TDC–II

PAPER–III

Unit–1

Chemical Kinetics

Rate of reaction—

$$r = \frac{dx}{dt}$$

Where,

dx = uniform change in concentration in infinitismal time dt sec.

$$A \longrightarrow B.$$

$$\frac{-d[A]}{dt} = \frac{+d[B]}{dt}$$

rate of dissociation of A $= \frac{-d[A]}{dt}$

rate of formation of B $= \frac{+d[B]}{dt}$

rate of reaction –

$$r = \frac{dx}{dt}$$

Unit :-

$$r = \frac{dx}{dt} = \frac{mol\ L^{-1}}{sec} = mol\ L^{-1}\ sec^{-1}.$$

Rate constant :-

Let us consider a reaction —

$$A \longrightarrow Product$$

$$r \propto [A]$$

$$r = K.[A]$$

where, K = rate constant

If $[A] = 1$

$r = K$

Again for the reaction —

$$A + B + \dots\dots \rightarrow \text{Product.}$$

$$r = K [A][B] \dots\dots$$

If $[A] = [B] = 1$

$r = K$

So, rate constant (K) may be defined as the rate of reaction when the concentration of each reactant is unity.

Unit

Let $nA \longrightarrow$ Product

$$r = K [A]^n$$

$$K = \frac{r}{[A]^n}$$

$$K = \frac{mol\ L^{-1}\ sec^{-1}}{(mol\ L^{-1})^n}$$

$$= \frac{mol\ L^{-1}\ sec^{-1}}{mol^n\ L^{-n}}$$

$$\boxed{K = mol^{1-n}\ L^{n-1}\ sec^{-1}}$$

Molarularity -

Molecularity of a chemical reaction may be defined as the total number of molecules taking part in the elementary step of a chemical reaction.

$$H_2 + I_2 \longrightarrow 2HI$$

$$\text{molecularity} = 1+1 = 2 \quad (\text{Bimolecular})$$

The molecularity doesnot exceed three or four values. This is due to the fact that simultaneous collision between more than three or four molecules is not probable.

Molecularity is a theoritical Concept. So, it cannot be defined for complex reaction. (multistep reaction)

Molecularity can may be defined for simple reaction i.e. elementary step reaction — one step reaction.

Order of Reaction :-

Let us consider a general reaction —

$$n_1 A + n_2 B + \ldots\ldots \longrightarrow \text{Product.}$$

then rate of reaction —

$$r = K[A]^{n_1}[B]^{n_2}$$

Order of reaction —

$$n = n_1 + n_2 + \ldots\ldots$$

where, n_1, n_2 .... are determined experimentally.

So, Order of reaction may be defined as the sum total of all the exponent (Power) raised to the concentration terms in the rate law equation. (Experimental rate).

Example–

(1) $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$

theoritical rate $r = K \cdot [H_2]^1 [Cl_2]^1$

theoritical order $n = 1+1 = 2$

But experimentally determined rate –

$$r = K [H_2]^0 [Cl_2]^0$$

So, order of reaction $n = 0$ Zero order reaction.

(2) $C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

Cane Sugar Glucose Fructose

experimental rate –

$$r = K [C_{12}H_{22}O_{11}]^1 [H_2O]^0$$

order, $n = 1+0 = 1$.

Order of reaction is an experimental quantity. It may have any values i.e. zero, fractional or intiger.

for Complex reactions (multi step reaction) slowest step is the rate determined step from which order of reaction may be evaluated.

Higher order of reactions are rare.

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