B.Sc. Part-1 Chemistry (Hons)

1[st] Paper

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❖ CHEMICAL KINETICS :

'The branch of Chemistry which deals with the rates of chemical reaction, the factors affecting the rate of reaction and the mechanism by which the reaction proceed is known as Chemical Kinetics'.

❖ RATE OF REACTION/ VELOCITY OF REACTION/ SPEED OF REACTION :

The rate of reaction may be defined as given below:-

The rate of reaction is defined as the change in the concentration of any one of the reactants or product per unit time.

Let us consider a reaction

$$A \rightarrow B$$

Rate of reaction = $-\dfrac{\textit{Decrease in concentration of reactant A}}{\textit{Time interval}}$

OR, **Rate of reaction** = $\dfrac{\textit{Increase in concentration of product B}}{\textit{Time interval}}$

Let $[R_1]$ & $[R_2]$ represent molar concentration of reactant and $[P_1]$ & $[P_2]$ represent molar concentration of products at time t_1 and t_2 respectively.

The change in concentration of reactant = $\Delta R = [R_2]-[R_1]$ and

The change in concentration of product = $\Delta P = [P_2]-[P_1]$

Time interval = $\Delta T = t_2-t_1$

The rate of reaction = $-\dfrac{\Delta R}{\Delta T} = \dfrac{\Delta P}{\Delta T}$

NOTE: We use +ve sign for increase in concentration and -ve sign for decrease in concentration.

Eg. $PCl_5 \rightarrow PCl_3 + Cl_2$

Rate of reaction = $- \frac{\Delta[PCl\ \ ]}{\Delta T} = + \frac{[PCl3]}{\Delta T} = + \frac{[Cl2]}{\Delta T}$

In general for the reaction,

$aA + bB \rightarrow cC + dD$

The rate of reaction is given by

Rate = $- \frac{1}{a}\frac{d[A]}{dt} = - \frac{1}{b}\frac{d[B]}{dt} = - \frac{1}{c}\frac{d[C]}{dt} = - \frac{1}{d}\frac{d[D]}{dt}$

Where d[A] & d[B] represent small decrease in the concentration of A & B respectively and d[C] & d[D] represent small increase in the concentration of products C & D respectively in the very small time dt.

If in very small time dt, dx is the very small increase in concentration of any product

Then rate of reaction can also be given by

$$\textbf{Rate} = \frac{\mathbf{dx}}{\mathbf{dt}}$$

❖ FACTORS AFFECTING THE RATE OF REACTION:

The rate of any reaction depends upon the following factors:

1) **Nature of reactants**.
2) **Concentration of the reactants :** Greater is the concentrations of the reactants, faster is the reaction.
3) **Temperature :** The rate of reaction increases with increase of temperature. Generally rate of reaction becomes double for 10^0 rise in temperature.
4) **Presence of Catalyst :** Catalyst generally increase the rate of reaction. But in some reaction it also decrease the rate of reaction.
5) **Surface area of the reactants :** Greater is the surface area, the faster is the reaction.
6) **Presence of light :** Photochemical reaction depend upon presence of light.

❖ RECALL MEMORY:

- If a reaction occurs in two or more steps then, slowest step of reaction is the rate determining step.
- Velocity Constant or Rate Constant may be defined as the rate of reaction when the molar concentration of each reactant is taken as unity. It is expressed by 'K' .
- Greater is the value of rate constant, faster is the reaction.

- Rate Constant depend upon temperature.
- If concentration of one or more reactant is too high then it cannot be taken in rate equation.

❖ ORDER OF REACTION:

It is defined as the sum of powers to which the molar concentrations in rate determining equation are raised to express the observed rate of the reaction.

E.g. $NH_4NO_2 \rightarrow N_2 + 2H_2O$

The rate law eq^n is

Rate = $K[NH_4NO_2]$

Order of reaction = 01

$2HI \rightarrow H_2 + I_2$

Rate α $[HI]^2$

∴ Order of reaction = 2

In general

$Aa + bB \rightleftharpoons$ Product

If Rate α $[A]^a$ $[B]^b$

The order of reaction = a + b

Order of reaction may be 0,1,2,3….

It may be fractional.

It can be determined experimentally.

❖ MOLECULARITY OF A REACTION:

Total number of atoms, ions or molecules of reactants appeared in balanced equation of a chemical reaction is known as Molecularity of the reaction.

E.g. $PCl_5 \rightarrow PCl_3 + Cl_2$

Molecularity of reaction = 1

$2N_2O_5 \rightarrow 4NO_2 + O_2$

Molecularity of reaction = 2

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

Molecularity of reaction =4 + 5 = 9

$$H_{2\,(g)} + Cl_{2\,(g)} \xrightarrow[hv]{} 2HCl$$

Molecularity of reaction = 1 +1 = 2

Reactions can be defined as basis of Molecularity of reaction. If Molecularity of reaction is one then **unimolecular reaction**.

If Molecularity of reaction is two then **bimolecular reaction**.

If Molecularity of reaction is three then **termolecular reaction**.

Molecularity of reaction is always whole number, never zero or fractional.

❖ DIFFERENCE BETWEEN ORDER OF REACTION AND MOLECULARITY OF REACTION :

ORDER OF REACTION	MOLECULARITY OF REACTION
1. Sum of the concentrations terms appeared in rate determining equation is known as order of reaction. E.g. $PCl_3 \rightarrow PCl_3 + Cl_2$ Rate α $[PCl_5]$ Order of reaction = 1 E.g. $H_2 + Cl_2 \overset{hv}{\Leftrightarrow} 2HCl$ Experimentally rate of reaction does not depend upon concentration of H_2 & Cl_2 . So order of reaction = Zero	1. Total number of atoms/ions/molecules which is essential to start the reaction or appeared in stoichiometry equation. E.g. $H_2 + Cl_2 \rightleftharpoons 2HCl$ Molecularity = 1+ 1 = 2
2. Order of reaction may be zero, fractional or whole number.	2. Molecularity of reaction may be always whole number never zero.
3. It can be determined experimentally.	3. This cannot be determined experimentally. Can be obtained from the stoichiometry of equation of reaction.
4. It is applicable to elementary as well as complex reactions.	4. It is not for complex reaction.
5. Order of reaction is variable.	5. Molecularity of reaction is invariable.

❖ EXPRESSION FOR VELOCITY CONSTANT OF FIRST ORDER REACTION :

‘A reaction is said to be first order if the rate of reaction depends upon only one concentration term’.

Let us consider a first order reaction expressed by-

$$A \rightarrow X$$

Let a moles/litre of the initial concentration of reactant 'A' after time t, x moles/ litre of A decomposed into product.

Hence concentration of 'A' after time 't' = (a-x)

According to Law of Mass Action,

$$\textbf{Rate of reaction} = \frac{dx}{dt} \ \alpha \ (a-x)$$

Or, $\frac{dx}{dt}$ = k(a-x) where k is the Velocity Constant

Or, $\frac{dx}{a-x} = k\,dt$

Integrating both sides,

$$\int \frac{dx}{a-x} = k \int dt$$

Or, -ln(a-x) = kt + C ————(i) where 'C' is the integration constant

When t = 0, then x = 0

Putting these values in eq^n (i), we get

Or, -ln(a-x) = k×0 + C

Or, -ln a = C

Substituting value of 'C' in eq^n (i), we get

-ln(a-x) = kt + [-ln a]

-ln (a-x) = kt – ln a

kt = ln a – ln (a-x)

$$k = \frac{1}{t} \ln\frac{a}{a-x}$$

$$k = \frac{2.303}{t} \log\frac{a}{a-x} \quad \text{————(ii)}$$

Eq^n (ii) is known as expression for the Velocity Constant of first order reaction.

❖ CHARACTERISTICS OF FIRST ORDER REACTION :

1. Unit of k :

We know that

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

Since $\frac{a}{a-x}$ is the ratio of two concentration terms, so unit of k is Time^{-1} would be in sec^{-1}, min^{-1}, hr^{-1} respectively in second, minute, hour.

Hence Velocity Constant (k) of first order reaction is independent of the units in which concentration are expressed.

2. Determination of k :

If $[A]_0$ is initial concentration of reactant and [A] is concentration of reactant after time 't'.

Then, $k = \frac{2.303}{t} \log\frac{[A]0}{[A]}$

Or, $\frac{k}{2.303} t = \log\frac{[A]0}{[A]}$

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

This eq^n is similar to eq^n of a straight line y=mx+c.

If log[A] is plotted against time 't' we will get given below graph:

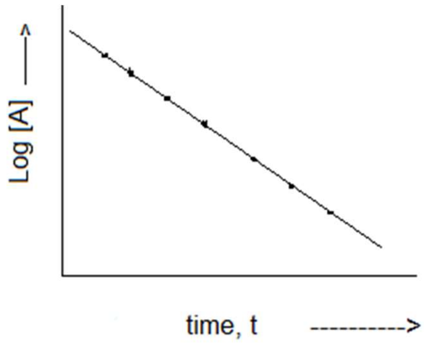

Fig.2.

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

From this eq^n we calculate value of 'k'
The time taken for any fraction of the reaction to complete is independent of the initial concentration.

Let us consider ‘a’ is the initial concentration of reaction after time taken for half completion of the reaction i.e. $T_{1/2}$ would be a/2.
We know that,

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

$$\text{Or, } T_{1/2} = \frac{2.303}{k} \log\frac{a}{a/2}$$

$$\text{Or, } T_{1/2} = \frac{2.303}{k} \log 2$$

$$\text{Or, } T_{1/2} = \frac{2.303 \times 0.301}{k} = \frac{0.693}{k}$$

$$\therefore T_{1/2} = \frac{0.693}{k}$$

Since ‘a’ does not appear in this eq^n, hence $T_{1/2}$ is independent of initial concentration of reactant and $T_{1/2}$ is defined as time required for the half completion of reaction OR

The time in which the concentration of a reactant of first order reaction is reduced to half of its initial concentration is known as Half life period of the reaction.

Similarly it can be proved that $t_{1/3}$, $t_{2/3}$, etc does not depend upon initial concentration of the reactant of first order reaction. Hence, the time taken for any fraction of the first order reaction to complete is independent of the initial concentration.

In general,

$$T_n = \frac{2.303}{k} \log n \;;$$

where for completion of ‘n’ fraction of reaction.

❖ FOR NUMERICAL PROBLEMS :

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

2. $T_{1/n} = \frac{2.303}{k}$ log n ,for completion of n^{th} fraction of the reaction

3. $T_{1/2} = \frac{0.693}{k}$

4. Amount of the substance left after n-half lives $= \frac{[A]0}{2^n}$

5. Average life = 1.44 × $T_{1/2}$

##########################THANKS#########################