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Subject : Chemistry

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Paper II : PHYSICAL CHEMISTRY

Unit IV

TOPIC : Order & Molecularity Of Reaction

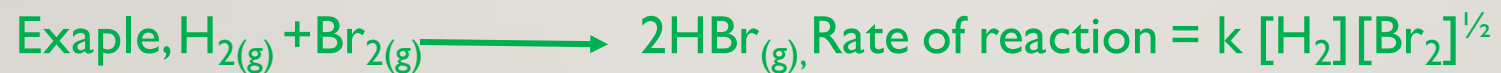
ORDER OF REACTION

- **The sum of all the powers of concentration terms appearing in the rate law expression is called as order of reaction**

- Consider, a reaction $aA + bB + cC \longrightarrow \text{Product}$

$$\text{Rate of reaction} = k [A]^p [B]^q [C]^r$$

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



Then order is, $1 + 1/2 = 1.5$

MOLECULARITY OF REACTION

- The number of molecules taking part in the rate determining step of a reaction is called as molecularity of reaction
- $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$ (Unimolecular)
- $\text{NO}_{(g)} + \text{O}_{3(g)} \longrightarrow \text{NO}_{2(g)} + \text{O}_{2(g)}$ (Bimolecular)
- $2\text{NO}_{(g)} + \text{O}_{2(g)} \longrightarrow 2\text{NO}_{2(g)}$ (Trimolecular)

ZERO ORDER REACTION

- Reaction is said to be zero order reaction if its **rate is independent of the concentration of the reactant.**
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Considered a reaction $A \longrightarrow \text{Product}$

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,

$$dx/dt = k_0[A]^0 = k_0 ; \text{Therefore, } dx = k_0 dt$$

After integration we get, $x = k_0 t + C$ (I); When $t=0$ & $x=0$, we get $0=0+C$
means, $C=0$ put this value in equation (I)

We get $x=k_0 t$ This 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 $A \longrightarrow \text{Product}$

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,

$$dx/dt = k_1[A]^1 = k_1(a-x), \quad dx/(a-x) = k_1 dt.$$

After integration we get, $-\log(a-x) = k_1 t + C$ 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)

$$-\log(a-x) = k_1 t - \log a ; \log(a/a-x) = k_1 t ; k_1 = 1/t \log(a/a-x) \quad \text{..... Equation (2)}$$

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.
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I. If initial concentration of both reactants are same

Considered a reaction $A + B \longrightarrow \text{Product}$

Initial concentration: $a \quad a \quad 0$

Concentration at time 't' $a-x \quad a-x \quad x$

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

$$\begin{aligned} dx/dt &= k_2[A][B]; & dx/dt &= k_2(a-x)(a-x) \\ & & &= k_2(a-x)^2 \end{aligned}$$

$dx/(a-x)^2 = k_2 dt$ After integrating this equation we get,

$$1/a-x = k_2 t + C \quad \text{..... Equation (1)}$$

When $t=0, x=0$ the equation become

$$1/a = 0 + C; \quad C = 1/a \text{ put this value in equation (1)}$$

$$1/a-x = k_2 t + 1/a$$

$$\text{Therefore } k_2 t = 1/a-x - 1/a = a-(a-x)/a(a-x)$$

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

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.
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Considered a reaction $A + B \longrightarrow \text{Product}$

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

$$\text{Rate} = K[A][B]$$

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,

$$\text{Rate} = K'[A]$$

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

Therefore it is called as pseudo-first order reaction.