Dr. Usha Kumari, Associate Professor

Dept of Chemistry, Magadh Mahila College
Patna University

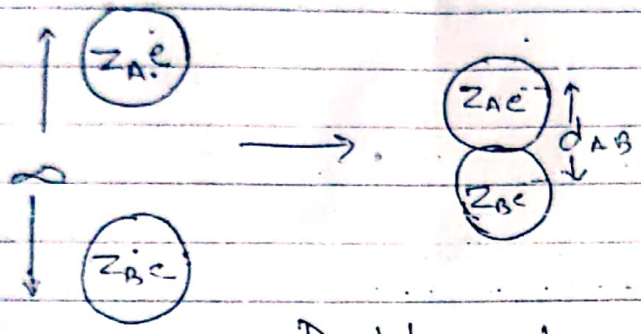
Email id: kumari.usha1963@gmail.com

CHEMISTRY
M.Sc Sem-4
Unit 3

A. Kinetics of condensed phase reaction
B. Fast reactions

Kinetics of ionic reaction :-

The electrostatic force between the ions are much stronger than the non-electrostatic force. A very simple model of reaction between the ions in solution is represented below -



Double sphere model

The reacting molecules are considered as conducting spheres, the radii are r_A & r_B and charges are $Z_A e$ & $Z_B e$, e being the electronic charge.

Initially, the ions are at infinite distance from each other and in the activated state they are considered to be intact and they are at the distance of d_{AB} apart. This model is considered as Double Sphere Model.

When the ions are at a distance of 'x' apart, then the force acting between them is equal to -

$$F = \frac{Z_A e \cdot Z_B e}{\epsilon x^2} \qquad \text{---(1)}$$

where, ϵ is dielectric constant of the medium.

The work that must be done in moving the ions together a distance of 'dx' will be -

$$dw = -\frac{Z_A Z_B e^2}{\epsilon x^2} dx \quad \text{---(2)}$$

[∵ dw = force × displacement]

The work that is done in moving the ions from an infinite distance to the final distance d_{AB} is -

$$w = \int_0^{d_{AB}} -\frac{Z_A Z_B e^2}{\epsilon x^2} dx$$

$$= -\frac{Z_A Z_B e^2}{\epsilon} \int_0^{d_{AB}} \frac{dx}{x^2}$$

$$= \frac{Z_A Z_B e^2}{\epsilon} \left[\frac{1}{x}\right]_0^{d_{AB}} \quad \left[\because \frac{dx}{x^2} = \frac{x^{-2+1}}{-1} = -\frac{1}{x}\right]$$

$$w = \frac{Z_A Z_B e^2}{\epsilon} \cdot \frac{1}{d_{AB}} \quad \text{---(3)}$$

There is also a non-electrostatic term Δh^*_{nes} in the calculation of free energy. The free energy of activation per molecule may be written as -

Date
Page

$$\frac{\Delta G^*}{N} = \frac{\Delta G^*_{ines}}{N} + \frac{Z_A Z_B e^2}{\epsilon d_{AB}} \quad \text{——— (4)}$$

where, N = total no. of particles.

According to the theory of absolute reaction rate, the rate constant is given as —

$$K' = \frac{KT}{h} e^{-\frac{\Delta G^*}{RT}}$$

where, K = Boltzmann Constant,
K' = Rate constant

or, $K' = \frac{KT}{h} e^{-\frac{\Delta G^*}{NKT}}$ ——— (5)

Putting the value of $\frac{\Delta G^*}{N}$ in eqⁿ (5), we get —

$$K' = \frac{KT}{h} e^{-1/KT\left(\frac{\Delta G^*_{ines}}{N} + \frac{Z_A Z_B e^2}{\epsilon d_{AB}}\right)}$$

$$K' = \frac{KT}{h} e^{-\frac{\Delta G^*_{ines}}{RT}} \cdot e^{-\frac{Z_A Z_B e^2}{\epsilon KT d_{AB}}} \quad \text{——— (6)}$$

Taking logarithm in both sides of eqⁿ we get,

$$\ln K' = \ln \frac{KT}{h} - \frac{\Delta G^*_{ines}}{RT} - \frac{Z_A Z_B e^2}{\epsilon KT d_{AB}} \quad \text{——— (7)}$$

Suppose,

$$\ln \frac{KT}{h} - \frac{\Delta G^{\ddagger}_{uncc}}{RT} = \ln K_0$$

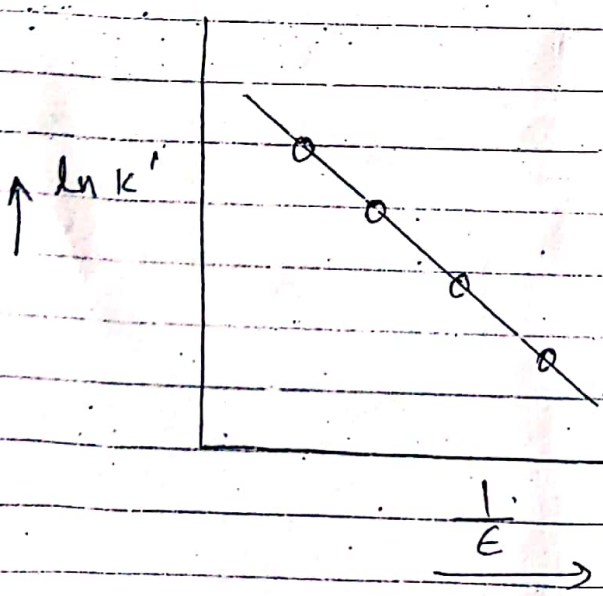
then eqⁿ (1) becomes -

$$\ln K' = \ln K_0 - \frac{Z_A Z_B e^2}{\epsilon K T d_{AB}} \quad \text{---} \quad (3)$$

The equation (3) indicates that the logarithm of the rate constant of a rxⁿ b/w the ions will vary linearly with the reciprocal of dielectric constant.

What will be the effect of dielectric constant on rxⁿ rate ? (इस तरह से ques पूछेगा तो पूरा ऊपर वाला topic लिखेंगे)

A plot of $\ln K'$ against the reciprocal of dielectric constant for the rxⁿ b/w the ions in solⁿ is given below —



Several tests of this relationship have been made. They are found to be in good agreement.

Effect of Ionic strength on the rate of rxn (Bronsted Bjerrum Equation)

A/c to Bjerrum, the reacting ions first form an activated complex which is in equilibrium with the reactant and then the activated complex decomposes to yield the products.

Consider a rxn as -

$$A^{Z_A} + B^{Z_B} \underset{K_2}{\overset{K_1}{\rightleftharpoons}} \left[AB^{Z_A+Z_B}\right]^* \xrightarrow{K_3} \text{Product}$$

Where, A & B are reacting species, Z_A & Z_B are charges on the respective species, AB is the activated complex, K_1 & K_2 & K_3 are rate const.

A/c to the law of mass action, the equilibrium constant is given as -

$$K^* = \frac{a_{AB}}{a_A \cdot a_B} \quad \text{---(1)}$$

where, $K^* = \frac{K_1}{K_2}$ is the equilibrium constant.

a_A, a_B & a_{AB} are the activities of reactan and the activated complex.

We know that,

activity = conc^n x activity coefficient

$$\Rightarrow \boxed{a = C\gamma}$$

$\therefore a_{AB} = C_{AB} \cdot \gamma_{AB}$

Similarly, $a_A = C_A \cdot \gamma_A$

$a_B = C_B \cdot \gamma_B$

Putting the value of activities in eq^n (1) we get -

$$K^* = \frac{C_{AB}}{C_A \cdot C_B} \times \frac{\gamma_{AB}}{\gamma_A \cdot \gamma_B}$$

$$\therefore C_{AB} = K^* \times \left(\frac{\gamma_A \cdot \gamma_B}{\gamma_{AB}}\right) C_A C_B$$

~~If the above reaction is elementary rx^n then~~, rate of the rx^n $= K_3 \cdot C_{AB}$ — (3)

Putting the value of C_{AB} from eq^n (2) in eq^n (3) we get

$$\text{Rate of rx}^n = K_3^* \times K^* \left(\frac{\gamma_A \gamma_B}{\gamma_{AB}}\right) C_A C_B$$

$$= K_0 \left(\frac{\gamma_A \gamma_B}{\gamma_{AB}}\right) C_A C_B \quad \text{— (4)}$$

where, $K_0 = K_3 \cdot K^* =$ Constant (suppose)

If the above rx^n is elementary rx^n then, experimental rate of rx^n is given by -

$$\text{Rate of rx}^n = K_r \cdot C_A C_B \quad \text{— (5)}$$

where, K_r = rate constant

Date
Page

From eqn (4) & (5) we get -

$$K_r C_A C_B = K_0 \left(\frac{\gamma_A \gamma_B}{\gamma_{AB}}\right) C_A C_B$$

$$K_r = K_0 \left(\frac{\gamma_A \gamma_B}{\gamma_{AB}}\right) \quad \text{——— (6)}$$

Taking logarithm in both sides of eqn (6) we get -

$$\log K_r = \log K_0 + \log \gamma_A + \log \gamma_B - \log \gamma_{AB} \quad \text{——— (7)}$$

A/c to Debye Huckel's theory, activity coefficient is related to ionic strength by the expression -

$$-\log \gamma = 0.509 \cdot Z^2 \sqrt{\mu}$$

where, Z is the charge upon the ion & μ is the ionic strength.

For A, B and AB, the activity coefficients may be expressed as -

$$-\log \gamma_A = 0.509 Z_A^2 \sqrt{\mu}$$

$$-\log \gamma_B = 0.509 Z_B^2 \sqrt{\mu}$$

$$-\log \gamma_{AB} = 0.509 (Z_A + Z_B)^2 \sqrt{\mu}$$

Putting these values in eqⁿ (7)

$$\log k_r = \log k_0 + 0.509 Z_A^2 \sqrt{\mu} - 0.501 Z_B^2 \sqrt{\mu} + 0.509 (Z_A + Z_B)^2 \sqrt{\mu}$$

$$= \log k_0 - 0.509 Z_A^2 \sqrt{\mu} - 0.509 Z_B^2 \sqrt{\mu} + 0.509 (Z_A^2 + Z_B^2 + 2 Z_A Z_B) \sqrt{\mu}$$

$$\log k_r = \log k_0 + 1.018 Z_A Z_B \sqrt{\mu} \quad -(8)$$

Eqⁿ. (8) is known as Bronsted- Bjerrum Eqⁿ.

The above eqⁿ shows that the rate const. of the rxⁿ depends upon the ionic strength.

Three cases may arise:

Case I: when $Z_A Z_B = 0$, it mean that one of the reactant is non-electro-lyte.

eg- $CH_2ICOOH + CNS^- \rightarrow CH_2(CNS)COOH + I^-$

In such case, the rate constant will be independent of ionic strength.

Date
Page

Case II: When $Z_A \cdot Z_B$ = +ve,

it means that Z_A & Z_B are of same sign then, the above eqⁿ. shows that the rate constant of the rxⁿ. will increase with the increase in ionic strength.

eg- $S_2O_3^{2-} + I^- \longrightarrow$ Product

$[Co(NH_3)_5Br]^{2+} + Hg^{2+} \longrightarrow$ Product

Case III: When $Z_A \cdot Z_B$ = -ve,

it means that Z_A and Z_B are of opposite sign. For such rxⁿ the rate const. will decrease with increase in ionic strength.

eg → $H_2O_2 + H^+ + Br^- \longrightarrow$ Product.

Transition State Theory in solution

→ Transition state theory in solution is simple in principle but is difficult to carry out quantitatively because of imperfect knowledge of liquid state. However, it is better to treat rxn. rates in solution using activity coefficients.

The fundamental postulate of transition state theory is that the reactant molecules after interaction form an activated ~~complex~~ molecule which is in equilibrium with the reactant molecule & the activated molecule decomposes into the products.

Consider a reaction as -

$$A + B \rightleftharpoons M^* \longrightarrow \text{Products}$$

The activated complex is an aggregate of atoms which may be thought to be similar to the ordinary molecule except it has one special vibration w.r.t which it is unstable. Such vibrations lead to the dissociation of the activated complex, into the product. If the frequency of this vibration is ν then the rate at which products are formed is given as -

$$\text{Rate} = \nu c^*$$

where, c^* = conc^n of activated complex

But in soln, equilibrium const. $K^* = \frac{a^*}{a_A \cdot a_B}$ — (2)

where, a_A, a_B & a^* are the activities of reactants and the transition state molecule.

Since,

activity = conc^n × activity coefficients

Therefore eq^n (2) takes the form

$$K^* = \frac{C^* \times \gamma^*}{C_A \cdot C_B \times \gamma_A \cdot \gamma_B}$$

or, $C^* = K^* \times \left(\frac{\gamma_A \gamma_B}{\gamma^*}\right) C_A C_B$

Putting the value of C^* in eq^n (1) we get,

$$\text{rate} = \nu \times K^* \left(\frac{\gamma_A \gamma_B}{\gamma^*}\right) C_A \cdot C_B \quad \text{— (3)}$$

If the rx^n is elementary rx^n,

$A + B \longrightarrow$ Products

then the rate of rx^n,

$$\text{rate} = K_r C_A C_B \quad \text{— (4)}$$

Where, K_r is the rate constant

With the help of eqⁿ (3) (3) & (4), we get

$$K_r C_A C_B = \nu K^* \left(\frac{\gamma_A \gamma_B}{\gamma^*}\right) C_A C_B$$

or, $$K_r = \nu K^* \left(\frac{\gamma_A \gamma_B}{\gamma^*}\right) \quad \text{— (5)}$$

The frequency of vibration is —

$$\nu = \frac{KT}{h}$$

where, K = Boltzmann const.

Putting the value of ν in eqⁿ (5) we get

$$K_r = \frac{KT}{h} K^* \left(\frac{\gamma_A \gamma_B}{\gamma^*}\right) \quad \text{— (6)}$$

The eqⁿ (6) is known as Eqⁿ for Transition state theory in solⁿ

* Fast Reactions :

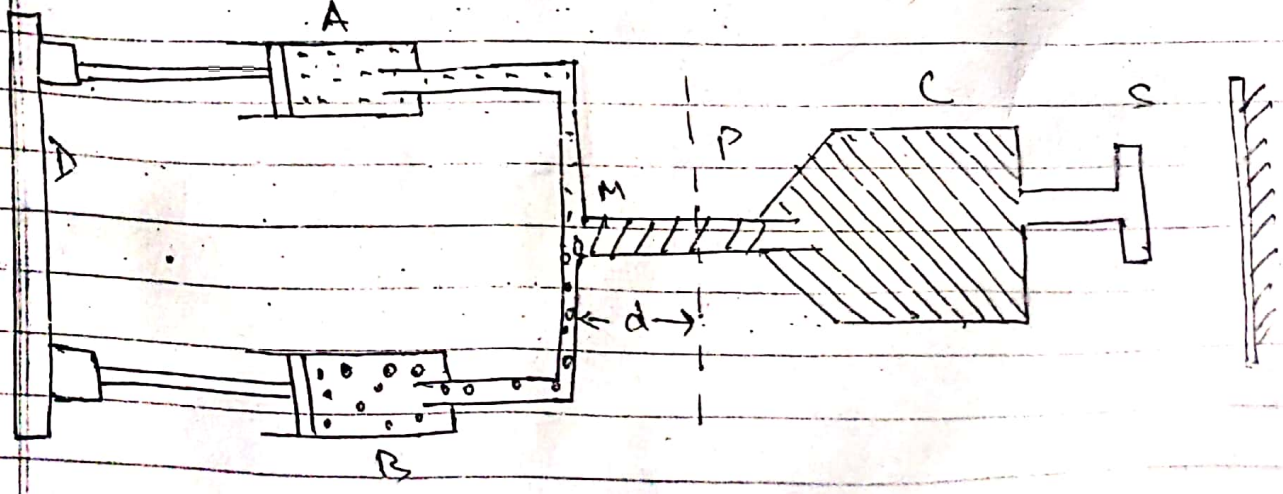
The reaction which takes place in time shorter than time required to mix the reactants and which cannot be investigated by conventional method, is called Fast reaction.

Powerful experimental techniques have been developed to study the kinetics of fast reactions. Some of the important methods are —

(1.) Stopped flow method
(2.) Flash Photolysis
(3.) Relaxation technique method

(1.) STOPPED FLOW METHOD

The stopped flow method is one of the most important method to measure the rate of fast reaction. The diagram of this method is as below —



A→ ::
B→ ::

Date
Page

Syringes A & B contain the separate reactants. These syringes are attached with valves. The solutions are forced into the mixing chamber (M) by means of common driving mechanism (D) consisting of an air driven system. The solution then enters into the stopping syring (C) whose plunger comes to rest against a fixed stop (S). This triggers the recording device.

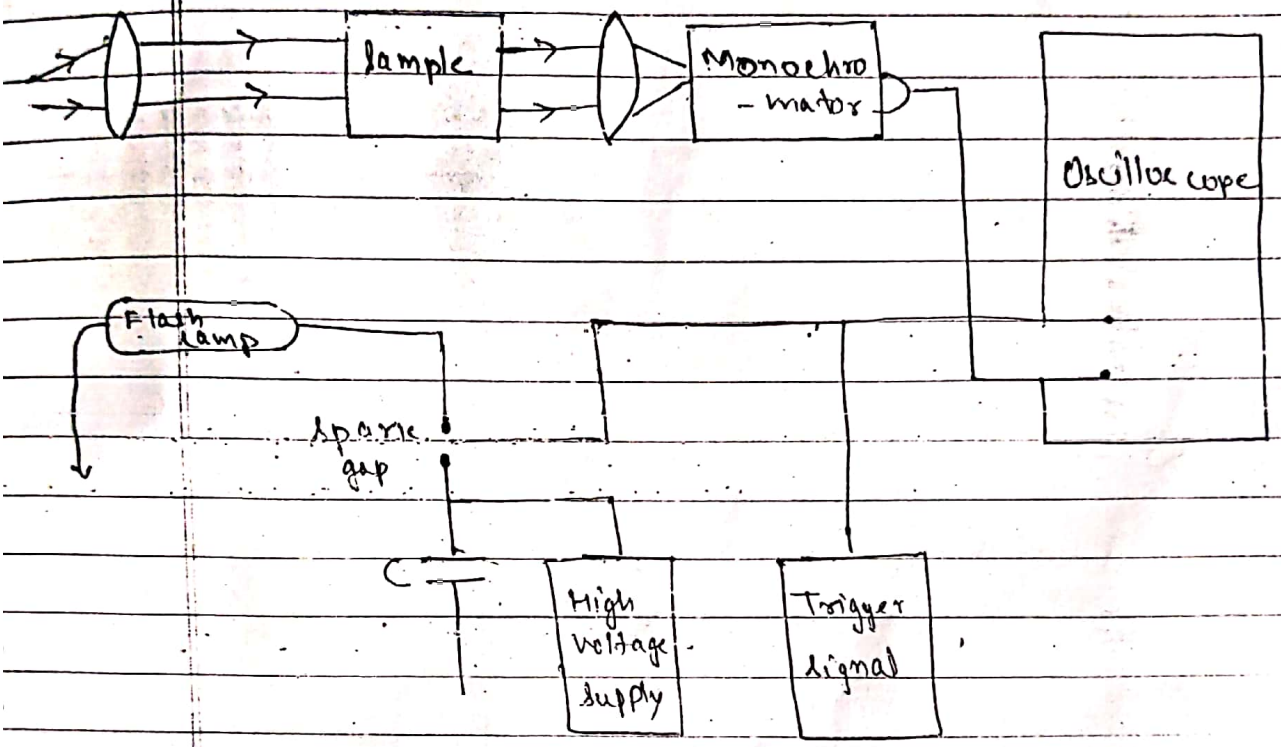
The rxn is observed in the stationary soln at a point (P) at a distance (d) from the mixing chamber. The method of detection utilises UV/visible spectrophometry. Kinetic data are obtained by measuring the value of an appropriate physical property as determined by various time after mixing the solutions with the help of suitable technique

(2) Flash Photolysis method

This method was developed by Norrish and Porter in 1949.

It may be mentioned that in a conventional photochemical rxn excited state molecules are obtained in such low conc that they cannot be studied directly. If a powerful flash of visible or UV radiation is used,

then then method is called Flash Photolysis. The apparatus used in this method is as below-



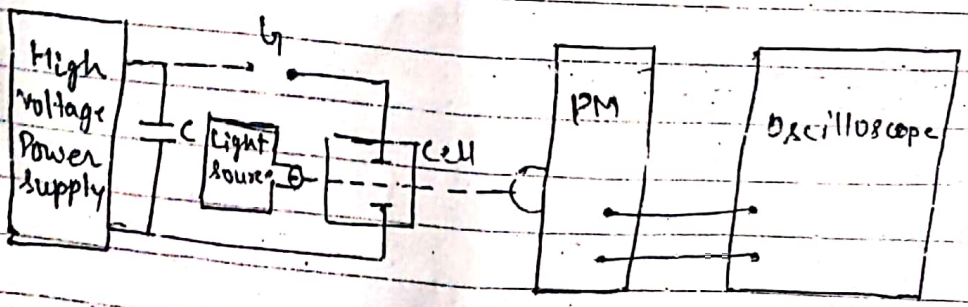
A condenser of high microfarad capacity is charged to 10000 volts by a high voltage supply by means of trigger signal a spark is produced in the spark gap which permits rapid passage of current through the flash lamp. The condenser discharges in few microseconds, the laser can produce a flash of the duration of few nanoseconds. Soon after, the capacitor discharges. The flash lamp is automatically triggered off. The rate of disappearance of the excited molecule is followed by the

rate of increase in the transmitted light which is measured with the help of an oscilloscope. In the experiment, the reactants are put in a cylindrical quartz vessel 50 cm long and 2 cm diameter which is mounted next to photolytic flash tube.

(3.) Relaxation technique

→ Eigen and his co-workers used relaxation technique to investigate fast reactions in solution. In this method the reacting system in equilibrium is subjected to a suitable variation in some physical parameters on which new equilibrium is established. The physical parameters may be temp., pressure, electric field.

When temp. is taken as physical parameter, the method is called Temperature jump method. The diagram of this method is as below -



A high voltage power supply charges a capacitor 'C', when a certain voltage is reached, the spark gap is breaks down discharging the

capacitor and sending a strong current through the cell containing the reactive system at equilibrium. As the current passes, the temp. of the system rises by about 10°C in a few microsecond. In this time interval, the conc^{n} of the reacting system adjust to a new equilibrium a/c to the temp. jump. As a result, the intensity of the light beam leaving the cell and entering the detector 'PM'. The output of the photomultiplier tube is displayed on oscilloscope. In this way the curve showing the variation of concentration versus time is displayed on oscilloscope screen.