B. Sc. Part II (Subsidiary)

Paper : Physical Chemistry

Topic : Chemical Kinetics

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Order and Molecularity of a Reaction :-

Order of a Chemical Reaction :-

Order of a reaction is the number of reactant molecules whose concentration determines the rate expression. It is essentially an experimental quantity.

Consider the following reaction :

$$aA + bB + cC + \ldots\ldots \rightarrow \text{Products}$$

Experimentally its rate law is

$$Rate = k[A]^a \cdot [B]^b \cdot [C]^c \cdots$$

where a, b, c, ... are the powers of concentrations of reactants A, B, C, ..., and also the partial orders with respect to reactants A, B, C, ...

The overall order (n) of the reaction is

$$n = a + b + c + \cdots$$

It must be remembered that n is purely an experimental quantity and can not be determined theoretically by observing the stoichiometry of a reaction.

The order of reaction may be a whole number (1 to 3), zero or even fractional. A reaction is said to be of the first order if its rate is given by the expression of the type: $r = k_1[A]$; of the second order if the rate is $r = k_2[A]^2$ or $r = k_2[A][B]$; of the third order if the rate is given by $r = k_3[A]^3$ or $r = k_3[A]^2[B]$ or $r = k_3[A][B]^2$ or $r = k_3[A][B][C]$ and so on. Generally order above third is very rare. For a zero order reaction, the rate equation is written as $r = k_0$. Here there is no concentration term i.e. in zero order reaction the rate of reaction is independent of concentrations of reactants. Some examples of reactions and its orders are given by

(a) $N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$

Rate $= k[N_2O_5]$ i.e. $n = 1$, hence it is a first order reaction.

(b) (i) $H_2(g) + I_2(g) \rightarrow 2HI(g)$

$r = k[H_2][I_2]$ i.e. $n = 1 + 1 = 2$

(ii) $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$

$r = k[NO_2]^2$ i.e. $n = 2$

These two reactions are of second order reaction

(c) $2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O$

$r = k[NO]^2[H_2]$ i.e. $n = 2 + 1 = 3$

It is a third order reaction.

(d) $NO_2(g) + CO(g) \xrightarrow[\text{at } 200^\circ C]{} NO(g) + CO_2(g)$

Here rate $= k[NO_2]^2$ (Experimentally found)

The rate does not depend on [CO], so this is not included in the rate law and the power of [CO] is understood to be zero. Thus this reaction is of zeroth order with respect to CO. The reaction is second order with respect to NO_2. The overall reaction order is $2 + 0 = 2$ i.e. second order reaction.

Molecularity of a Chemical Reaction:-

The total numbers of molecules or atoms which take part in a chemical reaction as represented by the chemical equation is known as the molecularity of reaction.

The term molecularity is often confused with order of a reaction. The order of reaction is determined only be those species whose concentration is changing during the course of reaction whereas molecularity of reaction is determined by all the species taking part in the overall reaction.

Consider, for example, inversion of cane sugar. It can be written as:

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Since, two molecules of reactants are taking part in this reaction, it is a bimolecular reaction (i.e. molecularity is 2). If the rate equation is written as

$r = k[C_{12}H_{22}O_{11}][H_2O]$, order seems to be two. But since water is present in large excess that its concentration does not change during the course of reaction, the rate equation becomes

$$r = k'[C_{12}H_{22}O_{11}]$$

and the reaction is found to be of first order with respect to sucrose.

Such reactions whose molecularity is two but the order is found experimentally to be one are known as pseudo-first order reactions

Order of a reaction can also be zero or even fractional but molecularity is always a natural number.

Order of a reaction can change with the conditions such as pressure, temperature and concentration but molecularity is invariant for a chemical equation.

To be continued.....