Dr S.K. Gupta
Deptt. of Chemistry
Marwari College, Doby

23-07-20.

Deg-I (H/s) Physical-Chemistry (Paper-II)

Chapter - Chemical-Kinetics

Topics - Kinetics of second order Reactions

Second-order-Rkn:-

Those Chemical reaction in which its reaction rate is determined by the variation of two-reactant terms.

Case-I when two same reactant is involved.

In general equation involving same reactant

$$2A \longrightarrow \text{Product}$$

let Initial Conc. of A = a mole/lit

Conc. of product from after time 't' = x mole/lit

Conc. of A after time 't' = (a-x) mole/lit

Applying law of Mass-Action.

Rate of Rkn. is expressed as

$$\frac{dx}{dt} \propto [A]^2$$

or, $\frac{dx}{dt} \propto (a-x)^2$

$\frac{dx}{dt} = K \cdot (a-x)^2$ | K = Rat. Const.

or, $\frac{dx}{(a-x)^2} = K \cdot dt$

Upon Integration,

$$\int \frac{dx}{(a-x)^2} = \int K \cdot dt$$

$-2+1$

or, $\frac{(a-x)}{-2+1} \times (-1) = Kt + C$

or, $\frac{1}{(a-x)} = Kt + C$ — (1) | C = Integ. Const.

When $t=0$, $x=0$

Putting the value in above expression

$$\frac{1}{a} = C \quad \text{— (2)}$$

Substituting the value of C in eqn (1)

$$\frac{1}{(a-x)} = Kt + \frac{1}{a}$$

$$Kt = \frac{1}{(a-x)} - \frac{1}{a}$$

$$Kt = \frac{a-(a-x)}{a(a-x)}$$

$\therefore Kt = \frac{x}{a(a-x)}$

$$\therefore \boxed{K = \frac{1}{t} \cdot \frac{x}{a(a-x)}} \quad \text{---(3)}$$

Eqn-(3) is the rate-expression of second order Reaction have same-Reactant.

Case-II when two different-reactants with different-Initial-Concns are involved.

General-eqn for such-Reaction,

$$A + B \longrightarrow \text{Product}$$

let initial-Concn of A = a moles/lit

" " " B = b moles/lit

After time 't' x moles/lit of Product formed, then Concn of A becomes = (a-x) moles/lit

" " " B " = (b-x) moles/lit

Applying Law of Mass-Action, We get-

Rate of Reaction,

$$\frac{dx}{dt} \propto [A][B]$$

$$\propto [a-x][b-x]$$

$$\frac{dx}{dt} = k(a-x)(b-x) \quad \text{---(4)}$$

Rearranging the eqn (4)

$$\frac{dx}{(a-x)(b-x)} = k \cdot dt \quad \text{---(5)}$$

Resolving the left-hand side by partial fraction, eqn (5) may be written as

$$\frac{1}{(a-b)}\left[\frac{1}{(b-x)} - \frac{1}{(a-x)}\right] dx = k \cdot dt$$

Integrating this equation. We get

$$\frac{1}{(a-b)}\left[\int \frac{dx}{(b-x)} - \int \frac{dx}{(a-x)}\right] = \int k \cdot dt$$

$$\frac{1}{(a-b)}\left[-\ln(b-x) - \{-\ln(a-x)\}\right] = kt + c$$

$$\frac{1}{(a-b)}\left[\ln(a-x) - \ln(b-x)\right] = kt + c$$

$$\text{or, } \frac{1}{(a-b)}\left[\ln\frac{(a-x)}{(b-x)}\right] = kt + c \quad \text{---(6)}$$

To eliminate the value of C,

when $t=0$, $x=0$

Putting this value in eqn (6)

$$\frac{1}{(a-b)} \ln \frac{a}{b} = C \quad \text{---(7)}$$

Putting this value in eqn (6)

$$\frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)} = Kt + \frac{1}{(a-b)} \ln \frac{a}{b}$$

$$\text{or } Kt = \frac{1}{(a-b)} \left[\ln \frac{(a-x)}{(b-x)} - \ln \frac{a}{b} \right]$$

$$Kt = \frac{1}{(a-b)} \left[\ln \frac{b(a-x)}{a(b-x)} \right]$$

$$\therefore \boxed{K = \frac{2.303}{t(a-b)} \left[\log \frac{b(a-x)}{a(b-x)} \right]} \quad \text{---(8)}$$

The above expression is rate-constant for second-order Reaction having different reactant & its different concentration.