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

Chapter - Chemical Kinetics

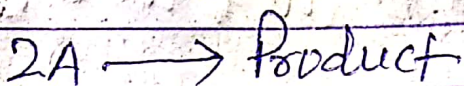
Topics - Kinetics of Second
order Reactions

Second-order Rxn:-

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



Let Initial Concⁿ of A = a mole/lit

Concⁿ of product form after time 't'
= x mole/lit

Concⁿ of A after time 't' = $(a-x)$ mole/lit

Applying law of Mass-Action.

Rate of Rxn. is expressed as
 $\frac{dx}{dt} \propto [A]^2$

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

$$\frac{dx}{dt} = K_1 (a-x)^2 \quad \left| \begin{array}{l} K = \text{Rate Const} \end{array} \right.$$

$$\text{or } \frac{dx}{(a-x)^2} = K_1 dt$$

Upon-Integration.

$$\int \frac{dx}{(a-x)^2} = \int K_1 dt$$

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

$$\text{or, } \frac{1}{(a-x)} = Kt + C \quad \text{--- (1)} \quad \left| \begin{array}{l} C = \text{Integr. Const.} \end{array} \right.$$

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)

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

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

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

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

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

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

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

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

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

To - eliminate the value of C .

when $t=0, x=0$

Putting this value on eqn (6)

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

Putting this value in eqn (6)

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

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

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

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

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

