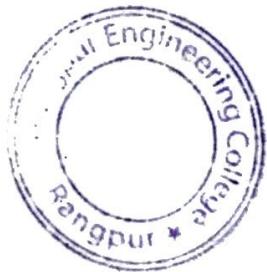


# Chemical Kinetics

## Lecture - ③

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Q1 1. What do you mean by rate of a reaction



Rate of a reaction: The rate of a chemical reaction is the decrease of concentration (in mol L<sup>-1</sup>) of the reactant or increase in the concentration of the product in unit time.

Let us consider the reaction



As the reaction proceeds, the concentration of A decreases and that of B increases. If the increase and decrease are simply stated as the change in concentration then,

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

where [ ] represents the concentration in 'moles/litre' and d represents infinitesimally small change in concentration.

The negative sign indicates that the concentration of the reactant A decreased with the progress of reaction and the positive sign indicates that the concentration of the product B increased with time.



2. Write rate law and define rate constant. OR Define rate constant.

Ans: The rate of a reaction is directly proportional to the reactant concentrations.

Let us consider the reaction



According to the rate law

$$\text{rate} \propto [A]$$

$$\text{or rate} = K[A]$$

where  $K$  is the proportionality constant and is called the rate constant. If the concentration is  $1 \text{ mol L}^{-1}$  then

$$\text{rate} = K$$

Thus, the rate of a unit molar concentration is called the rate constant.

3. what do you mean by order and molecularity of a reaction.

order of a reaction: The order of a reaction is defined as the sum of the powers of concentrations in the rate law.

Let us consider the reaction



According to the rate law

$$\text{rate} = k[A]^m[B]^n$$

The order of the reaction is  $(m+n)$ .

Molecularity of the reaction: The total number of molecules which take part in the reaction as represented by the chemical equation, is known as the molecularity of the reaction.



4. What do you mean by zero order reaction.

Ans: A zero order reaction is one whose rate is independent of reactant's concentration.

5. What is first order reaction and deduce mathematical formulation of first order reaction.

First order reaction: The reaction whose rate is proportional to the first power of the concentration of the only one reactants is called the first order reaction.

Mathematical formulation of first order reaction:

Let us consider a first order reaction



suppose that at the beginning of the reaction ( $t=0$ ), the concentration of A is  $a$  moles/litre.

At after time  $t$ ,  $x$  moles of A have changed, the

concentration of A is  $a-x$ . We know that for a first order reaction, the rate of reaction  $\frac{dx}{dt}$  is directly proportional to the concentration of the reactant. Thus,

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

where  $k$  is rate constant.

$$\text{or, } \frac{dx}{a-x} = k dt \quad \textcircled{1}$$

By integration of the equation  $\textcircled{1}$

$$\int \frac{dx}{a-x} = \int k dt$$

$$\text{or, } -\ln(a-x) = kt + I \quad \textcircled{2}$$

where  $I$  is the constant of integration. i.e.

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

substituting these values in the equation  $\textcircled{2}$   
we get,

$$I = -\ln a$$

substituting the value of  $I$  in the equation  $\textcircled{2}$   
we get.

$$-\ln(a-x) = kt - \ln a$$

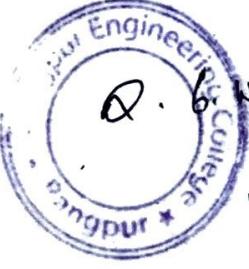
$$\text{or, } kt = \ln a - \ln(a-x)$$

$$\text{or, } kt = \ln \frac{a}{a-x}$$

$$\text{or}, K = \frac{1}{t} \ln \frac{a}{a-x}$$

$$\text{or}, K = \frac{2.303}{t} \log \frac{a}{a-x} \quad \dots \quad (3)$$

This is the mathematical formulation of first order reaction.

  
Q. b. What is second order reaction. Deduce mathematical formulation of second order reaction/s.

Second order reaction/s: The reaction/s whose rate are determined by the change of concentrations of two molecules of a reactant or more than a reactant/s.

Mathematical formulation of second order reaction/s:

Let us take a second order reaction of the type



Suppose the initial concentration of A is  $a$  moles/litre<sup>-1</sup>. If after time  $t$ ,  $x$  moles of A have reacted, the concentration of A is  $(a-x)$ . We know that for such a second order reaction, rate of reaction is proportional to the square of the concentration of the reactant. Thus

$$\frac{dx}{dt} = k(a-x)^2 \quad [\text{where } k \text{ is the rate constant}]$$

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

on integration, it gives

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

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

where  $I$  is the integration constant.

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

putting these values in the equation (1) we get

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

$$\text{or, } I = \frac{1}{a}$$

substituting the value of  $I$  in the equation (1)  
we get,

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

$$\text{or, } kt = \frac{1}{a-x} - \frac{1}{a}$$

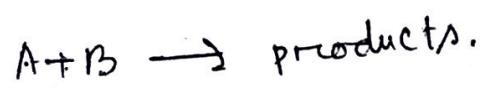
$$\text{or, } kt = \frac{x}{a(a-x)}$$

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

This is the mathematical formulation of second order



Q. Deduce the rate constant equation of the type.



Ans:  $A + B \rightarrow \text{products.}$

Suppose the initial concentration of A is  $a$  moles/litre<sup>-1</sup> and the initial concentration of B is  $b$  moles/litre<sup>-1</sup>. If after time  $t$ ,  $x$  moles of A and B react, the concentration of A is  $(a-x)$  and the concentration of B is  $(b-x)$ . Thus rate of reaction

$$\frac{dx}{dt} = K(a-x)(b-x)$$

where  $K$  is the rate constant.

$$\text{or, } \frac{dx}{(a-x)(b-x)} = K dt$$

$$\text{or, } \frac{1}{(a-b)} \left[ \frac{1}{b-x} - \frac{1}{a-x} \right] dx = K dt \quad \text{--- (1)}$$

on integration, it gives

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

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

where  $I$  is the integration constant.

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

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

putting these values in the equation ② we get.

$$\frac{1}{a-b} \ln \frac{a}{b} = I$$

$$\text{or, } I = \frac{1}{a-b} \ln \frac{a}{b}$$

substituting the value of  $I$  in the equation  
② we get.

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

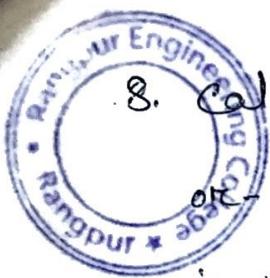
$$\text{or, } \frac{1}{a-b} \ln \frac{a-x}{b-x} - \frac{1}{a-b} \ln \frac{a}{b} = kt$$

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

$$\text{or, } K = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

$$\text{or, } K = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)} \quad \text{--- ③}$$

Equation ③ is the rate constant of  
 $A + B \rightarrow \text{products}$  type reaction.



8. Calculate the half-life of a first order reaction.

or - Show that half life for a first order reaction is independent of the initial concentration.

or - Show that half life is inversely proportional to  $K$ , the rate constant.

Ans:

The integrated rate equation for a first order reaction can be stated as

$$K = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{--- (1)}$$

where,  $a$  is the initial concentration and  $x$  is the concentration after time  $t$ . Half life,  $t_{1/2}$ , is the time when initial concentration reduces to  $\frac{1}{2}$  i.e.,

$$x = \frac{a}{2} \quad \text{and} \quad t = t_{1/2}$$

substituting these values in the equation (1) we get

$$K = \frac{2.303}{t_{1/2}} \log \frac{a}{a-a/2}$$

$$\text{or, } K = \frac{2.303}{t_{1/2}} \log \frac{a}{\frac{a}{2}}$$

$$\text{or, } K = \frac{2.303}{t_{1/2}} \log 2$$

$$\text{or, } t_{1/2} = \frac{2.303}{K} \times 0.301$$

$$\text{or, } t_{1/2} = \frac{0.693}{K} \quad \text{--- (2)}$$

equation ② is the half life of a first order reaction and the half life of a first order reaction is constant.

From equation ② we see that half life for a first order reaction is independent of the initial concentration.

From equation ② we see that half life is inversely proportional to K, rate constant.

f/ prove that half life of a second order reaction depends on initial concentration.

The integrated rate equation for a second order reaction can be stated as

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

where 'a' is the initial concentration and  $(a-x)$  is the concentration after time, t. Half life,  $t_{1/2}$  is the time when initial concentration reduces to

$\frac{1}{2}$ , i.e.,

$$x = \frac{a}{2}, \quad t = t_{1/2}$$

substituting these values in the equation ① we get

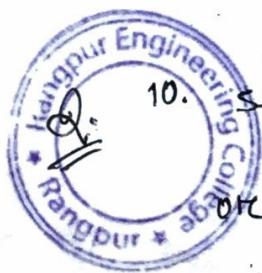
$$K = \frac{1}{t_{1/2}} \frac{\frac{a}{2}}{a(a - \frac{a}{2})}$$

$$\text{or, } t_{1/2} = \frac{1}{K} \frac{a}{a - \frac{a}{2}}$$

$$\text{or, } t_{1/2} = \frac{1}{k} \cdot \frac{a}{2} \cdot \frac{2}{a^2}$$

$$\text{or, } t_{1/2} = \frac{1}{k} \cdot \frac{1}{a} \quad \dots \quad (2)$$

from equation (2) we can say that half life of a second order reaction depends on initial concentration.



10. State and Explain transition state theory.

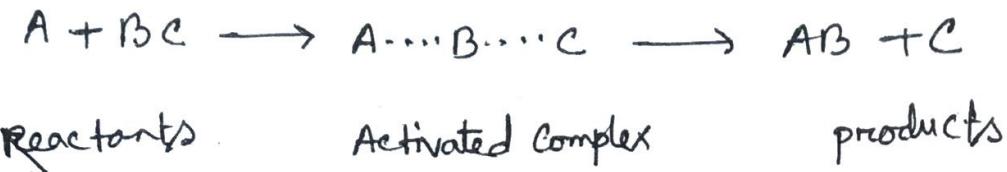
or explain activated complex and activation energy.

Ans: It is now believed that all chemical processes proceed through the formation of an intermediate activated complex or transition state. The activated complex is a grouping of atoms of reactant molecules which is unstable. The activated complex breaks up or decomposes at a definite rate to give the products of the reaction. Consider a reaction of the type



It is thought that at first an activated complex, having a structure intermediate between that of the reactants and products, is formed.

In the above example the reaction may be written as



The activated complex ( $\text{A} \cdots \text{B} \cdots \text{C}$ ) has a higher potential energy than either the reactants or products. The difference in energy between  $\text{A} + \text{BC}$  and the activated complex is equal to  $E_a$ , the energy of activation of the reaction. It is to be noted that to get from the reactant side to the product side the system has to cross over an energy barrier corresponding to the energy of the activated complex.

In spite of collision between molecules, reaction can not take place unless the energy barrier can be crossed. The difference between the energy of the reactants and that of the products is the enthalpy change of the reaction ( $\Delta H$ ).

If the energy level of the products is lower than that of the reactants, energy is given out during the reaction, the reaction being exothermic.

✓ If the energy level of the products is higher than that of the reactants, energy is given in during the reaction, the reaction being endothermic.