

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



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,

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

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

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

Where  $K$  is the rate constant for the 2nd order reaction

Rearranging eq<sup>n</sup>. (1) we have

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

Integrating this eq<sup>n</sup>, we get

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

(2)

$$\text{L.H.S.} \quad (q-x) \frac{1}{-1} \times (-1) = kt + I$$

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

Where  $I$  is integration constant

In the beginning, i.e. at time  $t=0$ ,  $x=0$   
Putting this value in eq<sup>n</sup>. (2) we get

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

Substituting this value of  $I$  in eq<sup>n</sup>. (2) we get

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

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

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

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

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  $q = c_0$  and  $(q-x) = c_t$  putting this value in eq<sup>n</sup>. (3), we get

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

expression for the

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

③

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  $t$

$$\text{Concentration of A} = (a-x) \text{ moles/litre}$$

$$\text{Concentration of B} = (b-x) \text{ moles/litre}$$

We know that,

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

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

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

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

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

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

(4)

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

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

Where  $I$  is the constant of Integration.

But at  $t=0, x=0$

Putting these values in eq<sup>n</sup> (3), we get

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

Putting this value in eq<sup>n</sup> (3), we get

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

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

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

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

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

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