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class \Rightarrow B.Sc. (Hons) Part I
 Subject \Rightarrow Chemistry
 Chapter \Rightarrow Chemical Kinetics
 Topic \Rightarrow Second order Reaction

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Second order Reaction

A reaction is said to be of the second order if the rate of reaction depends upon two concentration terms.

Case 1 \Rightarrow When only one reactant is involved

Let us consider a general reaction involving one reactant
 $2A \longrightarrow$ Products

Suppose the initial concentration of A = a moles/litre
 If after time t, x moles of A have reacted, the concentration of A = (a-x) moles/litre.

We know that for such a second order reaction, rate of reaction is proportional to the square of the concentration of the reactant, Thus,

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

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

$$\text{or } \frac{dx}{dt} = k(a-x)^2 \quad \text{--- (1)}$$

Where k is the rate constant for the 2nd order reaction.

Rearranging eqn. (1) we have

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

Integrating this eqn., we get

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

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$$\int \frac{(a-x)^{-1} \times (-1)}{-1} = kt + I$$

$$\text{or } \frac{1}{(a-x)} = kt + I \quad (2)$$

Where I is integration constant

In the beginning i.e. at time $t=0$, $x=0$
 Putting this value in eqn (2) we get

$$\frac{1}{a} = I$$

Substituting this value of I in eqn (2) we get

$$\frac{1}{a-x} = kt + \frac{1}{a}$$

$$\text{or } kt = \frac{1}{a-x} - \frac{1}{a} \quad (3)$$

$$\text{or } kt = \frac{a - (a-x)}{a(a-x)}$$

$$\text{or } kt = \frac{x}{a(a-x)}$$

$$\therefore k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

This is the integrated rate equation for a second order reaction.

If the initial concentration is written as c_0 and concentration at any instant of time t as c_t , then $a = c_0$ and $(a-x) = c_t$ putting this value in eqn (3), we get

$$k = \frac{1}{t} \left[\frac{1}{c_t} - \frac{1}{c_0} \right]$$

expression for the

This is another form of the rate constant of second order reaction.

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Case 2 \Rightarrow When: two different reactants with different initial concentrations are involved

General equation for such reaction is



Suppose the initial concentration of A = a moles/litre
 the initial concentration of B = b moles/litre,
 amount of A that reacts in time t = x moles/litre
 then the amount of B that would react in the same time would also be x moles/litre.

\therefore At any instant of time t
 Concentration of A = (a-x) moles/litre
 Concentration of B = (b-x) moles/litre

We know that,

$$\text{Rate of reaction } \frac{dx}{dt} \propto [A][B]$$

$$\text{or } \frac{dx}{dt} \propto (a-x)(b-x)$$

$$\therefore \frac{dx}{dt} = k(a-x)(b-x) \quad \text{--- (1)}$$

Where k is the rate constant.

Equation (1) may be rewritten as

$$\frac{dx}{(a-x)(b-x)} = k dt \quad \text{--- (2)}$$

Resolving the left hand side into partial fractions, equation (2) may be rewritten as

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

Integrating this equation, we get

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

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

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or, $\frac{1}{(a-b)} [\ln(a-x) - \ln(b-x)] = kt + I$

$\therefore \frac{1}{(a-b)} \left(\frac{\ln a-x}{b-x} \right) = kt + I$ ——— ③

Where I is the constant of Integration.

But at $t=0, x=0$

Putting these values in eqn ③, we get

$\frac{1}{(a-b)} \left(\ln \frac{a}{b} \right) = I$ ——— ④

Putting this value in eqn ③, we get

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

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

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

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

$\therefore k = \frac{2.303 \log \frac{b(a-x)}{a(b-x)}}{t(a-b)}$

This is the rate equation for a second order reaction.

unit \Rightarrow The unit of k for Second order reactions are $\text{conc}^{-1} \text{time}^{-1}$

Examples next class