + log 10^4 + log 2.303 + log 8.314]

= Antilog [0.0969 + 4 + 0.3622 + 0.9198]

= Antilog - 5.3789]

= 239.2 kJ mol^{-1}

Ans: The energy of activation of the reaction is 239.2 kJ mol^{-1}.

★ Q.7 The energy of activation for a first order reaction is 104 kJ/mol. The rate constant at 25º C is 3.7 × 10^{-}s^{-1}. What is the rate constant at 30ºC? (R = 8.314J/Kmol)

Solution:

Activation energy

(E_a) = 104 kJ mol^{-1} = 104×10^3 J mol^{-1}

Rate constant $(k_1) = 3.7 \times 10^{-5}s^{-1}$

Temperatures ; T_1 = 25 + 273 = 298 K, T_2 = 30 + 273 = 303 K

R = 8.314 J K^{-1} mol^{-1}

Rate constant (k_2) at 30 ºC

$$\log_{10}\frac{k_2}{k_1}=\frac{E_a}{2.303R}\left(\frac{T_2-T_1}{T_2T_1}\right)$$

$$\log_{10}\frac{k_2}{3.7\times10^{-5}s^{-1}}$$

$$=\frac{104\times10^3\,Jmol^{-1}}{2.303\times8.314JK^{-1}mol^{-1}}\left(\frac{303K-298K}{303K\times298K}\right)$$

$$\log_{10}\frac{k_2}{3.7\times10^{-5}s^{-1}}=\frac{104000}{2.303\times8.314}\times\frac{5}{303\times298}$$

$$=\frac{104000}{2.303\times8.314}\times\frac{5}{303\times298}$$

$$=\frac{520000}{2.303\times8.314\times303\times298}$$

$$=\frac{52\times10^4}{2.303\times8.314\times303\times298}$$

= Antilog [(log 52 + log 104) –
(log 2.303 + log 8.314 + log 303 +log 298)]
= Antilog [(1.7160 + 4) –
(0.3622 + 0.9198 +2.4814 + 204742)]
= Antilog [(5.7160) – (6.2376)]
= Antilog [– 0.5216]

$$\log_{10}\frac{k_2}{3.7\times10^{-5}}=0.301$$

Taking Antilog on both side we get

$$\frac{k_2}{3.7\times10^{-5}}=\text{antilog}(0.301)$$

$$\frac{k}{3.7\times10^{-5}}=2$$

$k = 2 \times 3.7 \times 10^{-5}$
$k = 7.4 \times 10^{-5}s^{-1}$

Ans: The rate constant of the reaction is $7.4 \times10^{-5}s^{-1}$.

★Q.8 What is the energy of activation of a reaction whose rate constant doubles when the temperature changes from 303 K to 313 K?

Solution:

Rate constants; $k_2 = 2k_1$,
Temperatures : $T_1 = 303$ K, $T_2 = 313$ K
Activation energy of the reaction *(E_a)*

$$\log_{10}\frac{k_2}{k_1}=\frac{E_a}{2.303R}\left(\frac{T_2-T_1}{T_2T_1}\right)$$

$$\log_{10}=\frac{E_a}{2.303\times8.314JK^{-1}mol^{-1}}\left(\frac{313K-303K}{313K\times303K}\right)$$

$$\log_{10}=\frac{E_a}{2.303\times8.314Jmol^{-1}}\left(\frac{10}{313\times303}\right)$$

$$0.3010=\frac{E_a}{2.303\times8.314}\times\frac{10}{313\times303}$$

$$E_a=\frac{0.3010\times2.303\times8.314\times313\times303}{10}$$

$0.3010 \times 2.303 \times 8.314 \times 313 \times 303$
= Antilog [log 0.3010 + log 2.303 + log 8.314
+ log 313 + log 303]
= Antilog [– 5214 + 0.3622 + 0.9198 +
2.4955 +2.4814]
= Antilog [–1.5214 + 6.2589]
antilog [4.7375]
$E_a = 54.63\ kJmol^{-1}$

Ans: The energy of activation of the reaction is 54.63 mol^{-1}.

Problems for practice

1. What is the activation energy for a reaction if its rate is doubled when the temperature is raised from 200 K to 400 K?

Ans : E_a = 434.65 KJ mol^{-1}

2. The rate constant for a first order decomposition reaction is given by

$\log k = 10-\frac{1000}{T}$. Then what will be activation energy in Kcal/ mol ?

Ans : E_a = 4.6 Kcal/ mol

3. The rate constant of a first order reaction at 25°c is 0.24 s^{-1} . If the energy of activation of the reaction is 88 KJ mol^{-1} at what temperature would this reaction have rate constant of $4\times10^{-2}\,s^{-1}$.

Ans : T_2 = 283.6 K

4. The rate constant for a first order reaction becomes six times when the temperature is raised from 350 K to 400 K. Calculate the activation energy for the reaction.

Ans : E_a = 41.721 KJ mol^{-1}.

6.8 Effect of catalyst on the rate of reaction

Q.61 Define catalyst.

Ans:

i. A catalyst is a substance added to the reactants that increases the rate of the reaction without itself being consumed in the reaction. Here MnO_2 is the catalyst.

$$2KClO_{3(s)} + 3O_{2(g)} \xrightarrow{MnO_2} 2KCl_{(s)}$$

ii. It has been observed that the decomposition rate increases with the addition of catalyst.

iii. A catalyst provides alternative pathway associated with lower activation energy.

iv. the potential energy barriers for the catalysed and uncatalysed reactions.

v. The barrier for uncatalysed reaction (E_a) is larger than that for the same reaction in the presence of a catalyst E_a.

Note :

It has been observed that the decomposition rate increases with addition of catalyst.

Q.62 How catalyst increases the rate of reaction? Explain with the help of potential energy diagram for cataylsed and un catalysed reactions.

Ans:

i. Consider the decomposition of H_2O_2 in aqueous solution catalysed by I- ions.

$$2H_2O_{2(l)} \xrightarrow{I} 2H_2O_{(l)} + O_{2(g)}$$

ii. At room temperature the rate of reaction is slower in the absence of catalyst with its activation energy being 76 kJ mol^{-1}.

iii. In the presence of iodide ion/ the catalyst I^- the reaction is faster since the activation energy decreases to 57 kJ mol^{-1}.

Q.63 Explain graphically the effect of catalyst on the rate of reaction.

Ans:

i. A catalyst lowers the threshold energy.

ii. Consequently more molecules acquire the minimum amount of energy and tend to cross the energy barrier.

iii. A fraction of activated molecules is greater for the catalyzed reaction.

iv. The rate of catalyzed reaction thus is larger than the reaction with no catalyst.

❍❍❍