

## M.Sc-1<sup>st</sup> Year-PHYSICAL CHEMISTRY-AS-2145

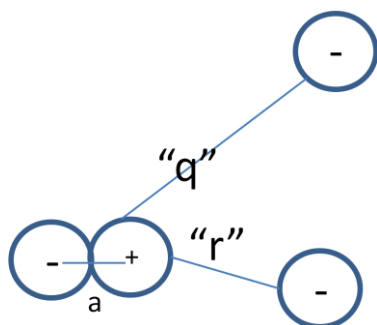
(Dr. K.V.S.Ranganath)

1. What is an oscillatory reaction: The oscillatory reaction is the variation of concentration of intermediates with time. It is very difficult to find one reaction, which goes reversible by itself. Auto catalysis is the key step in the oscillatory reactions. The most important characteristic of oscillatory reaction is steady state approximation is not applicable.

Example: Oxidation of malonic acid by  $Ce^{3+}/Ce^{4+}$  in the presence of  $H_2SO_4$

2. Physical Interpretation of Bjerrum's critical distance: The concept of association of ions to form ion pairs was studied by Bjerrum. The probability of finding two oppositely charged ions together is a minimum, can be obtained

$r_{min} = z_+ z_- \epsilon^2 / 2DKT$ . According to Bjerrum, all ions lying within a sphere of radius  $r$  should be regarded as associated to form ion-pair, whereas those outside this sphere may be considered to be free. The higher value of " $r_{min}$ ," the greater the probability of the occurrence of ion-pairs.



Where "a" is the minimum distance to form ion pair and "q" is the maximum distance to form ion pair. Force of attraction is strong if ions are at a distance of "r". The probability of formation of ion pair according to Bjerrum is given by  $4C\pi\lambda^3 \int e^{-y} y^4 dy$

3. According to Debye-Huckel theory, oppositely charged ions attract one another. As a result anions, are more likely to be found near cations in solution and vice-versa. Finally, over period of the time, it leads to the formation of ionic atmosphere. The energy, and therefore the chemical potential of any given central ion are lowered as a result of electrostatic attraction with its ionic atmosphere. This model leads to the result that at very low concentrations the activity coefficient can be calculated from Debye-Huckel Limiting Law:

$\log \gamma_{\pm} = -(z_+ z_-) A I^{1/2}$ , where  $A = 0.509$  and "I" is the dimensionless ionic strength of the solution. This indicates that log of activity coefficient must decrease linearly with square root of ionic strength. At infinite dilution, where the interionic forces are negligible; I is 0 and  $\gamma_{\pm}$  tends to 1.

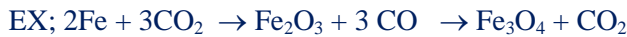
It gives the concept of ion pair formation; charging process; asymmetric and electrochromic effects explained by D-H theory. The Debye-Huckel Onsager equation is:  $\log \gamma_{\pm} = -(z_+ z_-) A I^{1/2} / (1 + B I^{1/2})$ .

The slope of  $\log \gamma_{\pm}$  vs  $\sqrt{I}$ : straight line  
slope does not depend on particular electrolyte; but only on valence.

At infinite dilution, where the interionic forces are negligible:  $I \rightarrow 0$   
 $\therefore \log \gamma_{\pm} \rightarrow 0$  (or)  $\gamma_{\pm} \rightarrow 1$

#### 4. Simultaneous reaction:

The general representation of simultaneous reaction is given by:



#### 5. Activity Coefficient:

The activity coefficient ( $\gamma_i$ ) measures the degree of departure of substance behavior from ideal or ideally dilute behavior. It is the ratio of  $a_i/x_i$ ; where  $a_i$  is the activity and  $x_i$  is the mole fraction. In ideal solution, the activity coefficient is one. ( $\gamma_i = a_i/x_i$ );  $\gamma_i$  is equal to one for ideal.

#### 6. Bimolecular Surface Reactions:

(i) Ethylene hydrogenation over platinum surfaces

(ii)  $\text{NH}_3$  synthesis catalyzed by iron

(iii) Oxidation of CO on transition metals.

(iv) Cyclohexene hydrogenation on Pt surface.

#### 7. Organic decomposition:

The breakdown of organic raw material into the final product of composting is known as organic decomposition. In organic decomposition, kinetics and mainly elementary processes believed to be playing a major part.

Ex: Pyrolysis of ethane. (main products are ethylene and hydrogen), but significant amounts of methane and butane are also formed.

#### 8. Sticking probability:

**The rate at which a surface is covered by adsorbate depends on the ability of the substrate to dissipate the energy of incoming particle as thermal motion as it crashes on to the surface. If the energy is not dissipated quickly, the particle migrates over the surface until a vibration expels it into the overlying gas or it reaches an edge. The portion of collision with the surface that successfully lead adsorption is called sticking probability. It is given by  $s =$**

**Rate of adsorption of particles by the surface**

**Rate of collision of particles with the surface before adsorption**

#### 9. Significance of excessive function:

It is thermodynamic properties of a solution of two liquids are often expressed in terms of excess function. The excess entropy  $S^E$  of a mixture is defined as the difference between the actual Entropy of the solution and the entropy of a hypothetical ideal solution with the same

Temp, Pressure and composition:  $S^E = S - S^{id}$ . Similarly we can also define excess functions of other parameters like enthalpy, volume, Gibbs free energy.

10. The decomposition of  $\text{PH}_3$  on tungsten is **First order at low pressures and zero-order at high pressures**

**Long Answer:**

2. Consider 1 mole of an electrolyte dissociating into  $v^+$  cations and  $v^-$  anions

$$G = n_s \mu_s + n \mu = n_s \mu_s + n_+ \mu_+ + n_- \mu_-$$

We know to define the activities: (“+” is for cation and “-“ is for anion)

$$\mu = \mu^\circ + RT \ln a; \quad \mu_+ = \mu_+^\circ + RT \ln a_+$$

$$\mu_- = \mu_-^\circ + RT \ln a_-; \quad \mu_{\pm} = \mu_{\pm}^\circ + RT \ln a_{\pm}$$

Relationship between a and  $a_{\pm}$ : (activity and mean activity)

We know:  $\mu_{\pm} = \mu / v$ ; where v is the valency.

$\mu = \mu^\circ + RT \ln a = v (\mu_{\pm}^\circ + RT \ln a_{\pm})$ . The relation between activity and mean activity of electrolyte is  $(a_{\pm})^v = a$

Activity Coefficient varies with concentration of a solution:

The Debye-Huckel limiting law shows that the activity coefficient is related to the **ionic strength, I** in the following way:

$$\ln \gamma = -A z_+ z_- I^{1/2}$$

where A is a constant (= 1.172 at 298 K),  $z_+ z_-$  the **valence factor** and I is the ionic strength which is define by the equation:

$$I = \frac{1}{2} \sum z_i^2 m_i$$

where  $m_i$  is the concentration of the *i*th ion concentration. The summation,  $\Sigma$ , is taken over all the possible ions in the solution.

For very concentrated solutions, using concentration based on weight of solvent may offer a better approximation than using concentration based on volume. However, at this level, we are only introducing the concept of ionic strength for the calculation of the activity coefficient.

Equivalent conductivity is the conductance of volume of a solution containing one equivalent mass of a dissolved substance when placed between two parallel electrodes; which are at distance of 1 cm apart. It increases on dilution because of decrease in conductivity is more compensated with increase in value of (1/c) on dilution.

When association occurs; At higher concentration; a non conducting pair is formed and this reduces equivalent conductance. Ion pair is more predominant in low dielectric solvent media. Conductance decreases with increase in conc. and at low dielectric constant

### 3. Fuoss model

#### The Fuoss Approach to Ion-pair formation:-

- \* Defect of Bjerrum is that identifies as ion pairs, ions are not in physical contact; the ion pair is counted as an ion pair as long as  $q < V$ .
- \* A second defect is the arbitrary final integral is terminal at 'q', i.e., the distance 'q'.
- \* Ion pair is defined in straightforward manner. For a period of time that two oppositely charged ions are in contact and at a distance of apast  $q = a$ , the two ions function as neutral dipole, considered as ion pair
- \* If  $N_{IP}$  is average n.o of ion pairs and  $N_i$  is the average n.o of ions  
 $\Theta = N_{IP} / N_i$   
 Suppose  $z^+$  +ve ions and equal n.o of -ve ions exist in a volume "V" of solution. let  $z_{IP}$  ion pairs be there, there will be  $z_{FI} = z - z_{IP}$ .  
 Now suppose one add  $z_2$  +ve ions and a similar n.o of anions.  
 $z_2 = z_{2FI} + z_{2IP}$

\* Fuoss approach, the ion association constant is

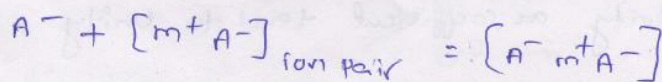
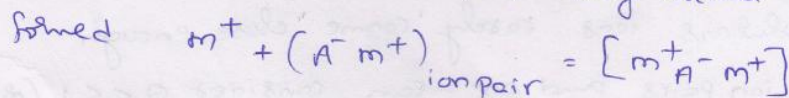
$$K_A = \frac{4\pi N_A}{3000} a^3 e^b \quad \text{where } q = a : b = \frac{z_+ z_- e_0^2}{\epsilon a kT}$$

Bjerrum constant is  $k_B = 4\pi C \int_0^b e^{-\frac{q}{a}} e^{-\frac{q}{a}} dq$

#### From Ion pairs to triple ions:-

The coulombic attractive forces given by  $\frac{z_+ z_- e_0^2}{\epsilon q^2}$   
 $\frac{z_+ z_- e_0^2}{\epsilon q^2}$  is large when dielectric constant is small.

suppose electrostatic forces are sufficiently strong, it may well happen that ion-pair "dipoles" may attract ions and triple ions formed



triple ion formation has been suggested for which  $\epsilon < 15$ .

for  $\epsilon < 10$ ; larger ionic clusters may be possible.



#### 4. Composite Reactions: Composite reactions are consecutive, simultaneous and opposing reactions

Composite reactions:-

(i)  $A + B \rightarrow C$   
 $R \propto [A][B] \Rightarrow R = k[A][B]$   
 $R$  is rate of reaction  $\downarrow$   $k$  is rate constant.

(ii)  $2A \rightarrow B$   
 $R \propto [A]^2 \Rightarrow R = k[A]^2$

The most obvious indication that a mechanism is composite is when the kinetic equation is inconsistent with the stoichiometric equation for the reaction.

Ex:  $2NO + 2H_2 \rightarrow N_2 + 2H_2O$   
 Actual:  $\nu = k[NO]^2[H_2]^2$ , but  $\nu = k[NO][H_2]$   
 This is due to

$2NO + H_2 \rightarrow N_2 + H_2O_2$  slow  
 $H_2O_2 + H_2 \rightarrow 2H_2O$  fast

Ex:  $2Icl + H_2 \rightarrow I_2 + 2Hcl$   
 $\nu = k[Icl][H_2]$ , this is due to  
 $Icl + H_2 \rightarrow HI + Hcl \rightarrow$  slow  $\therefore \nu = k[Icl][H_2]$   
 $HI + Icl \rightarrow Hcl + I_2 \rightarrow$  fast

parallel :-  $A \rightarrow Y$  } parallel. or simultaneous  
 $A \rightarrow Z$

$A + B \rightarrow Y$ ;  $A + C \rightarrow Z$  B & C compete with one another

$A + B \rightleftharpoons Z \rightarrow$  opposing reaction

$A \rightarrow X \rightarrow Y \rightarrow Z \rightarrow$  consecutive reactions

Ex:  $Cl + O_3 \rightarrow ClO + O_2$  } competing (or parallel)  
 $Cl + CH_4 \rightarrow Hcl + CH_3$

consecutive reaction:

$A \xrightarrow{k_1} X \xrightarrow{k_2} Z$

If initial conc. of 'A' is  $[A]_0$  and its conc. at any time 't' is 'A', the rate equation for 'A' is

$-\frac{d[A]}{dt} = k_1[A]$   
 $[A] = [A]_0$  when  $t = 0$  gives  $-\int_{[A]_0}^A \frac{d[A]}{[A]} = k_1 \int_0^t dt \Rightarrow [A] = [A]_0 e^{-k_1 t}$

The net rate of formation of 'X' is  $\frac{d[X]}{dt} = k_1[A] - k_2[X]$

$\therefore \frac{d[X]}{dt} = k_1[A]_0 e^{-k_1 t} - k_2[X]$

This contains variables  $[X]$  & 't' and integration gives

$\frac{d[X]}{dt} + k_2[X] = k_1[A]_0 e^{-k_1 t}$

$\therefore [X] = [A]_0 \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$

The equation for 'Z' can be obtained  $[A] + [X] + [Z] = [A]_0$

$\therefore [Z] = [A]_0 - [A] - [X]$

Insertion of  $[A]$  &  $[X]$  values in above equation gives

$[Z] = \frac{[A]_0}{k_2 - k_1} [k_2(1 - e^{-k_1 t}) - k_1(1 - e^{-k_2 t})]$

Two limiting cases:  $k_1$  is small &  $k_2$  is large  $\rightarrow$  steady state approximation

$k_2$  is small &  $k_1$  is large  
 reactant is rapidly converted into intermediate 'X' which slowly forms 'Z'

Example for consecutive reactions:

$^{239}_{84}Po \xrightarrow{23.5 \text{ min}} ^{239}_{85}Np \xrightarrow{2.35 \text{ days}} ^{239}_{92}Pu$

$^{218}_{84}Po \xrightarrow{3.1 \text{ min}} ^{214}_{82}Pb \xrightarrow{26.8 \text{ min}} ^{214}_{83}Bi$

#### 4b Kinetic Chain Length:

Chain length is defined as the ratio of rate of formation of product to the rate of initial radical formation

$$v = R_p / R_i \quad (\text{OR})$$

Number of propagation steps per initiation step (OR)

Ratio of the rate of propagation step to the rate of initiation

$$\text{Chain length } (v) = v_{\text{propagation}} / v_{\text{Initiation}} = v_{\text{propagation}} / v_{\text{termination}}$$

5. (a) The adsorption of a gas is described by the Langmuir isotherm with  $K = 0.75 \text{ kPa}^{-1}$  at  $25^\circ\text{C}$ . Calculate the pressure at which the fractional surface coverage is (i) 0.15 and (ii) 0.95

The Langmuir adsorption isotherm is given by  $\theta = Kp / 1 + Kp$

“ $\theta$ ” is the fraction of the surface covered;  $K$  is the equilibrium constant; ‘ $p$ ’ is the pressure of the gas.

From the above equation,  $P = \theta / (1-\theta)K$ ;  $P = 0.15 / (1-0.15) * 0.75$ ;

$$P = 0.15 / 0.64 = 0.23 \text{ Pa.}$$

$$P = 0.95 / (1-0.95) * 0.75 = 0.95 / 0.38 = 2.5 \text{ Pa.}$$

- (b) If “ $I$ ” is the inhibitor on a unimolecular surface reaction of a gas molecule “ $A$ ”, the fraction of surface covered by  $A$  is?

$$\frac{KP}{1 + KP + KI}$$

Where “ $I$ ” is the pressure of the inhibitor and “ $K$ ” is the equilibrium constant.

6. Write the rate expressions for chemisorptions and desorption processes?

Rates of chemisorption:-

Transition State Theory of surface reactions:-

Let  $N_s$ ,  $N_g$ ,  $N^\ddagger$  be the n.o of base sites, gas molecules and activated molecules



$$\frac{c^\ddagger}{c_g c_s} = \frac{q^\ddagger}{q_g q_s} e^{-E/RT}$$

$c^\ddagger$  is conc of activated complexes  
 $c_s$  is <sup>conc.</sup> n.o of base sites  
 $c_g$  is conc. of gas molecules

$\Rightarrow$  ' $q_g$ ' can be factorized into translational, vibrational and rotational factors.

$\Rightarrow$  If the activated complex is localized on surface, it has no translational or rotational, but it undergoes vibrational motion.

$\therefore$  loose vibration is  $kT/h\nu$ ; where ' $\nu$ ' is frequency of vibration.

$$\therefore \frac{c^\ddagger}{c_g c_s} = \frac{\nu^\ddagger (kT/h\nu)}{q_g q_s} e^{-E/RT}$$

$$\therefore \nu c^\ddagger = c_g c_s \frac{kT}{h} \frac{\nu^\ddagger}{q_g q_s} e^{-E/RT}$$

where ' $\nu$ ' is the frequency of vibration of activated complexes

product of conc. of  $c^\ddagger$  complexes and frequency of their transformation.

i.e. adsorption process; which is given by on rightside.



### Rate of Desorption:-

\* Desorption of undissociated molecules held in a layer.

\* Desorption from such a layer involves an activation in which the molecule has acquired the necessary configurational and activation energy to escape from the surface.

$$\therefore k = \frac{c_{\neq}}{c_a} = \frac{N+1/S}{N/S} = \frac{q^{\neq}}{q_a} e^{-E_a/RT}$$

"E" is the molecular activation energy for desorption at absolute zero

$$\therefore c_{\neq} = c_a \times \frac{q^{\neq}}{q_a} e^{-E_a/RT}$$

$$= c_a \times \frac{q^{\neq}(RT/h\nu)}{q_a} e^{-E_a/RT}$$

$$\nu c_{\neq} = c_a \times \frac{RT}{h} \frac{q^{\neq}}{q_a} e^{-E_a/RT}$$

$$\underline{\underline{\nu_{-1}}} = c_a \times \frac{RT}{h} \frac{q^{\neq}}{q_a} e^{-E_a/RT}$$

The rate expression for bimolecular surface reaction of A and B gas molecules assuming that Langmuir-Hinshelwood mechanism are following

The rate expression when two molecules adsorbed on the surface of the catalyst is

$$\frac{kK_A K_B [A][B]}{(1+K_A[A]+K_B[B])^2}$$



6. What is non-ideal solution? Explain activity, activity coefficients and chemical potential?

An ideal solution is a model system in which every component has its chemical potential.  $\mu_i = \mu_i^\circ + RT \ln x_i$ ; where  $\mu_i^\circ$  is the chemical potential of the pure substance and  $x_i$  is the mole fraction of the substance. A non-ideal solution is the one that is not an ideal solution and which does not obey neither Raoult's law nor Henry's law. For non-ideal solution, chemical potential is given by  $\mu_i = \mu_i^\circ + RT \ln a_i$ ; where  $a_i$  is the activity of  $i^{\text{th}}$  ion.  $a_i$  replaces  $x_i$  in the expression for  $\mu_i$  in a non-ideal solution.  $a_i = x_i$  for ideal solution; when  $a_i = 0$ :  $\mu_i = \mu_i^\circ$

$$\mu_i - \mu_i^{\text{Id}} = (\mu_i^\circ + RT \ln a_i) - (\mu_i^\circ + RT \ln x_i) = RT \ln (a_i/x_i)$$

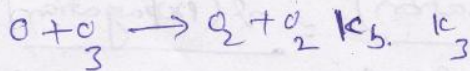
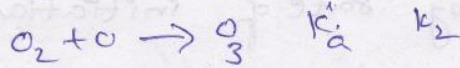
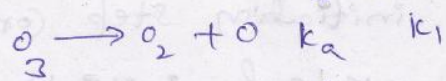
$(a_i/x_i)$  is the measure of departure from ideal behaviour and it is known as activity coefficient ( $\gamma_i$ )

For non-ideal solutions:  $\mu_i = \mu_i^\circ + RT \ln \gamma_i x_i$ ; if  $\gamma_i = 1$  for ideal solution. If only single component is present in the system, then  $x_i = 1$  and  $\gamma_i$  is also one; then  $\mu_i = \mu_i^\circ + RT \ln \gamma_i$ . It becomes  $\mu_i = \mu_i^\circ$

$\mu = (\partial G / \partial n_i)_{T, P, i \neq j}$  It is a measure of reactivity of a component in the solution. Thermodynamic function of a substance in a system that is the partial differential of the Gibbs functions of the system with respect to the number of moles of the substance. Symbol  $\mu$

8.

Derive the rate law for decomposition of ozone in the reaction  $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$  on the basis of mechanism.



$$\frac{d[\text{O}]}{dt} = k_a[\text{O}_3] - k_a'[\text{O}_2][\text{O}] - k_b[\text{O}][\text{O}_3] = 0$$

$$[\text{O}_2] = \frac{k_a[\text{O}_3][\text{O}]}{k_a'[\text{O}_2] + k_b[\text{O}]}$$

$$[\text{O}] = \frac{k_a[\text{O}_3]}{k_a'[\text{O}_2] + k_b[\text{O}_3]} = \frac{k_1[\text{O}_3]}{k_2[\text{O}_2] + k_3[\text{O}_3]}$$

$$\frac{d[\text{O}_2]}{dt} = k_a[\text{O}_3] - k_a'[\text{O}_2][\text{O}] + k_b[\text{O}][\text{O}_3]$$

$$= k_a[\text{O}_3] - k_a'[\text{O}_2] \frac{k_a[\text{O}_3]}{k_a'[\text{O}_2] + k_b[\text{O}_3]} + k_b[\text{O}_3] \frac{k_a[\text{O}_3]}{k_a'[\text{O}_2] + k_b[\text{O}_3]}$$

$$\frac{d[\text{O}_2]}{dt} = \frac{-2k_a k_b [\text{O}_3]^2}{k_a'[\text{O}_2] + k_b[\text{O}_3]} = \frac{-2k_1 k_3 [\text{O}_3]^2}{k_2[\text{O}_2] + k_3[\text{O}_3]}$$