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Subject : Chemistry

Class : B.Sc. Ist Year Semester II

Paper II : PHYSICAL CHEMISTRY

Unit IV

TOPIC : Order & Molecuarity Of Reaction

ORDER OF REACTION

- **The sum of all the powers of concentration terms appearing in the rate law expression is called as order of reaction**
- Consider, a reaction $aA+bB+cC \longrightarrow$ Product

  Rate of reaction = $k [A]^p [B]^q [C]^r$

Hence, Order of reaction: $(p+q+r)$

Exaple, $H_{2(g)} + Br_{2(g)} \longrightarrow 2HBr_{(g)}$, Rate of reaction = $k [H_2] [Br_2]^{½}$

Then order is, $1+½= 1.5$

MOLECULARITY OF REACTION

- The number of molecules taking part in the rate determining step of a reaction is called as molecularity of reaction
- $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$ (Unimolecular)
- $NO_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2(g)}$ (Bimolecular)
- $2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$ (Trimolecular)

ZERO ORDER REACTION

- Reaction is said to be zero order reaction if its **rate is independent of the concentration of the reactant.**

Considered a reaction A $\longrightarrow$ Product

Initial concentration: a 0

Concentration at time 't' a-x x

Let, the reaction is of zero order. Hence, rate of reaction is given by,

$dx/dt = k_0[A]^0 = k_0$; Therefore, dx =k0dt

After integration we get, $x = k_0t+C$ .... (1); When t=0 & x=0, we get 0=0+C means, C=0 put this value in equation (1)

We get $x=k_0t$ Thise is called as integrated form rate expression for zero order reaction.

FIRST ORDER REACTION

- The reaction in which rate depends upon only the concentration of one of the molecule is called as first order reaction.

Considered a reaction $A \longrightarrow$ Product
Initial concentration: a 0
Concentration at time't' a-x x
Let, the reaction is of first order. Hence, rate of reaction is given by,
$dx/dt = k_1[A]^1 = k_1(a-x)$, $dx/(a-x) = k1dt$.
After integration we get, $-\log(a-x) = k_1t + C$ .... Equation (1)
When $t=0$, $x=0$ equation (1) become, $-\log(a-0) = 0+C$; $C=-\log a$
Put the value of C in equation (1)
$-\log(a-x) = k_1t - \log a$; $\log(a/a-x) = k_1t$; $k_1 = 1/t \log(a/a-x)$ .... Equation (2)
Converting equation (2) into common logarithm, we get
$K_1 = 2.303/t \log_{10}(a/a-x)$
This is called as integrated form of rate expression for first order reaction.

SECOND ORDER REACTION

- When rate of reaction depends upon concentration of 2 molecules, it is called as second order reaction.

1. **If initial concentration of both reactants are same**

Considered a reaction $A + B \longrightarrow Product$

Initial concentration:	a	a	0
Concentration at time 't'	a-x	a-x	x

Let, the reaction is of second order. Hence, rate of reaction is given by,

$dx/dt=k_2[A][B]$; $dx/dt= k_2(a-x)\ (a-x)$

$= k_2(a-x)^2$

$dx/(a-x)^2 = k_2dt$ After integrating this equation we get,

$1/a-x = k_2t+C$ .... Equation (1)

When t=0, x=0 the equation become

$1/a =0+C$; $C=1/a$ put this value in equation (1)

$1/a-x = k_2t+1/a$

Therefore $k_2t= 1/a-x -1/a = a-(a-x)/a(a-x)$

$t= 1/t\ x/a(a-x)$

PSEUDO ORDER REACTIONS

- In some reactions, one of the reactants is present in large excess. Such concentration Of reactant does not change during the course of reaction. The experimentally observed order is less than expected. Such reactions are called as pseudo-order reaction.

Considered a reaction $A + B \longrightarrow$ Product

If it is second order reaction, the rate is given by

Rate= K[A][B]

But, Amount of B is taken excess, the experimentally observed rate becomes independent of concentration of B and so the rate can be written as,

Rate =K`[A]

Hence, actual reaction is second order, but in practice it will be 1st order.

Therefore it is called as pseudo-first order reaction.