First Year

Paper III : Physical Chemistry I

Unit: I

Thermodynamics:

Thermodynamics of systems of variable composition. Partial Molar quantities, a partial. Molar volume. Experimental determination, chemical potential, Gibbs Duhem equation - Thermodynamic properties of real gases - Fugacity, determination of fugacity of real gases. The concept of activity for condensed states. Thermodynamic equation of states- derivation and application. Maxwell's thermodynamic relations.

Thermodynamic properties at absolute Zero:

De Dondee treatment of chemical equilibrium - non-equilibrium thermodynamics, entropy production, onsager reciprocal relationship.

Three component systems - partially miscible three liquid systems, formation of one Pair, two pairs and· three pairs of partially miscible liquids. Systems composed of two solids and a liquid. crystallisation of pure component only, formation of solid solution and partial miscibility of solids Phases.

Unit II

Quantum Mechanics - I

Postulates of quantum Mechanics. Schrodinger time-independent equation - wave function; operators - linear and hermitian operator, method of setting up quantum mechanical operators. Eigen function and Eigen values. Degeneracy, Orthogonality and normalisation of wave function. Commuting and non - commuting operators. Non- commuting operators and uncertainty principle.

Application of quantum mechanics of simple system - free particle, particle in 1D. Box. particle in 3D (Cubic box and rectangular) Box, simple harmonic oscillator rigid rotatar and hydrogenatom.

Unit III

Quantum Mechanics - II

Approximation method - perturbation theory (first order only) and varriation method secular equation and secular determinants. Helium atom and effective nuclear charge. Electron spin and paul's principle. Slater deteminant, Born - Oppenheimer approximation. Hatree Fock self consistent field method of many electron systems.

I.CAO approximation MO method for H_2^+ and H_2. VB treatment of hydrogen moleclde. Hybridisation Huckel theory of conjugated systems, bond order and charge density calculation, Application to ethylene and butadiene

UnitIV

Statistical Thermodynamics:

Aim of statistical thermodynamics. Boltzman distribution law and its derivation. Partition function. Derivation of expression for translational rotational and vibrational partition functions. Thermodynamic properties. from partition function. Quantum statists - Fermi Dirac and Bose - Einstein statistics. Population inversion. Negative Kelvin temperature - Ensembles. Einstein and Debye theories of heat capacity of solids.

Unit V:

Electrochemistry

Debye - Huckel theory of ion iteraction, derivation and experimental verification. Activity co-efficient Debye Huckel Limiting Law. Modification of Debye Huckel Limiting law. Kinetics of electrode, processes - Bulter - volmer equation Tafel curves, Electrical double layer - zeta potential- electrokinetic phenomena.

Voltammetry and polarography - current - voltage relationships, dropping mercury electrode, half - wave potential. Applications of polargraphy. Coulometry - primary and secondary coulometric analysis, amperometric titrations, chronopotentiometry - cyclic voltammetry, Electrochemical enerrgy conversion storage and fuel cells, Thermodynamics of fuel cells.

References:

1. S. Glasstone - Thermodynamics for chemists.
2. S. Glasstone - An introduction to electrochemistry.
3. B. Viswanathan, etal Electrochemistry.
4. D.R.Crow, Principles and Applications of electrochemistry.
5. L. Antropov, Theoretical electrochemistry.
6. A.K.Chandra, Introductory quantum Chemistry.
7. J. Rajaram and J. Kuriacose, Chemical Thermodynamics
8. IN. Levine, Quantum Chem.istry.

SYLLABUS

UNIT - I

Partial Molar properties

As the thermodynamic properties E,H,S, A and G change with the change in the mass of system, they are extensive properties. When the various equations involving these thermodynamic properties were derived, an important assumption was made that the system under consideration was a closed system (ie) a system in which mass and composition do not vary. In order to extend results so obtained to open systems G.N.Lewis introduced thermodynamic property, say X, which was called Partial molar property. This property must be a function not only of temperature and pressure but also of the number of moles of various components present in the system.

Let us consider an extensive property such as volume, free energy, entropy, energy content, etc be represented by X. Suppose there are 'n' constituents in the system having $n_1, n_2 \ldots n_3 \ldots$ moles of individual components. Then the property X is a function of temperature, pressure as well as of the amounts of different constituents. Thus

$$X = f(T, P, n_1, n_2, n_3 \ldots) \qquad \ldots..(1)$$

If there is a small change in the T, P and the amounts of constituents, then change in property X is given by

$$dx = \left(\frac{\partial X}{\partial T}\right)_{p,n_1,n_2,n_3\ldots} dT + \left(\frac{\partial X}{\partial T}\right)_{T,n_1,n_2,n_3\ldots} dP + \left(\frac{\partial X}{\partial n_1}\right)_{T,p,n_2,n_3\ldots} dn_1 + \left(\frac{\partial X}{\partial n_2}\right)_{T,p,n_1,n_3\ldots} dn_2 + \ldots \quad (2)$$

The first term on R.H.S, gives the change in the value of X with temperature when pressure and composition are kept constant. The second term on R.H.S. gives the change in the value of X with pressure when T and composition are kept constant. The remaining quantities give the change in the value of X with a change in the amount of a constituent, when T, P and the amounts of other constituents are kept constant. If T and P of the system are kept constant, then dT = 0, dP = O. So the . eq (2) becomes.

$$dx_{T,P} = \left(\frac{\partial X}{\partial n_1}\right)_{T,p,n_2,n_3....} dn_1 + \left(\frac{\partial X}{\partial n_2}\right)_{T,p,n_1,n_3....} dn_2 + ...$$

First quantity on right hand side is partial molar quantity of component 1, the second quantity for the component 2 and so on.

These are represented by putting a bar over the Symbol of that particular property (ie) $\bar{X}_1, \bar{X}_2$, for the 1st,2nd component etc., respectively Thus,

in general, for any component i

$$\left(\frac{\partial X}{\partial n_1}\right)_{T,p,n_2,n_3....} = \bar{X}_1 \left(\frac{\partial X}{\partial n_2}\right)_{T,p,n_1,n_3....} = \bar{X}_2 \left(\frac{\partial X}{\partial n_i}\right)_{T,p,n_1,n_2....} = \bar{X}_i$$

Chemical Potential (or) partial Molar free energy

Consider the extensive property, free energy. Let it be represented by 'G'. Suppose that the system consists of 'n' constituents, the amounts of which present in the system are n_1, n_2, n_3 .... moles. Then the property 'G' is a function not only of temperature and pressure but of the amounts of the different constituents as well, so that we can write.

$$G = f(T, P, n_1, n_2, n_3 ...) \quad .....(3)$$

Now, if there is a small change in the temperature, pressure and the amounts of the constituents, then the change in the property G is given by

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,n_1,n_2,n_3....} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,n_3....} dp + \left(\frac{\partial G}{\partial n_1}\right)_{T,p,n_1,n_2,n_3....} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_1,n_3....} dn_2 + ...(4)$$

On the right hand side, the first quantity gives the change in the value of G with temperature when P and composition are kept constant; the second quantity gives the change in the value of G with P when temperature and composition are kept

constant; the remaining quantities give the change in the value of G with a change in the amount of a constituent, when T, P and the amounts of other constituents are kept constant.

If the temperature and pressure of the system kept constant, then

$$dT = 0 \text{ and } dP = 0$$

So, the equation (4) becomes

$$(dG)_{T,P} = \left(\frac{\partial G}{\partial n_1}\right)_{T,p,n_2,n_3....} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_1,n_3....} dn_2 + ...(5)$$

Each derivative on the right hand 'side is calleo partial molar property and is represented by putting a bar over the symbol of that particular property i.e., $\overline{G}_1$, $\overline{G}_2$ for the 1st, 2nd component etc., respectively. Thus

$$\left(\frac{\partial G}{\partial n_1}\right)_{T,p,n_2,n_3....} = \overline{G}_1 ; \left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_1,n_3....} = \overline{G}_2$$

In general, for any component ı

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_1,n_2,n_3} = \overline{G}_i$$

This quantity is called partial molar free energy or chemical potential and is usually represented by the symbol μ . Thus

$$\mu_1 = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_1,n_2,n_3} = \overline{G}_i$$

Gibb's - Duhem Equation

Free energy (G), being an extensive property, depends' not only upon the temperature and pressure of the system but also upon the composition of the system. If the system consists of a number of constituents, the amounts of which are n_1, n_2,n_3.... moles respectively, then we can write.

$$G = f(T, P, n_1, n_2, n_3, ...) \qquad ..... (3)$$

For small changes in T, P and the quantity of different constituents, the small change in free energy can be obtained by the partial differentiation of equation (3). This gives

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,n_1,n_2,n_3 ...} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,n_3 ...} dp + \left(\frac{\partial G}{\partial n_1}\right)_{T,p,n_2,n_3 ...} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_1,n_3 ...} dn_2 + ... (6)$$

If temperature and pressure are kept constant then $dT = 0$, $dP = 0$

Equation (6) becomes $(dG)_{T,P} = \left(\frac{\partial G}{\partial n_1}\right)_{T,p,n_2,n_3 ....} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_1,n_3 ....} dn_2 + ...$

$$(dG)_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + ... \qquad (7)$$

For a system of definite composition, represented by the number of moles n., n2, n3 etc., equation (7) on integration gives

$$G_{T,P,N} = n_1\mu_2 + n_2\mu_2 + ...$$

Differentiating this equation under conditions of constant T and P but varying , composition, we get

$$(dG)_{T,P} = (n_1 d\mu_1 + \mu_1 dn_1) + (n_2 d\mu_2 + \mu_2 dn_2) + ...$$

$$= (\mu_1 dn_1 + \mu_2 dn_2 + ...) + (n_1 d\mu_1 + n_2 d\mu_2 + ...) .... (8)$$

Comparing equation (4) and (5), we get

$$n_1 d\mu_1 + n_2 d\mu_2 + ... = 0 \qquad ....(9)$$

Equation (9) is known as Gibbs - Duhem equation and is valid at constant temperature and pressure for any homogeneous system.

Concept of fugacity: Making use of the free energy function G, Lewis introduced the concept of fugacity for representing the actual behaviour of real gases which is distinctly different from the behaviour of ideal gases.

Variation of free energy with pressure at constant 'T' is given by the following equation

$$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad \text{.................(10)}$$

This equation is applicable to all gases whether ideal or non ideal.

If one mole of a pure gas is under consideration, then V refers to molar volume. For an ideal gas, the above equation may be put as

$$(dG)_T = RT.\, dP/P$$

and for 'n' moles

$$(dG)_T = nRT.\, dP/P$$

$$(dG)_T = RT\ d(\ln P) \qquad \text{..................(11)}$$

Integration of equation (11) yields

$$G = G^* + nRT \ln P \qquad \text{.....(12)}$$

where G*, the integration constant, is the free energy of 'n' moles of the ideal gas at temperature T when the pressure 'P' is unity.

Equation (12), evidently gives the free energy of an ideal gas at temp 'T' and pressure P.

Integration of equation (11) between P_1I and P_2 at constant 'T' yields

$$\Delta G = \int_{P_1}^{P_2} nRT \frac{dP}{P} = nRT \ln \frac{P_2}{P_1}. \qquad \text{..................(13)}$$

The corresponding equation for 1 mole of the gas would be

$$\Delta G = RT \ln P_2/P_1 \qquad \text{........ (14)}$$

The equations (12) and (14) are not valid for real gases, Since V is not exactly equal to RT/P

In order to make these simple equations applicable to real gases, Lewis introduced a new function 'f called fugacity function. It takes the place of 'P' in equation (11) which, for real gases, may be expressed as

$$(dG)_T = nRTd(\ln f) \qquad \text{......... (15)}$$

and equation (12) integrating may be represented as

$$G = G^* + nRTd(\ln f) \qquad \text{......... (16)}$$

where G* is the free energy of n moles of a real gas when its fugacity happens to be 1.

Thus fugacity is a sort of "fictitious pressure" which is used in order to retain for real gases-simple forms of equations which are applicable to ideal gases only.

The equation (16), evidently gives the free energy of a real gas at temperature 'T' and pressure P at which its fugacity can be taken as f.

The equation (15) on integration between fugacities f_1 and f_2 at constant temperature, yields.

$$\Delta G = nRT \ln f_2/f_1 \qquad \text{........... (17)}$$

The corresponding equation for one mole of the gas would be

$$\Delta G = RT \ln f_2/f_1 \qquad \text{........... (18)}$$

As discussed above, the equations (17) and (18) are applicable in the case of real gases.

Fugacity at low pressures

The ratio f/P where P is the actual pressure, approaches unity when P approaches zero since in that case a real gas approximates to ideal behaviour. The fugacity function, therefore, may be defined as

$$\lim_{p \to 0} f/p = 1$$

Evidently at low pressures, fugacity is equal to pressure. The two terms differ materially only at high pressures.

Determination of Fugacity of a Gas

The well known equation, for one mole of a gas may be put as

$$G = G^* + RT \ln f \quad \text{.........(19)}$$

Differentiation of equation (19) with respect to pressure at constant temperature and constant number of moles of the various constituents (ie) in a closed system, gives.

$$\left(\frac{\partial G}{\partial P}\right)_T = RT\left(\frac{\partial \ln f}{\partial P}\right)_T$$

It follows that

$$\left(\frac{\partial \ln f}{\partial P}\right)_T = \frac{V}{RT} \text{...........(20)} \left(\sin ce \left(\frac{\partial G}{\partial P}\right)_T = V\right)$$

Thus at a definite temperature, equation (20) may be written as

$$RT\, d(\ln f) = VdP \quad \text{.............(21)}$$

•Since one mole is under consideration, v is the actual molar volume of the gas.

Knowing that for an ideal gas, V = RT/P the quantity a, defined as departure from ideal behaviour at a given temperature is given by

$$\alpha = \frac{RT}{P} - V \qquad \text{......(22)}$$

multiplying by dP throughout, we get

$$\alpha\, dp = RT \quad \frac{dP}{P} - V\, dp \quad \text{......(23)}$$

combining equations (21) & (23)

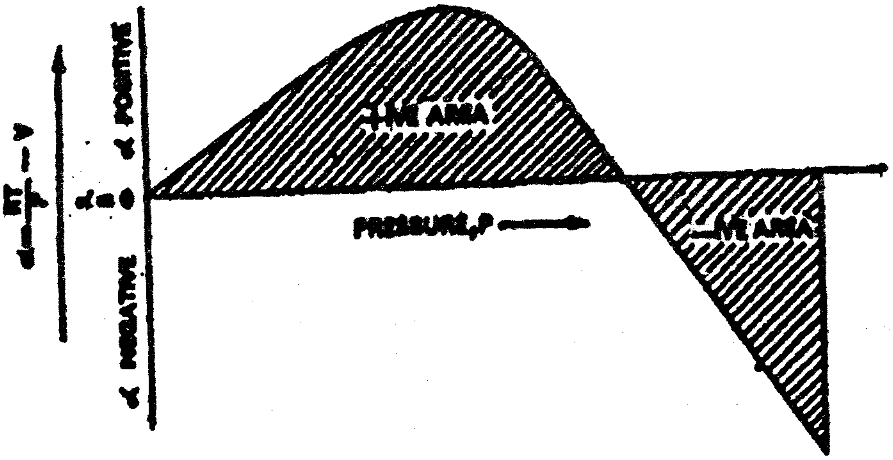
$$RT\ d(\ln f) = RT\ \frac{dP}{P} - \alpha\ dP_{\alpha} \qquad \text{......(24)}$$

$$d(\ln P) = d(\ln P) - \frac{dP}{RT} \qquad \text{......(25)}$$

Integrating equations (25) between pressures 0 and p, we have

$$\ln f = \ln p - \frac{1}{RT}\int_{0}^{P} \alpha\ (dp) \qquad \text{......(26)}$$

Now α as given" by equation (22), can be determined experimentally, at di pressures. These values of α are then plotted against corresponding pressure, as shown in the above Figure.



Plot of x (=RT/P -V) versus P for the determination of a gas

Now α as given " by equation (22), can be determined experimentally, at different pressures. Theses values of α are then plotted against corresponding pressure, as shown in the above Figure. The area under the curve between pressure $\alpha = 0$ and any given pressure P, yield the value of the integral $\int_0^P \alpha \, dP$ *as* illustrated by the shaded portion in the above Figure. Incoporating this value in equation (26), the fugacity f can be evaluated at any given pressure 'P' of the gas.

Concept of Activity:

It may be pointed out that since the absolute value of free energy or chemical potential is not known, it is not possible to evaluate μ^* of a substance. This difficulty has been overcome by referring all free energy or chemical potential measurements for any given substance to a standard reference point. Lat μ_i^0 be the chemical potential of a substance i in pure state and lef f_i be its fugacity.

So, the well known equation $\mu_i = \mu_i^* + RT \ln f_i$ becomes

$$\mu_i^o = \mu_i^{*o} + RT \ln f_i^o \qquad \text{........ (27)}$$

Let μ_i be the chemical potential of the same substance in some other state.

$$\mu_i = \mu_i^* + RT \ln f_i \qquad \text{........ (28)}$$

The difference between chemical pótential of a substance in any state and that in the pure sate is given by

$$\mu_i - \mu_i^o = RT \ln fi / f_i^o$$

$$\mu_i = \mu_i^o + RT \ln f_i / f_i^o \qquad \text{........ (29)}$$

We may introduce here a new term, activity, a and define it as

$$a = f / f_i^o \qquad \text{....... (30)}$$

for a substance i, as :

$$a_i = f / f_i^{\circ} \qquad \text{........ (31)}$$

Activity of a substance in any given state is thus defined as the ratio of the fugacity of the substance in that state to the fugacity of the same substance in the pure state.

So, the equation (29) becomes

$$\mu_i = \mu_i^{\bullet} + RT \ln a_i \qquad \text{........ (32)}$$

Activity coefficient: For an ideal gas, activity is numerically equal to its pressure (i.e.,) a = p, For real gases, however, activity is only proportional to its pressure

(i.e:,)

$$a \propto P \; (\text{or}) \; a = \gamma P$$

Where γ is known as the activity coefficient.

Thermodynamic Equation s of state

Entropy being a state function, for a pure substance, its value will depend on any two of the three variables, T, P, and V. Variation of S with 'T' and 'V'

$$S = f(T,V)$$

$$ds = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \qquad \text{........ (33)}$$

For a reversible Process in which only Pdv work and heat are interchanged with the surroundings

$$\Delta E = q - W$$

$$d_{Qrev} = dE + Pdv$$

$$TdS = dE + PdV \; (\text{or}) \; dE = TdS - PdV \qquad \text{......... (34)}$$

$$dS = 1/T \; dE + P/T \; dV \qquad \text{......... (35)}$$

Let us assume

$$E = f(T, V)$$

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dv \qquad \text{.........} (36)$$

Eliminating dE between equations (34) and (36)

$$\left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dv = Tds - Pdv$$

$$dS = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V dT \quad \text{[illegible]} \qquad \text{.........} (37)$$

Equating the coefficients of dT and dV in equations (37) and (33)

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V = \frac{C_V}{T} \qquad \text{.........} (38)$$

$$\left(\frac{\partial S}{\partial V}\right)_V = \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] \qquad \text{.........} (37)$$

From Equation (38)

$$\left(\frac{\partial E}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

Differentiating with respect to 'V' at constant T

$$\left(\frac{\partial^2 E}{\partial V . \partial T}\right) = T\left(\frac{\partial^2 S}{\partial V . \partial T}\right)$$

Similarly Equation (39) becomes

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left[\left(\frac{\partial S}{\partial V}\right)_T - P\right]$$

Differentiating with respect to 'T' at constant V

$$\left(\frac{\partial^2 E}{\partial V . \partial T}\right) = T\left(\frac{\partial^2 S}{\partial V . \partial T}\right) + \left(\frac{\partial S}{\partial V}\right)_T - \left(\frac{\partial P}{\partial T}\right)_V$$

E being a state function, the order of differentiation is immaterial and so equating the two second differential Co-efficients.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \text{........ 40)}$$

Equation (40) is one form of Maxwell's Relation.

Substituting equation (38) and (40) in equation(33)

$$ds = C_V \frac{dT}{T} + \left(\frac{\partial P}{\partial T}\right)_V \partial V \qquad \text{........ (41)}$$

For constant volume process, dV = 0 and equation (41) reduces to

$$ds = C_V \frac{dT}{T} \qquad \text{........ (42)}$$

For n moles of an ideal gas PV = nRT

$$\left(\frac{\partial P}{\partial T}\right) = \frac{nR}{V}$$

So, equation (41) becomes

$$dS = nC_V \frac{dT}{T} + nR.\frac{dV}{V} \qquad \text{........ (43)}$$

Substituting for $\left(\frac{\partial S}{\partial V}\right)_T$ from (39) in equation (40)

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \frac{P}{T}$$

(or)

$$\left(\frac{\partial E}{\partial V}\right)_T = \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] \qquad \text{........ (44)}$$

Equation (44) is known as the thermodynamic equation of state and is applicable to all systems, ideal or real

Variation of 'S' with Temperature and Pressure

$S = f(T,P)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \qquad \text{........ (45)}$$

$H = E + PV$

Complete differential gives

$dH = dE + PdV + VdP = TdS + VdP = (. TdS = dE+PdV)$

$$TdS = dH - VdP \qquad \text{........ (46)}$$

$H = f(T,P)$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad \text{........ (47)}$$

From (46) and (47)

$$Tds = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP - VdP$$

$$dS = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP \qquad \text{........(48)}$$

Comparing equation s (45) and (48)

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P = \frac{Cp}{T} \qquad \text{........ (49)}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] \qquad \text{........ (50)}$$

From equation(50)

$$\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

Differentiating with respect to 'p' at constant T

$$\left(\frac{\partial^2 H}{\partial P.\partial T}\right)_P = T\left(\frac{\partial^2 S}{\partial P.\partial T}\right)$$

From equation (50)

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V \qquad \text{........ (A)}$$

Differentiating with respect to 'T' at constant P

$$\left(\frac{\partial^2 H}{\partial T.\partial P}\right) = T\left(\frac{\partial^2 S}{\partial T.\partial P}\right) + \left(\frac{\partial S}{\partial P}\right)_T + \left(\frac{\partial V}{\partial T}\right)_P$$

H being a state function, the second differential coefficients can be equated.

so,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{........ (51)}$$

Equation (51) is another form of Maxwell's relations

Inserting equations (49) and (51) into equation (45)

$$dS = C_P\frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P .dP \qquad \text{........ (52)}$$

For n moles of an ideal gas

$$V = nRT/P \text{ and } \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

So, equation (52) becomes

$$ds = nC_P\frac{dT}{T} - nR.\frac{dP}{P} \qquad \text{........ (53)}$$

Substituting equation (51) in to (A)

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

Equation (54) is another thermodynamic equation of state

Maxwell Relations

Maxwell used the two laws of thermodynamics and deduce six fundamental differential relations among the basic thermodynamic coordinates. These relations are known as Maxwell's thermodynamical relations and are applicable to all thermodynamical systems.

The state functions E, H, P, V, T, A, G and S are related by means of four fundamental equations I to IV.

$$dE = Tds - PdV \quad ..... (I)$$

$$dH = TdS + VdP \quad ..... (II)$$

$$dA = - PdV = SdT \quad ..... (III)$$

$$dG = VdP - SdT \quad ..... (IV)$$

These equations (I) to (IV) is in the form of $dx = Mdy + NdZ$, where 'X' is a single valued function of the variables Y and Z (ie) a thermodynamic property of a closed system and dx is an exact differential. M and N are also functions of Y and Z such that

$$\left(\frac{\partial X}{\partial Y}\right)_z = M \left(\frac{\partial X}{\partial Z}\right)_Y = N$$

$$\frac{\partial^2 X}{\partial Y \partial Z} = \left(\frac{\partial M}{\partial Z}\right)_Y \quad .... (55)$$

$$\frac{\partial^2 X}{\partial Y \partial Z} = \left(\frac{\partial N}{\partial Y}\right)_Y \quad .... (56)$$

It follows Euler's criterion that

$$\left(\frac{\partial M}{\partial Z}\right)_y = \left(\frac{\partial N}{\partial Y}\right)_z$$

The same above procedure were applied and considering the Euler's criterion for the above four equations, we get the four different forms of Maxwell's Relations.

Example

$$dE = TdS - PdV \qquad \ldots\ldots\ldots (57)$$

Equation (57) differentiated with respect to 'S' at constant V

$$\left(\frac{\partial E}{\partial S}\right)_V = T \qquad \ldots\ldots\ldots (58)$$

Equation (57) differentiated with respect to 'V' at constant S

$$\left(\frac{\partial E}{\partial V}\right)_S = -P \qquad \ldots\ldots (59)$$

Equation (58) differentiated with respect to 'V' at constant S

$$\left(\frac{\partial^2 E}{\partial V . \partial S}\right)_V = \left(\frac{\partial P}{\partial V}\right)_S \qquad \ldots\ldots\ldots (60)$$

Equation (59) differentiated with respect to 'S' at constant V

$$\frac{\partial^2 E}{\partial V . \partial S} = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \ldots\ldots\ldots (61)$$

Comparing equation (60) to (61) with Euler's criterion then we get

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_P$$ - Maxwell's Relation - I

Similarly when same procedure were applied to equations (II), (III) and (IV), we get the remaining forms of Maxwell's relations

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$ Maxwell's Relation - II

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$ Maxwell's Relation - III

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$ Maxwell's Relation - IV

ENTROPY PRODUCTION

The branch of science dealing with the study of thermodynamic properties of the systems which are not in equilibrium and involve transport processes which are irreversible is termed as Non-equilibrium or Irreversible thermodynamics or Thermodynamics for Irreversible processes.

The entropy of an isolated system in equilibrium is maximum. Hence if such a system is not in equilibrium, the entropy will increase but may not decrease i.e., equilibrium lies in the direction of increasing entropy. This is termed as "entropy production."

The concept of entropy production in an irreversible process may be understood in a simple manner as follows. It is known that

$$dS \geq \frac{dQ}{T}$$

or which can be rearranged in the form

$$dS - \frac{dQ}{T} \geq 0$$

The quantity on the left is greater than or equal to zero.So we may write

$$dS - \frac{dQ}{T} = d\sigma \qquad \text{........} (62)$$

where $d\sigma$ will be either zero or positive.

If it is assumed that the system is in contact with a reservoir at T, and a quantity of heat dQ flows into the system, then a quantity, -dQ, flows in the reservoir. If the quantity, -dQ, is transferred reversibly to the reservoir, then the entropy change of the reservoir is

$$dS = -\frac{dQ}{T} \qquad \text{........} (63)$$

so that the Eq. (62) can be written as

$$dS + dS_{res} = d\sigma \qquad \text{........} (64)$$

The quantity $d\sigma$ refers to the entropy increase of the system plus that of the surroundings (the reservoir). The $d\sigma$ is called the entropy production of the process. For an irreversible process, the entropy production is positive while for a reversible process, the entropy production is zero.

Onsager Reciprocal Relations

These are also relations in which thermodynamics of irreversible processes is based. Onsager gave the following fundamental theorem pertaining to such irreversible processes:

If one makes a 'proper choice' of the fluxes J_i and X_i, the matrix of phenomenological coefficients L_{ik} would be symmetric, i.e.,

$$L_{ik} = L_{ki}\left(i, k = 1, 2, ...n\right) \qquad ..... (65)$$

These identities are termed as Onsager reciprocal relations. The notion of proper choice of fluxes and forces may be explained as follows.

If the state of the system (local temperature, pressure etc.) may be described by a number of parameters $A_1, A_2, \ldots A_n$ with their equilibrium values $\mathring{A}_1, \mathring{A}_2, \ldots \mathring{A}_n$, then deviation of state parameters from their equilibrium values is termed as state variable α. Hence.

$$\alpha_i = A_i - \mathring{A}_1 \, (i = 1, 2, ...n)$$

Now we will define the proper choice of fluxes and forces as the time derivative of the state variable α_i:

$$J_i = \alpha_i \left(i = 1, ...n\right) \qquad ..... (66)$$

and the following combination of the state variables α_i :

$$X_i \, \frac{\partial}{\partial \alpha_1}(\Delta S)\left(i = 1, 2, ...n\right) \qquad ..... (67)$$

where ΔS represents the deviation of the eneropy from the equilibrium value.

As entropy gets increased in irreversible process, this change in entropy ΔS from the equilibrium value can be put as a function of the state variables, i.e.,

$$\Delta S = \frac{\partial}{\partial \alpha_1}(\Delta S)\,\alpha_1 + \frac{\partial(\Delta S)}{\partial \alpha_2}\alpha_2 + ...$$

$$= \sum_i \alpha_i \, \frac{\partial(\Delta S)}{\partial \alpha_i}$$

$$= \sum_i J_i X_i \qquad \text{.... (68)}$$

In order to illustrate the above derived quantities e.g, fluxes and forces, we will consider a system which is composed of two parts, both enclosed within the same rigid adiabatic enclosure. Suppose the two parts are at uniform temperatures T_1 and T_2, if dQ represents. the amount of heat flow from part at temperature T_2 to that at T_1 then increase in entropy of the system would be given as follows:

$$dS = dQ\left[\frac{1}{T_1} - \frac{1}{T_2}\right] = dQ \cdot \frac{T_2 - T_1}{T_1 T_2}$$

$$= dQ \cdot \frac{\Delta T}{T^2}$$

Where $T_2 - T_1 = \Delta T$ and $T = \sqrt{(T_1 T_2)}$.

Hence rate of entropy production would be as follows :

$$S = Q\frac{\Delta T}{T^2} \qquad \text{..... (69)}$$

As heat flow, called flux, denoted by Q occurs due to temperature gradient, called force, denoted by ΔT, we can put

$$Q = J, \text{and } \frac{\Delta T}{T^2} = X_i \qquad \text{..... (70)}$$

so that eq. (69) would becomes as follows :

$$S = Q_i X_i$$

This is thus as eq. (68)

On Putting relations (70) in the following equation

$$J_i = \sum_{k=1}^{n} L_{ik} X_k \,(i = 1, 2, \ldots. n)$$

we get

$$Q = L\frac{\Delta T}{T^2}$$

THREE COMPONENT SYSTEMS C=3

(a) General. Phase Rule; F = 3 - P + 2 =5 -P

If F = 0, P is maximum, thus for invariant system five phases must be present together. The invariant system will exist at a quintuple point. Out of five phases for three component system, the maximum number of liquid phase would be only three, vapour phase only one (since vapours are miscible completely) and solid phase only 1.

Thus at quintuple point 3 liquid, one vapour and one solid phase may be present or 3 solid, 1 liquid, and 1 vapour phase or any other combinatior

As the number of phase diminishes the variance of the system increases. Maximum number of degree of freedom (variance) is 5 - 1 =4. Thus for the complete description of the phase diagram of a ternary system four variables viz. , the temperature, pressure and the mole fractions of any two components must be known. The phase diagram needed will be four dimensional, which in not easy to draw. This problem can be solved by keeping the temperature and the pressure constant. In considering a three-component system, the vapour phase is considered to be absent and such a system is called a condensed system.

(b) Graphical Representation: For a three - component system having a single homogeneous phase, the degree of freedom is given by.

$$F= C +2-P=3+2-1 = 4$$

The four variables are pressure, temperature and concentrations of any two of the three components. The graphical representation of a system having four coordinates is not possible. However, if pressure and temperature are kept constant then the degree of freedom reduces to two and the system can be represented on a two-dimensional plane. Several schemes have been in use for representing the equilibria in three component systems, but the equilateral triangle method suggested by Gibbs and Roozeboom is extensively used.

The Triangular Diagram

The composition of a three-component system is shown in a triangular diagra using the Gibbs-Roozeboom triangle (Fig. 3.43).

The various properties of equilateral triangle are then used to discuss the phase digram of a three component system.

(i) The vertices A, B, C of the equilateral triangle represent the three pure components.

(ii) The sides of the triangle represent the compositions of different binary systems. Side AB represents the composition of the binary system (A +B). On line AB, the concentration of the component C is zero. Line AC represents the composition of the binary system (A +C) and the composition of component B will be zero. Similarly side BC corresponds to the composition of the binary system (B +C), the component A being absent on this line and on any line drawn parallel to AB the concentration of C is constant; on lines parallel to AC, the concentration of component B is constant, and on lines parallel to BC, the concentration of A is constant.

(iii) Any point within the equilateral triangle will represent the composition of a mixture of three components. The composition of each component can be determined as follows;

Calculation of the concentration of each component

In a mixture, the composition of each component is given by the distance of the point (within the triangle) from the sides of the triangle opposite to the respective veritices A, B, C. This distance is measured along the line parallel to the sides of triangle. The mole fraction of component C in the mixture (P) is the distance of P from line AB measured parallel to AC or BC i.e.,

$X_C = PX_1 = PX_2 = X_1X_2$

Similarly $X_A = BX_2$ and $X_p = AX_1$

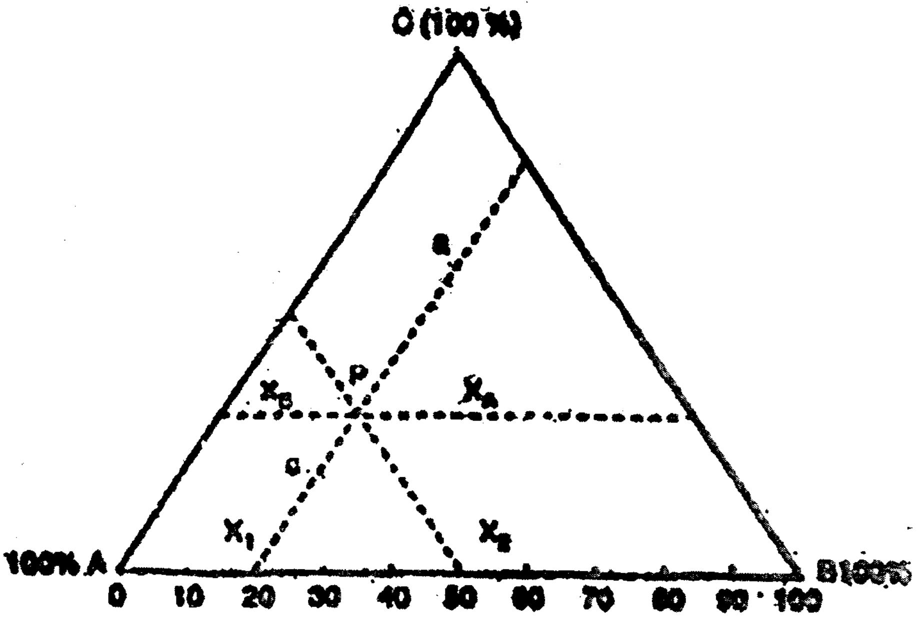


Fig.2 Graphical representation of the composition of a ternary system at constant 'T' and 'P'

Location of the point within the triangle when the composition of each component is known separately. Let $X_A = a$, $X_B = b$ and $X_C = c$, be the mole fractions of the three components A, Band C respectively. The point representing the gross composition of the ternary mixture can be located within the triangle as shown in Fig.2.

The sides of the triangle are equally divided into 100 or 10, or 5 parts. A portion $BX_2 = a$ is measured off on the AB which will give the concentration of A ; a portion $AX_1 = b$ measured off on the line AB will be concentration of component B. The remainder length $X_1X_2 = c$ will be equal to the concentration of the- third component C. The lines parallel to the sides of the triangle are drawn from points X_1 and X_2. The point of intersection of the two parallel lines will represent the gross composition of the ternary mixture as shown in Fig.3.

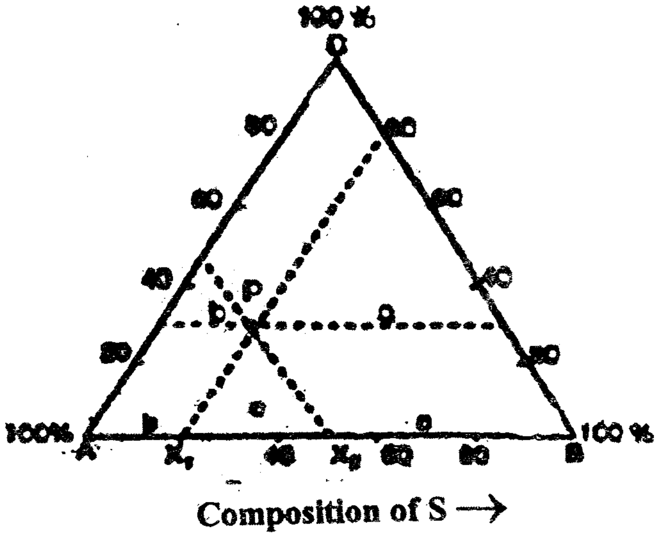


Fig.3. Location of a point within the triangular diagram

We have already indicated that unless the equilibrium system of a three-component system is considerably simplified by imposing a number of restrictions, it is not possible to study the equilibrium by constructing phase diagrams. The vapour phase is considered to be absent and now it is also assumed that no solid phase is involved in the equilibrium, i.e., the system consists of three liquid phases only.

THREE - COMPONENT LIQUID SYSTEMS

Systems consisting of three liquids can be divided into three main categories depending on the nature of the substance, and the experimental temperature.

1. Two liquids A - C, and B-C are completely miscible, and A-B only partially miscible. Example: (i) Water -Chloroform-Acetic Acid, (ii) Acetone - Water-Phenol.

2. One pair B-C is completely miscible. The pairs A - C, and A-B are only partially miscible. Example. Water-Phenol-Aniline.

3. All are only partially miscible.

4. All are completely miscible into each other.

One Pair of Partially Miscible Liquids. Of the three components A,B and C, one is completely miscible with the other two separately and the other two are only partially miscible between themselves, e.g., A is completely miscible with either B or C, but B is only partially miscible with C, Examples of such systems are $CH_3COOH + CHCl_3 + H_20$, $ROH + C_6H_6 + H_2O$ and $C_2H_5OH + CH_3COOC_2H_5 + H_2O$.

Suppose a mixture of Band C is taken at a constant temperature. As the two liquids are mutually partially miscible, the mixture will form two conjugate solutions given by the points b and c (Fig. 4). As some A is added to the system, A will distribute itself between the two layers (A is completely miscible with Band C) and the layers become conjugate ternary solutions. The compositions of these two solutions are given by the points b' and c'. The tie line b'c' will not be parallel to BC because the distribution of A among the two layers is unequal.

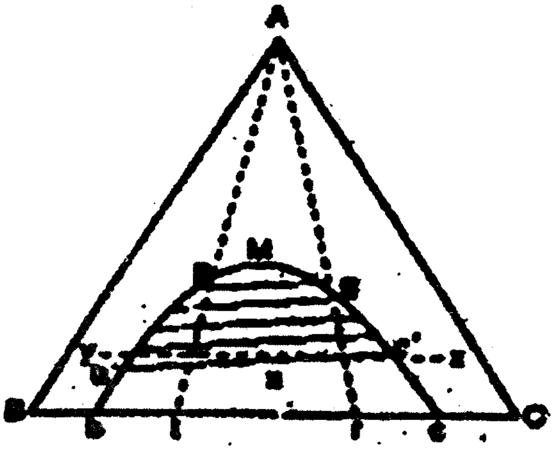


Fig.4. Properties of a three component liquid system of one pair of partially miscible liquids

At any point x on this tie-line, the relative amounts of the conjugate solutions b' and c' are given by c' x / b' x. As the amount of A is increased the miscibility of Band C increases until at the point P, the liquids become completely miscible. This is called the critical point or plait point. The curve obtained by joining different points indicating compositions of the two layers i.e. b P c, is . called a binodal curve. The binodal curve passes through a maximum at M. M generally does not coincide with the plait point P.

Any point outside the curve bPMc represents a one phase system, all the' three liquids being completely miscible among themselves. As pressure, and temperature are fixed, the degree of freedom of this region must be 2. Inside the binodal curve the system is a two-phase and consequently F = 1. An example of the system described is B= $CHCl_3$, C = H_2O and A = CH_3COOH. If the initial composition of the mixture of Band C is r, then as increasing amounts of A are added, the composition of the whole system changes along rA. It may be seen from the points of intersection of rA and the tie lines that as A is increased, the proportion of the left hand layer decreases until at the point S, the two layers coincide to form a single phase. Thus between S and A, the system is homogeneous and one phase. The same is observed for any line rA except when the line passes through the plait point P, e.g., tP A, along tP A, instead of one layer disappearing steadily, two layers remain, but their composition approach each other and becomes identical at P.

When the proportion of A is kept constant and Band C are varied, the system changes along the line YZ. Thus at Y, the system is one-phase and as C is added more and more another phase appears as the binodal curve is reached. Within the binodal curve the system remains two-phase and then again becomes one-phase when the proportion of C increases beyond the binodal curve. This change, however, is observed only with systems containing lesser amount of A than that corresponds to the maximum point M. When the original composition lies between P and M, then the conversion of one liquid layer to two takes place for a, system which always contains more of the component A than that at the plait point P. Such solutions are said to show retrograde solubility.

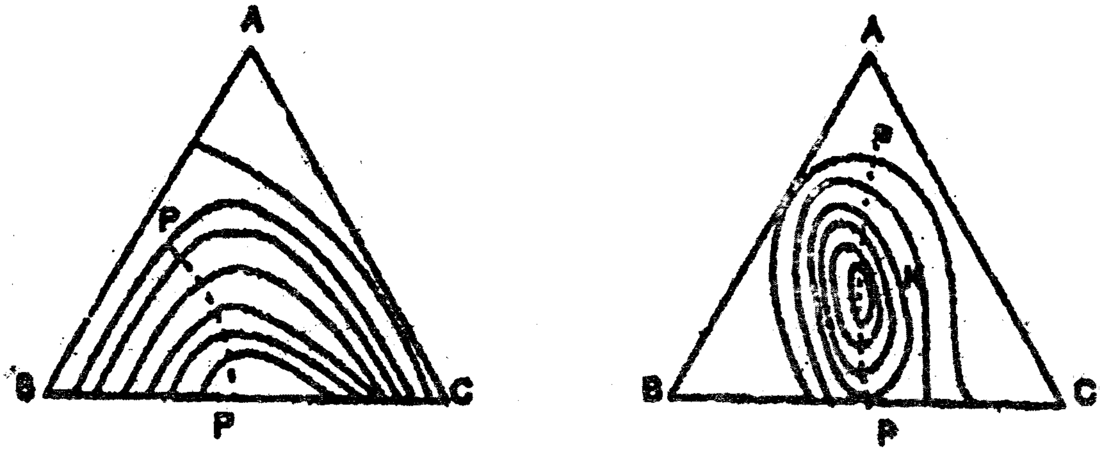


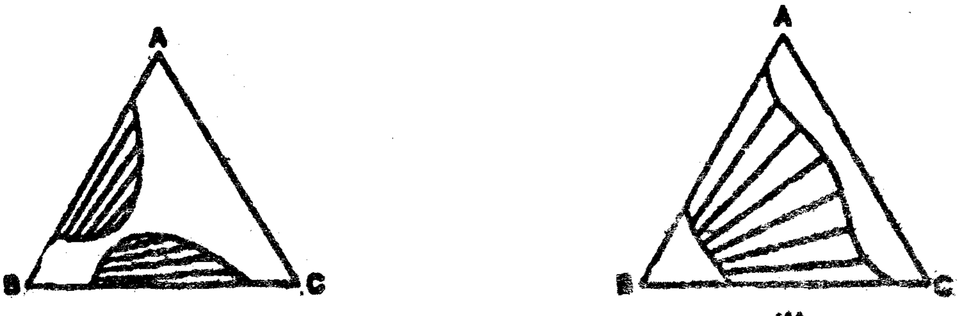
Fig 5 Binary and ternary solution temperatures for three-component liquid systems consisting of one partially miscible liquid pair.

The influence of temperature on the mutual solubilities may be studied by drawing a number of isothermal binodal curves in a triangular diagram. Two types of behaviour are found. Solubility generally increases with temperature and hence the area enclosed by the binodal curves becomes smaller and smaller until the curve coincides with the line BC (Fig. 5a). At this temperature, Band C becomes completely miscible and hence the temperature is the critical solution temperature of Band C. The plait points lie on PP' and P' gives the critical solution temperature. This type of behaviour is shown by the system water -aniline-phenol at 50°C.

For systems like water-acetone-phenol, the influence of temperature is given by Fig.5(b). Here, the plait points lie on PKP' and K represents the ternary critical solution temperature above which the three liquids are freely miscible. The binodal curves are of closed type and hence such a system has two plait points for each binodal curve.

Two Pairs of Partially Miscible Liquids.

Out of three liquids A, Band C, when two liquids A and B as well as Band C are partially miscible, there may be two binodal curves, as in Fig. 6(a), with their tie-lines and plait points. One example of such a system is water-ethanol-succinic nitrile between 13° and 31 ° C. At lower temperatures, the partial miscibility zone increases and the two curves may coalesoe to form a band as in Fig.6(b). The band diagram may also be obtained from a system forming only one partially miscible liquid pair. Thus it is not possible to say whether a band diagram will split up into a diagram containing 'to binodal curves on increasing the temperature. Binodal bands are given by systems like ethyl acetate- water-butanol or 2- methyl-propanol or 2-methyl-propan-2-ol etc., at 0 and 20°C. Points inside the band denote two-phase and outside the band one phase systems



(b)

Fig 6. Figures showing (a) two binodal curves and (b) binodal band

Three Pairs of Partially Miscible Liquids. Three separate binodal curves are possible for three pairs of partially miscible liquids. Points inside the binodal curves represent a pair of conjugate ternary liquids in equilibrium [fig.6)]. If the miscibility is very poor and the temperature is low then the three binodal curves may coalesce to produce a diagram as depicted in Fig.6 (b). The clear areas except DEF represent homogeneous one-phase system, the area shaded by the tie lines represent two phase systems and the area DEF represents thtee liquid phases. At constant temperature and pressure for three-phase, three-cpmponent system $F=0$ and so the composition of the three liquid layers at equilibrium must be definite at a definite temperature. The example of systems behaving like this is water-ether-succinio nitrile.

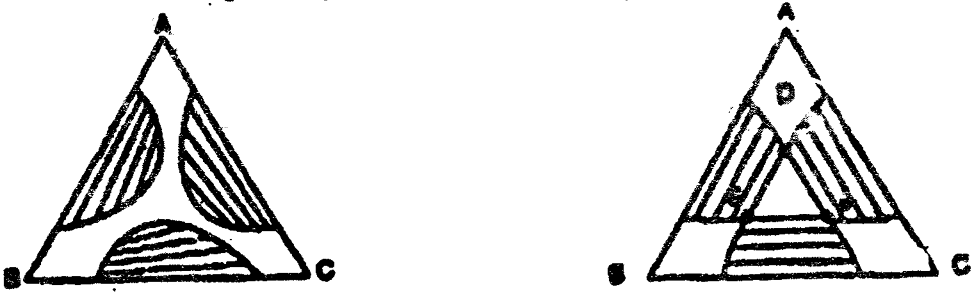


Fig. 7 (a) Three binodal curves and (b) Coalescence of three binodal curves

Two salts and water:

Type I: No Chemical Combination.

The isothermal equilibrium of this type is shown in the Fig. 8 & 9. In this diagram, points D and E represent solubilities of Band C respectively at the given temperature. When C is added to the solution saturated with B the concentration of the latter changes and follows the line DF. Similarly when added to the saturated solution of C, the composition of the solution changes along . EF. At the point F, the solution becomes saturated with both B and C. At point, the composition must be constant. That is why the point F is called the isothermal invariant point.

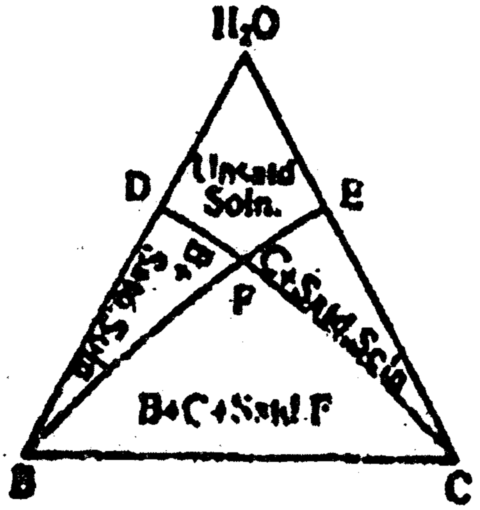


Fig. 8

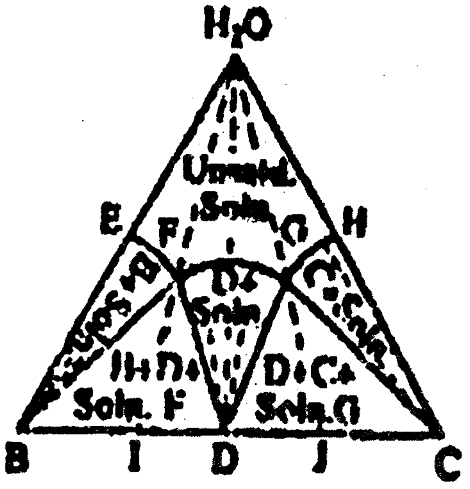


Fig.9

The area above the lines DF and FE contains only unsaturated solution. In the area DFB, there exists an equilibrium with saturated solution of composition lying along DF. The points of convergence of various sets of the lines within this area determine the nature of the solid phases, with which various solution are saturated

Corresponding to area DFB is area EFC in which the saturating phase is C.

The area a BFC is a three-phase region. At any point within his area there will be found solid B and solid C in equilibrium with saturated solution of composition F.

Examples: (i) Ammonium chloride-ammonium nitrate-water.

(ii) Sodium chloride-sodium nitrate-water.

(iii) Ammonium chloride - ammonium sulphate-water.

Type II: Double salt formed

Let us consider the first case when two salts B and C combine to form a double salt. Let the general formula of this salt be $B_n C_m$ When this double salt is formed, the composition of this will fall on the line BC [See Fig. 9].

In this diagram, point D indicates the composition of the double salt and line FG the compositions of solutions saturated with the compound. F and G are the two isothermal invariant points. The first of these solution is saturated with B and D, and the second with D and C.

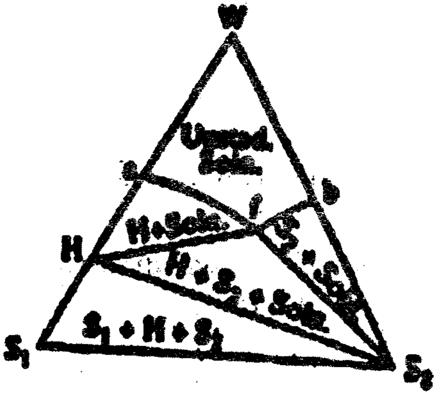
Within the area BEF there exist B and solutions. In area BFD these exists D and solution F. In the area DFG there are D and solution. In the area DGC there are D, C and solution G. In the area GHC there are C and solution and in area above the curve EFGH there is only unsaturated solution.

Example: $H_20 - AgN0_3 - NH_4N0_3$

This is an example in which the double salt of $AgN0_3$ is formed.

Type III: One salt forms a hydrate.

Suppose one of the salts say S_1 forms a hydrate in the presence of all amounts of S2. Its composition is given by point H on the line WS_1 So that WH represents the amount of anhydrous salts and HS_1 gives the amount crystallisation in the hydrate. The equilibrium diagram is as shown in Fig. 10.



In this diagram, point 'a' represents the solubility of hydrate H in water at a fixed temperature. As it is the actual solid phase in contact with the solution, it represents the composition of the solution in equilibrium with the solid hydrate. Along the saturation curve bf of S_2, no hydrate is formed.

The point 'f' is said to be non-variant because both the hydrate and solid S_2 are in equilibrium with solution and vapour.This can be easily followed from the phase rule.

$$F=C-P+2=2-3+2 = 1$$

Thus, at the fixed temperature the system is non-variant.

Any point within the area H S_1 S_2 will yield the composition of the system of completely mixture of H_1 S_1 and S_2, This is because the system does not contain sufficient water or convert all the solid S_1 into its hydrates.

Example:

System of H_20-Na_2S0_4-NaCl in which the hydrate Na_2S0_4- $10H_2O$ is formed.

Type IV: Double salt forms a hydrate :

Two cases may arise:

(i) Hydrated double salt is not decomposed by water.

(ii) Hydrated double salt is decomposed by water.

Let us consider these cases one by one.

Case (i).

The equilibrium diagram for this system is as shown Fig. 11. In system, the salt S_1 forms a hydrate H having a saturation curve ac whereas the salt S_2 is anhydrous at the given temperature. However, these two salts can form hydrated double salt. D having the formula,

$$xS_1yS_2zW$$

Where x, y and z are integers. The values x, y and z fix the position of the point D within the triangle.

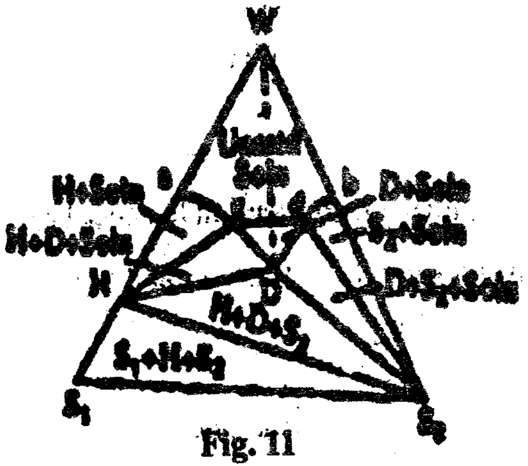


Fig. 11

As the hydrated double salt can exist as a separate solid phase, it means that it must have its own saturation curve. As the DW line cuts the saturation curve cd of the hydrated double salt, it means that the double salt does not get decomposed by water.

Within the area CdD, compound D is in equilibrium with solution along cd and may be recovered from these mixture. Points c and d are is thermal invariant points. Point c is saturated with the mixtures of H and D whereas point d is saturated with mixtures of solids D and S_2. All mixtures are completely solid below tie lines HD and DS_2.

Within the triangle HDS_2 the solid phases are H, D and S_2.

Example.

Alums having composition. such as $X_2SO_4, Y_2(SO_4)_3, 24H_2O$ are examples of this type because these are not decomposed by water.

Case (ii).

Now consider the case when the hydrated double salt is decomposed by water. The equilibrium diagram for this system is shown in the fig. 12.

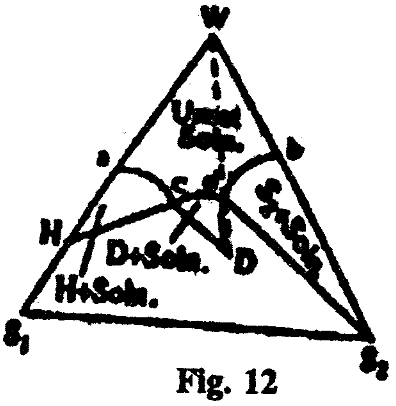


Fig. 12

In Fig. 12 the straight line DW is not meeting the saturated curve cd of the double salt, indicating that double salt is not decomposed by water. Thus, under certain conditions the preparation of the double salt is not Possible

Examples.

An example of this is $MgCl_2$. $CaCl_2$. $6H_20$ Another example of this type is $MgS0_4 \cdot Na_2S0_4 H_20$.

Category III. Formation of solid solutions.

When two solid components 8_1 and 8_2 are completely miscible in each other in the solid phase, a series of solid solutions ranging in concentration from pure S_1 to Pure S_2can be recovered from a solution of these in water. As under these conditions only two phases appear in the system no invariant point is observed. The equilibrium diagram for such a system is shown in Fig.13.

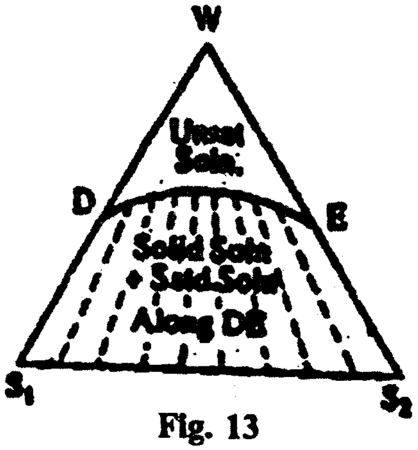


Fig. 13

In this diagram, the line DE gives the composition of saturated solution in equilibrium with solid solutions of S_1 and S_2 of compositions given by the dotted lines. In the area above DE, only unsaturated solutions can be obtained. Below this line DE, two phases occur i.e., the saturated solutions along DE and the solid solutions in equilibrium with each other.

Partial miscibility of solid phases

Fig. 14 shows the phase diagram for a system in which the solid phases S_1 and S_2 are partially miscible in each other. Under these conditions two sets of solid solutions would be formed.

(i) One of S_2 in S_1, lying between points S_1 and D and

(ii) Another of S_1 in S_2 lying between points S_2 and E..

The line FG gives the compositions of saturated solution In equilibrium with the first series of these solutions while curve HG with the second series of solid solutions.

Between points D and E mixtures of S_1 and S_2 will yield two solids of which one has the composition D and the other E. G is an isothermal invariant point because at this point the solid solutions D and E will be in equilibrium with the solution and vapour phase. If one considers any point within the triangle GDE, it gives composition of solutions in equilibrium with two solid solutions D and E.

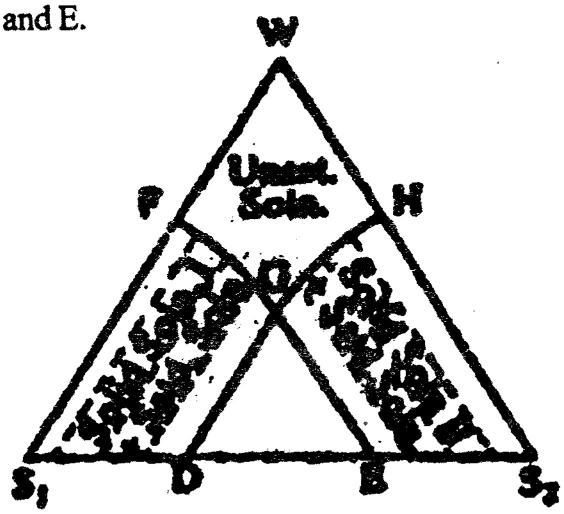


Fig. 14

UNIT - II

The Postulates of Quantum Mechanics:

The formulation of Quantum mechanics for the wave mechanical treatment of the structure of atom rests upon a few postulates.

Postulate 1 :

The state of a system is described by a wave function ψ (x, y, z, t) which contains all the information about the system.

Postulate 2 :

A physically observable quantity A of a system can be characterized in quantum mechanics by a linear operator $\hat{A}$ This operator corresponding to the classical expression for A is found by replacing each cartesian coordinate and each momentum component ϕ_x in that expression by x and

$$h/2\pi i \cdot \frac{\partial}{\partial x}$$ respectively.

Postulate 3 :

The allowed values of an observable A are the eigen values a_i in the operator equation. $\hat{A}\, \psi_i = a_i\, \psi_i$

Postulate 4 :

The average value of the property, associated with the operator $\hat{A}$ is given by

$$\langle A \rangle = \frac{\int \psi^{*} \hat{A}\, \psi\, d\tau}{\int \psi^{*}\, \Psi\, d\tau}$$

where ψ is the system state function

Postulate 5 :

The wave function that represents the state of the system changes with time according to the time dependent Schrodinger equation

$$\frac{-ih}{2\pi}.\frac{\partial\Psi(x,y,z,t)}{\partial t}=\hat{H}\psi(x,y,z,t)$$

where $\hat{H}$ is the Hamiltonian operator of a system

Operators

An operator is a symbol for a rule of transforming a given mathematical function into another function.

Ex. $\hat{A}$ denotes an operator which transforms the function f(x) into the function g(x), then we write $\hat{A}$ f(x) = g(x)

Let $\hat{A}$ be d/dx and $f(x) = ax^2$ then

$\hat{A}$ $f(x) = d/dx\,(ax^2) = 2a\,x$, i.e., $g(x) = 2ax$

Linear operator

An operator is said to be linear if its application on the sum of two functions gives the result which is equal to the sum of the operations on the two functions separately if

$\hat{A}\,[f(x) + g(x)] = \hat{A}\,f(x) + A\,\hat{A}\,(x)$

$\hat{A}\,Cf(x) = C.\,\hat{A}\,f(x)$, where C is a constant.

Example

1. d/dx is a linear operator because $d/dx\,(ax^m + bx^n)$

$$\frac{d}{dx}\left(ax^m\right)+\frac{d}{dx}\,bx^n$$

2. Square root is not a linear operator because

$$\sqrt{f(x)+g(x)}\neq\sqrt{f(x)}+\sqrt{g(x)}$$

Hermitian property of operators

The quantum mechanical operator satisfies the following condition known as Hermitian condition.

1. If an operator $\hat{A}$ has two eigen function ψ and ϕ and if

$$\int \psi(\hat{A}\phi)d\tau = \int(\hat{A}\psi)\phi d\tau$$

when ψ and ϕ are real.

$$\int \psi^*(\hat{A}\phi)d\tau = \int(\hat{A}\psi)^*\phi d\tau$$

when ψ and ϕ are complex, ψ^* is the complex conjugate of ψ and $d\tau$ is the volume element of space in which the function is defined, then the operator $\hat{A}$ is called Hermitian operator. Example: Examine if $\frac{d^2}{dx^2}$ is a Hermitian operator

If $\psi = e^{ix}$ and $\phi = \sin x$

$$\int \psi^*(\hat{A}\phi)d\tau = \int e^{ix}\frac{d^2}{dx^2}(\sin)dx = -\int e^{ix}\sin x\,dx$$

$$\int \phi(\hat{A}\psi)^*d\tau = \int \sin x\left[\frac{d^2}{dx^2}e^{ix})^*\right]dx = \int \sin x\left(i^2e^{ix}\right)dx = -\int \sin x e^{-ix}dx$$

The two integrals are the same $\frac{d^2}{dx^2}$ *is Hermitian.*

Eigen values and Eigen function

If an operator $\hat{A}$ operates on a well behaved (i.e., finite, continuous and single valued) function ψ_i to give the same function ψ_i but multiplied by a constant factor 'a' then constant factor is 'a' called the eigen value of the operator and the function ψ_i is called the eigen function $\hat{A}\psi_i = a\psi_i$

This is known as an eigen value equation

Example: If $\psi_i = e^{-ax}$ $\hat{A} = d/dx$

then $\frac{d}{dx}\left(e^{-ax}\right) = -a\left(e^{-ax}\right)$

e^{-ax} is an eigen function of d/dx and the corresponding function eigen value is -a.

Method of setting up quantum mechanical operator

1. First write the expression for the physical quantity in classical terms i.e., in terms of Cartesian coordinates of position (x,y,z) and momenta (P_x,P_y,P_z).
2. Replace there coordinates and momenta by their corresponding operators
3. Operator for a coordinate of position (say x) is multiplication by that variable x itself.
4. Operator for a coordinate of momentum (say p^x) $\frac{h}{2\pi i} \cdot \frac{\partial}{\partial x}$

Ex:- the kinetic energy of a single particle moving in one direction say x.

$$\hat{T}_x = \frac{1}{2} m V_x^2 = \frac{m^2 V x^2}{2m} = \frac{P_x^2}{2m}$$

Therefore, the K.E. operator

$$\hat{T} = -\frac{h^2}{8\pi^2 m} \frac{\partial^2}{\partial x^2}$$

$$\hat{T}_x = \frac{1}{2m}\left(\frac{h}{2\pi i} \cdot \frac{\partial}{\partial x}\right)^2$$

Degeneracy:

For every eigen function (well behaved wave function) there must be a corresponding eigen value (energy value). It means that each energy state of the system must have a wave function which will be the characteristic of the system. In other words among the various stationary states it may happen that some of them correspond to the same energy eigen values, but differ in the values of some other physical quantities. Such energy eigen values or energy levels of the system are said to be degenerate. It means that degenerate states of the system would be energetically identical.

If E_1, E_2, E_3 .... represent quantised energy levels, then corresponding to each of there values, there is atleast one eigen function ψ_n.

$$\hat{H}\psi_n = E_n\psi_n$$

ψ_n represent a set of eigen function ψ_1, ψ_2, ψ_3............

If for each energy state, if there is only one wave function, then the set of eigen functions and the energy states are non degenerate.

On the other hand if there are more than one wave function for an energy state such that

$\hat{H}\psi_1 = E\psi_1, \hat{H}\psi_2 = E\psi_2, \hat{H}\psi_3 = E\psi_3$ then it is degenerate.

Degenerate States are energetically identical.

Normalized and Orthogonal function

If $\psi^2 dx$ or $\psi\psi^* dx$ represents the probability of finding the particle at any point x, then the integration are the entire range of possible location, i.e., the total probability must be unity because the particle has to be somewhere within that

range i.e., $\int\psi^2\,dx = 1$ or $\int\psi\psi^*\,dx = 1$

In three directions $\int\psi^2\,d\tau = 1$ $(d\tau = dx, dy, dz)$ A wave function which satisfies the (above equation is known as normalized wave function and this condition is called normalisation condition. There may be many acceptable solutions to Schrodinger equation $\hat{H}\psi = E\psi$ for a particular system. Each wave function ψ has a corresponding energy value E. For any wave functions ψ_i and ψ_j corresponding to the energy values E_i and E_j respectively, the following condition must be fulfilled. $\int\psi_i\psi_j\,d\tau = 0$

Such a condition is called condition of orthogonality of the wave functions, the two functions ψ_i and ψ_j are said to be orthogonal to each other.

Commutative and Non-commutative property

When a series of operations are performed on a function successively the result depends on the sequence in which the operations are performed; in other words, in operator algebra it is not necessary that

$\hat{A}\hat{B}\, f(x)=\hat{B}\hat{A}\, f(x)$ for example let $\hat{A}$ denote $\frac{d}{dx}$ $\hat{B}$ stands for $3x^2$, and the function f(x) be sin x, then

$$\hat{A}\hat{B}\, f(x)=\frac{d}{dx}\left[3x^2.(\sin x)\right]=\frac{d}{dx}\left(3x^2 \sin x\right)=6x\sin x+3x^2\cos x$$

and

$$\hat{B}\hat{A} f(x)=3x^2.\frac{d}{dx}(\sin x)=3x^2\cos x=3x^2\cos x$$

If two operators are such that the result of their successive application is the same irrespective of the order of operations then the two operators arti said to be commutative. In the above example, the two operator are non-commutative.

Eg.,

$\hat{A}$ stand for 3+

$\hat{B}$ stand for 4+

f(x) = ax

$$\hat{A}\hat{B} f(x)=3+4+(ax)=3+(4+ax)=7+ax$$

$$\hat{B}\hat{A} f(x)=4+3+(ax)=4+(3+ax)=7+ax$$

Then $\hat{A}$ and $\hat{B}$ are commutative.

The Heisenberg uncertainty principle

According to classical mechanics one can determine, simultaneously and precisely both the position and the momentum of a body at any point in space. However, with microparticles, owing to the presence of both wave and particle characterization, their properties are different from those of macroscopic particles. As a result, it is not possible to determine accurately the position and momentum of a microparticle simultaneously. This gives rise to an uncertainty in either the position or the momentum which is however not a matter of imperfection of the experimental technique but a result of the interaction of the system with the measuring techniques.

According to Heisenberg that the product of the uncertainty in position (Δx) and the uncertainty in momentum (Δpx) along the x direction of a body, in equal to or greater than Planck's constant h

$$\Delta x.\Delta px \geq h$$

or

$$\boxed{\Delta x.\Delta px \geq \frac{h}{4\pi}}$$

Non - commuting operators and uncertanity principle:-

If the operators for two observables commute, then the two observables can have precise value simultaneously.

If the two operators do not commute, then it is not possible for the corresponding observables to have precise values simultaneously.

Consider the operators for position along the x axis X and the x component of momentum $\hat{P}_x$

$$\hat{X}\hat{P}_x\psi - \hat{P}_x\hat{X}\psi = -ith\left(x\frac{\partial y}{\partial x} - \frac{\partial}{\partial x}(X\psi)\right)$$

$$= -ith\left[-\psi\right] = it\psi$$

These operators do not commute. Consequently x and P_x cant have precise values simultaneously.

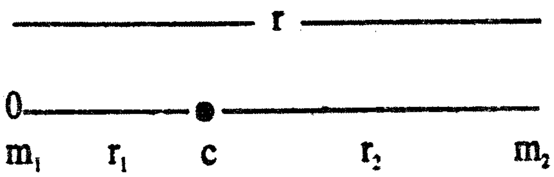
This is the basis for the uncertainity principle of Heisenberg.

Application of wave mechanics to rigid rotator

Rigid rotator - two or more particles system, in which the distance between the particles is assumed to remain fixed during rotation and cannot vary with time. The theory of such a rigid rotator is useful in dealing with the rotational spectra of diatomic molecules.

Let us consider a two particle rigid rotator like a diatomic molecule with masses mt and m2 and separated by fixed distance 'r'. The rigid rotator is a twobody problem and can be reduced to two separate one-body problems.

1. The translational motion of the system can be treated by using the total mass of the two particles and
2. The rotational motion of the particle can be obtained by considering a reduced mass μ



Let us consider the centre of mass C, of this two body problems, located at the origin of the cartesian coordinates, and let the distance of m_1 from the centre of mass be r_1 and the distance of m_2 be r_2

$$m_1r_1 = m_2r_2 \qquad ......(1)$$

$$r_1 + r_2 = r \qquad ......(2)$$

from equation (1) and (2) we get

$$m_1(r-r_2) = m_2 r_2$$

$$(m_1+m_2)r_2 = m_1 r$$

$$r_2 = \frac{m_1 r}{m_1+m_2} \qquad ......(3)$$

Similarly

$$r_1 = \frac{m_2 r}{m_1 + m_2} \qquad \text{......(4)}$$

The moment of inertia (I) of the rotating body, about the centre of mass is

$$I = m_1 r_1^2 + m_2 r_2^2 \qquad \text{......(5)}$$

Substituting the values of r_1 and r_2 in this equation we get

$$I = \frac{m_1 m_2}{m_1 + m_2} r_2 = \mu r^2 \qquad \text{.......(6)}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \text{ is the reduced mass}$$

Since the distance between the two particles is fixed, the potential energy is treated as zero. Therefore, the rigid rotator has only kinetic energy. The kinetic energy (T) of the rotation is then given by

$$T = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 \qquad \text{.......(7)}$$

Where V_1 and V_2 are the linear velocities of masses m_1 and m_2 respectively. Then in terms of angular velocity, we can write

$$T = \frac{1}{2} m_1 \omega^2 r_1^2 + \frac{1}{2} m_1 \omega^2 r_2^2 \qquad \text{......(8)}$$

$$v = \omega r$$

$$T = \frac{1}{2} \omega^2 \left(m_1 r_1^2 + m_1 r_2^2 \right) = \frac{1}{2} \omega^2 I \qquad \text{......(9)}$$

Where ω is the angular velocity. Since, angular momentum L is related to the moment of inertia, I through the relation

$$L = \omega I$$

$$T = \frac{L^2}{2I} = \frac{L^2}{2 \mu r^2} \qquad \text{......(9a)}$$

Now let us conside the two particle rigid rotator from the quantum - mechanical standpoint. The Hamiltonian operator $\hat{H}$ will contain only the kinetic energy operator. Hence

$$\hat{H} = \frac{\hat{L}}{2\mu r^2} = -\frac{h^2}{8\Pi^2\mu}\nabla^2 \qquad \text{.....}(10)$$

Where the operator corresponding to angular momentum is

$$\hat{L}^2 = -\frac{h^2}{4\Pi^2\mu} r^2\nabla^2 \qquad \text{.....}(11)$$

To solve this problem it is most convenient to use the expression of $\hat{L}^2$ in spherical polar coordinates. Therefore, Schrodinger's equation $\hat{H}\psi = E\psi$ may be written as

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\psi}{\partial\theta}\right] + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\Pi^2 I}{h^2}E\psi = 0 \qquad \text{.....}(12)$$

This equation contains two angular variables ψ and ϕ . It is solved once again by the method of separation of variables we look for a solution of form.

$$\psi = \theta(\theta)\phi(\phi) \qquad \text{......}(13)$$

Substitute this in the above equation we get

$$\frac{\sin\theta}{\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\theta}{\partial\theta}\right] + \frac{8\Pi^2 I}{h^2}\sin^2\theta = \frac{1\partial^2\phi}{\phi\,\partial\phi^2} \qquad \text{......}(14)$$

Setting both sides of equation (14) equal to a constant m^2, we get the pair of differential equations, each in one variable, as

$$\frac{\partial^2\phi}{\partial\phi^2}m^2\phi = 0 \qquad \text{.......}(15)$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\theta}{\partial\theta}\right] + \left[\beta - \frac{m^2}{\sin^2\theta}\right]\theta = 0 \qquad \text{......}(16)$$

where $\beta = \frac{8\pi^2 I}{h^2}E$ ......(17)

Equation (15) has the solution

$$\phi(\phi)=C\exp(\pm im\phi) \qquad ......(18)$$

This is an acceptable wave function provided m is an integer. This condition arises because ϕ is required to be single valued. Thus

$$\phi(\phi)=\phi\ (2\pi+\phi)$$

$$\exp(im\phi)=\exp\left[im\ \phi+2\pi\right] \qquad ....(19)$$

This requires exp (2πmi)] to be unity, in other words

$$\text{Cos}\ 2\pi m+i\sin 2\pi\ m=1$$

This is true if m = 0, ±1, ±2,±3, ... etc.,

The normalization condition gives the value $(2\pi)^{-1/2}$. The normalized solutions of equation (15) are

$$\phi\pm m(\phi)\ \frac{2}{\sqrt{(2\pi)}}\exp(\pm im\phi) \qquad ....(19a)$$

$$(m=0,1,2,3\ ....)$$

Equation (16) has its solutions the associate Lengendre polynomials $pi^{|m|}$ $(\text{Cos}\,\theta)$ where l is either zero or a positive integer and further $\ell\geq|m|$. The normalized solutions are given by

$$\theta(\theta)=\theta_{\ell}^{l,m}(\theta)=\sqrt{\frac{2\ell+1}{2}\frac{(\ell-|m|)!}{(\ell+|m|)!}}\ p_{\ell}^{|m|}(\cos\theta) \qquad ......(20)$$

The restriction on l leads to quantisation of the kinetic energy of rotation, whose values are given by

$$E=\frac{\ell(\ell+1)h^2}{8\pi^2 I} \qquad ......(21)$$

Equation. (21) is obtained from Equation (17) by substituting $\ell(\ell+1)$ for β. The total wave function of a rigid rotator is then given

$$\psi=(\theta,\phi)=\theta_{\ell\pm m}(\theta)\phi_{\pm m}(\phi)=Y_{l,\pm m}(\theta,\phi) \qquad ......(22)$$

The function $Y_{l,\pm m}$ are called spherical harmonics. The following are a few spherical harmonics.

$$Y_{0,0} = \frac{1}{2\sqrt{\pi}}; Y_{\ell} \pm 1 = \frac{\sqrt{3}}{2\sqrt{2\pi}} \text{Sin}\theta \exp(\pm i\phi)$$

$$Y_{1,0} = \frac{\sqrt{3}}{2\sqrt{\pi}} \text{Cos}\theta; Y_{2,0} = \frac{\sqrt{5}}{4\sqrt{\pi}}(3\text{Cos}^2\theta - 1)$$

$$Y_2 \pm 1 = \frac{\sqrt{15}}{4\sqrt{2\pi}} \text{Sin } 2\theta \exp(\pm i\phi);$$

$$Y_2 \pm 2 = \frac{\sqrt{15}}{4\sqrt{2\pi}} \text{Sin}^2 \theta \exp(\pm 2i\phi) \qquad \ldots\ldots(23)$$

From equation (21), the energy of a rotator does not depend on the quantum number m. The lowest state has zero energy and this is permissible according to the uncertainty principle because there is no variation in wave function, $\frac{Y_{0,0}}{Y_{0,0}}$ on the surface of the sphere.

Application of wave mechanics to harmonic oscillator

A diatomic molecule having masses m_1 and m_2 executes periodic motion with respect to centre of gravity. Such a motion is known as simple harmonic motion. In this problem a diatomic molecule is approximated to simple harmonic oscillator. Using Schrodinger equation for simple harmonic oscillator, E & ψ can be evaluated. The E values give the possible vibrational energies of the diatomic molecule, which will be useful in understanding of vibrational spectrum. Using the Eigen function, the allowed vibrational transitions can be predicted. The simple harmonic oscillator obeys classical Hooke's law.

1) Construction of Hamiltonina operator for simple harmonic oscillator

$$\hat{H}_{SHO} = \frac{-h^2}{8\pi^2\mu} \cdot \frac{\partial^2}{\partial X^2} + \frac{1}{2}kx^2$$

μ : reduced mass

The simple harmonic oscillator obeys classical Hooke's law:

$$f \; \alpha \; x$$
$$f = -kx$$

f = restoring force

k = force constant

x =displacement

The vibrational frequency of simple harmonic oscillator is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\nu^2 = \frac{1}{4\pi^2}\frac{k}{\mu}$$

$$k = 4\pi^2\nu^2\mu$$

$$P.E = \frac{1}{2}kx^2$$

Substitute the k value we get

$$P.E = \frac{1}{2}4\pi^2\nu^2\mu x^2$$

$$P.E = 2\pi^2\nu^2\mu x^2 \qquad \text{......(2)}$$

Substitute this value in the equation (1) we get

$$\hat{H}_{SHO} = \frac{-h^2}{8\pi^2\mu}\frac{\partial^2}{\partial X^2} + 2\pi^2\nu^2\mu x^2 \qquad \text{......(3)}$$

Schrodinger Equation for a simple harmonic oscillator

$$\hat{H}\psi = e\psi$$

Substitute the value of equ (3) in equ (4) we get

$$= \frac{-h^2}{8\pi^2\mu}\frac{\partial^2}{\partial X^2} + 2\pi^2\nu^2\mu x^2\psi = E\psi$$

Multiply throughout by $\frac{-8\pi^2\mu}{h^2}$

$$\frac{\partial^2\psi}{\partial X^2} + \frac{8\pi^2\mu}{h^2}\left[E - 2\pi^2\nu^2\mu x^2\right]\psi = 0$$

rewriting equ (5) we get

$$\frac{\partial^2\psi}{\partial X^2} + \left[\frac{8\pi^2\mu E}{h^2} - \frac{16\pi^4\nu^2\mu^2x^2}{h^2}\right]\psi = 0 \qquad \text{......(5)}$$

Let $\frac{8\pi^2\mu E}{h^2} = a$

$$\frac{4\pi^2 \mu \nu}{h} = b$$

Substituting this in the above eqn. we get

$$\frac{\partial^2 \psi}{\partial x^2} + \left[a - b^2 x^2\right]\psi = 0$$

Let $q = \sqrt{b}.x$

$$q^2 = bx^2$$

Once x is replaced by q

$\frac{\partial^2 \psi}{\partial x^2}$ must be replaced by $\frac{\partial^2 \psi}{\partial q^2}.b$

Replacing $\frac{\partial^2 \psi}{\partial x^2} = b.\frac{\partial^2 \psi}{\partial q^2}$ in equation (6) we get

$$b\frac{\partial^2 \psi}{\partial q^2} + \left[a - b^2 x^2\right]\psi = 0$$

Dividing throughout by b we get,

$$\frac{\partial^2 \psi}{\partial q^2} + \left[\frac{a}{b} - bx^2\right]\psi = 0$$

Where $bx^2 = q^2$

The above equation becomes

$$\frac{\partial^2 \psi}{\partial q^2} + \left[\frac{a}{b} - q^2\right]\psi = 0$$

Case: I Limit is Aysmtotic equation by b we get,

When $x \rightarrow$ large

$q \rightarrow$ large

$q^2 \rightarrow$ large

i.e., q^2 becomes $q^2 >> a/b$

Equation (7) becomes

$$\frac{\partial^2 \psi}{\partial q^2} + - \left[-q^2\right]\psi = 0$$

$$\frac{\partial^2 \psi}{\partial q^2} - q^2\psi = 0$$

(or)

$$\frac{\partial^2 \psi}{\partial q^2} = q^2\psi$$

The solution for the above equation

$$\psi = e^{\pm q^2/2}$$

There are two limiting solutions

$\psi = e^{+q^2/2}$ and $\psi = e^{-q^2/2}$

As the acceptable eigen functions or well behaved functions are considered in quantum mechanics. It should be single valued, continuous and finite.

$$\psi = e^{-q^2/2} \qquad \text{......(8)}$$

This is called asymptotic solution of equation (7)

The equation 7 is transformed into a differential equation in equation in f(q) and that diff. equation is

$$\frac{\partial^2 f}{\partial q^2} - 2q\frac{\partial f}{\partial q} + \left[\frac{a}{b} - 1\right] f = 0 \qquad \text{......(9)}$$

This is known as Hermitte equation.

The recurasion formula for the equation (9) is

$$\frac{A_{K+2}}{A_k} = \frac{2K - \left(\frac{a}{b} - 1\right)}{(K+2)(K+1)} \qquad \text{......(10)}$$

Put $A_{K+2} = 0$ and $K = n$ in equa (10)

i.e., $2n - \left(\frac{a}{b} - 1\right) = 0$

$$(2n+1) = \frac{a}{b}$$

where $a = 8\pi^2\mu E$

$$b = \frac{4\pi^2\nu\mu}{z}$$

substitute these values in the equation $(2n+1)=\frac{a}{b}$

$$2n+1 = \frac{8\pi^2\mu E}{h^2}\ \frac{h}{4\pi^2\mu\nu}$$

$$2n+1 = \frac{2E}{h\nu}$$

$$E = \frac{(2n+1)h\nu}{2}$$

$$E = h\nu\left(n+\frac{1}{2}\right)$$

When n = 0, 1,2, ... n

N = vibrational quantum number

Eigen function for simple Harmonic oscillator

Consider equation (9)

$$\frac{\partial^2 f}{\partial q^2} - 2q\frac{\partial f}{\partial q} + \left[\frac{a}{b}-1\right]f = 0$$

as the value of K are limited be n. f(q) becomes Hn(q)

W here $H_n(q) = A_0 + \frac{Aiq}{A_1q} + A2q^2 + \ldots Anq^n$ Hermitte polynomial

As $\frac{a}{b}-1=2n$ from recursion formula equation (9) becomes

$$\frac{\partial^2 H}{\partial q^2} - 2q\frac{\partial H}{\partial q}\ 2nH = 0$$

Solving its equation. We get Hermitte polynomial

$$H_n(q) = (-1)^n . e^{q^2} . \frac{\partial^n\left(e^{-q^2}\right)}{\partial q^n}$$

$$\psi_{S\mu O} = A\,H_n(q).e^{-q^2/2}$$

where A is normalization constant.

$$A = \frac{1}{\left[\sqrt{\pi}.2^{n}\left[n\right]^{2}\right]}$$

substituting this in the above equation we get

$$\psi_n \text{ for SHO} = \frac{1}{\left[\sqrt{\pi}.2^{n}\left[n\right]^{1/2}\right]}\left[(-1)^{n}\frac{\partial^{n} e^{q^2}\left[e^{-q^2}\right]}{\partial q^{n}}\right]\left[e^{-q^2/2}\right]$$

Case I n - 0 $E_0 = 1/2hv$

The corresponding eigen function is ψ_0

$$\psi_0 = \frac{1}{\left[\sqrt{\pi}.2^{0}\left[0\right]^{1/2}\right]}\left[(-1)^{0}\frac{eq^{2}\partial^{0}}{\partial q^{0}}\left(e^{-q^2}\right)\right]\left[e^{-q^2/2}\right]$$

$$\psi_0 = \frac{1}{\left[\pi^{1/4}\right]}\left[1.e^{q^2} - e^{-q^2}\right]e^{-q^2/2}$$

$$\psi_0 = \frac{1}{\left[\pi.^{1/4}\right]}\left[1.e^{0}\right]e^{-q^2/2}$$

$$\psi_0 = \frac{1}{\pi^{1/4}}e^{-q^2/2}$$

$$\psi_0 = \frac{1}{\pi^{1/2}}e^{-q^{2/2}}$$

$$q^2 = bx^2$$

$$\psi^2{}_0 = \frac{1}{\sqrt{\pi}}.e^{-bx^2} \quad \text{If } x = 0$$

$$\psi^2{}_0 = \frac{1}{\pi^{1/2}} = A^2$$

As the potential energy of simple harmonic oscillate = $\frac{1}{2}kx^2$, which in of the form $Y = ax^2$, Which represents a parabola, the P.E should vary with displacement in a parabolic manner

The free particle

One of the simplest applications of the Schrodinger equation is found in the treatment of a free particle. In the free particle system, a particle of mass m and the potential energy of such a particle is taken to be zero for convenience and the total energy is entirely kinetic energy.

The Schrodinger equation for such a system in one dimentsion is given by

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} E \psi = 0 \qquad ......(1)$$

This is second order linear differential equation and general solution is

$$\psi = A \exp\left(i\left(\frac{8\pi^2 mE}{h^2}\right)^{1/2} x\right) + B \exp\left[-i\left(\frac{8\pi^2 mE}{h^2}\right)^{1/2} x\right] \cdots \quad (2)$$

where A and B are two arbitrary constants. For the probability of finding a particle to remain finite as x goes to infinity, the necessary condition is that the energy, E must be positive.

If E < 0, then the first term in equation (2) will be infinite as x approaches minus infinity, and the second term becomes infinite as x approaches plus infinity. Thus the restriction on the energy of a free particle less in $E \geq 0$. In this condition the arbitrary constant A and B can now have any values. Therefore, for the free particle, energy in not quantised and it can have any value greater than zero, and energy spectrum will be continuous. This conclusion is in agreement with the observed spectra of an atom. The dissociation of an electron from the atom and the radioactive emission of alpha rays and beta rays are some of the examples of free particle.

WAVE MECHANICAL TREATMENT OF A PARTICLE IN ONE DIMENSIONAL BOX

Potential box

A potential box is a system in which potential energy is zero within a closed region and infinite $(v = \infty)$ everywhere else.

Particle in a one-dimensional potential box

The simplest problem related to that of a particle in a microscopic system (say, electron in the atom) involves the calculation of the wave function and energy of the particle (electron) constrained to move within a certain distance in given direction, back and forth. To tackle this problem, let us consider a particle (electron) in a one dimensional box as shown in Fig. (1).

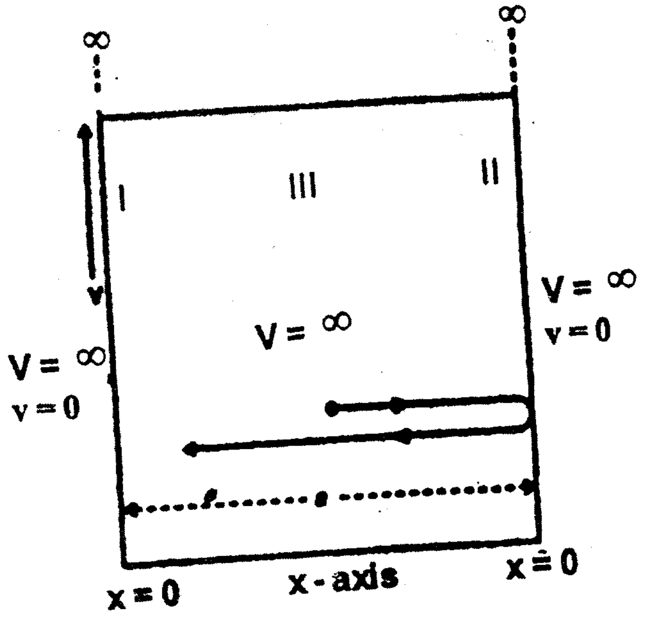


Fig.I. (ii). Wave Mechanical treatment of a particle in a one - dimensional potential box. The two walls of the box are I and II.

The particle is restricted to move along x-axis, back and forth. The width of the box is 'a' and height is ∞ . Suppose that particle does not lose energy when it collides against the walls of the box, so its energy remains constant (Fig. 1) . Consider the wave mechanical treatment of a particle in one -dimensional potential box. The two walls of the box are I and II are constant. Then this box is represented by a potential box of width 'a' with potential walls of infinity (∞) height at $x = 0$ and $x = a$. Hence potential energy (v) of particle becomes infinity ($v = \infty$) on the sides I ($x = 0$) and II ($x = a$) of the box and is constant inside the box. For sake of convenience it can be taken as zero ($V = 0$) inside the box so that there is no restriction on the movement of the particle in the box. Outside the box the potential energy is ∞, i.e., $V = \infty$ at $x < 0$ (i.e., negative side of x-axis) and at $x > a$. Therefore, the wave function ψ and probability of finding the particle (i.e., ψ^2) must be zero when $x < 0$, $x = 0$ and $x \geq a$. In other words, the particle is confined in the box and can not escape the box, i.e., particle does not exist outside the box.

The Schrodinger's wave equation w.r.t. space is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

For the particle moving only in x-direction, this equation becomes

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

Now, within the box $V = 0$. Therefore we get

$$\frac{\partial^2 \psi}{\partial x^2} \quad \frac{8\pi^2 m}{h^2} E\psi = 0$$

$$\boxed{\frac{\partial^2 \psi}{\partial x^2} = -\left(\frac{8\pi^2 m E}{h^2}\right)\psi} \qquad \text{.......(1)}$$

or solution of Equation (1). Since π, m, E and h are constant, equation (1) can be written as

$$\frac{\partial^2 \psi}{\partial x^2} = -k^2 \psi \qquad \text{......(2)}$$

$$k^2 = \frac{8\pi^2 m E}{h^2}$$

Where, the general solution of equation (2) is

$$\psi = C_1 e^{ikx} + C_{2e}^{-ikx} \qquad \text{......(3)}$$

where C_1 and C_2 = Constants

An equivalent and more convenient form of equation (3) is

$$\psi = A \operatorname{Sin}(kx) + B \cos(kx) \qquad \text{......(4)}$$

Where A and B = Arbitrary constants

Equation (4) represents all the solutions of equation (2) which are mathematically satisfactory. However, these solutions (wave functions) do not necessarily satisfy our boundary conditions, and we now must examine equation (4) in view of these requirements. Differentiating equation (4) with respect to x we get.

$$\frac{\partial^2 \psi}{\partial x^2} = -k^2 (A \sin kx + B \cos kx) \qquad \text{......(5)}$$

By applying boundary conditions that at x= 0, ψ = 0, the equation (5) becomes

$$0 = -k^2 (A \sin kx + B \cos kx)$$

As $\sin 0 = 0$ and $\cos 0 = 1$, we get

$$0 = -k (0 + B)$$

i.e., $B = 0$ ......(6)

Putting B = 0 in equation (4), we get

$$\psi = A \text{ Sin } kx \qquad \text{......(7)}$$

Applying the other boundary condition that at x =a, ψ = 0 the equation (7) becomes

$$0 = A \sin ka \qquad \text{......(8)}$$

Since A $\neq$ 0 (otherwise wave equation (7) vanishes if A == 0 then equation (7) yields $\psi = 0$ which means that probability of finding the particle in the box will be zero ($\psi^2 = 0$) which is not acceptable because the particle has been considered to be present inside the box the equation (8) gives

$$\sin ka = 0 \qquad \text{.......(9)}$$

$$ka = \pi \text{ or } n\pi \quad (\because \sin \pi = \sin n\pi = 0)$$

$$k = \frac{n\pi}{a} \qquad \text{------ (10)}$$

where n =an integer, i.e., n = 1,2,3, ...

Substituting value of k from equation (10) in (7), we get

$$\boxed{\psi = A\sin\left(\frac{n\pi x}{a}\right)} \qquad \text{......(11)}$$

The equation (11) gives a family of acceptable wave functions corresponding to n =1, n =2, n=3 .... etc. These single valued and finite functions are called eigen functions.

Expression for Energy of the Particle according to equation (10).

$$k = \frac{n\pi}{a} \qquad \therefore k^2 = \frac{n^2\pi^2}{a^2}$$

Also $$\therefore k^2 = \frac{8\pi^2 mE}{h^2}$$

$$\frac{8\pi^2 mE}{h^2} = \frac{n^2\pi^2}{a^2}$$

$$\boxed{E_n = \frac{n^2h^2}{8ma^2}}$$

Where n = 1,2,3 ...

Hence

Equation (11) gives allowed (permissible) values of energy corresponding to n = 1,n = 2, n =3, ... etc.

E_n stands for the energy of particle in nth level hence symbol E_n is used in place of E. Since n, called the quantum number, can assume only integral values, it is clear that the particle may have only certain discrete values for E. These are the eigen values for E.

E cannot be zero because in that case, $\psi = A \sin 0 = 0$, everywhere in the box. Clearly this is impossible. Hence, n = O is not permissible.

From the above discussion it becomes clear that the concept of energy quantization is inherent in the wave mechanics.

Normalization of Equation (11) The mathematical process or operation for calculating the value of 'A' in equation (11) is called normalization, which can be done as follows :

The probability that the particle is within the space x and (x + dx) for a one-dimensional box given by $\psi^2 dx$. As a consequence of these assumption

$$\int_{-\infty}^{+\infty} \psi^2 dx = 1$$

Imposing the condition that probability of finding the particle within the box, i.e., between x = 0 and x = a, is unity (because our problem requires that the particle must be somewhere inside the box), the above equation changes to

$$\int_0^a \psi^2 dx = 1$$

From equation (9)

$$\psi = A \sin kx$$

Hence $$\int_0^a A^2 \sin^2 kx \, dx = 1$$

or $$A^2 \int_0^a \sin^2 kx \, dx = 1$$

Since $$\sin^2 kx = \tfrac{1}{2}[1 - \text{Cos}\, 2kx]$$

Hence, $$\frac{A^2}{2} \int_0^a (1 - \cos 2kx) dx = 1$$

$$\frac{A^2}{2}\left[\int_0^a dx - \int_0^a \cos 2kx\, dx\right] = 1$$

$$\frac{A^2}{2}\left[a - \frac{1}{2k}(\sin 2kx - \sin 0)\right] = 1$$

$$\frac{A^2}{2}\left[a - \frac{1}{2k}\sin 2kx\right] = 1 \qquad (\because \sin 0 = 0)$$

From equation (11)

$$k = \frac{n\pi}{a}$$

Hence $\frac{A^2}{2}\left[a - \frac{1}{2k}\sin 2n\pi\right] = 1$

But $\sin 2n\pi = 0$

Hence, equation (13) becomes

$$\frac{A^2 a}{2} = 1$$

$$\boxed{A = \sqrt{\frac{2}{a}}}$$

Hence, general solution of Schrodinger's wave equation for a particle (say, electron) in a one-dimensional box is given by

since n = 1,2,3 ... an integer

Hence equation (11) is written as

$$\psi_n = \sqrt{2/a}\,.\sin\left(\frac{n\pi x}{a}\right) \qquad \text{.......(15)}$$

As we know that

$$k = \frac{n\pi}{a} \quad \text{and } k = \sqrt{\frac{8\pi^2 mE}{h^2}}$$

$$\frac{n\pi}{a} \quad \text{and } k = \sqrt{\frac{8\pi^2 mE}{h^2}}$$

Therefore equation (15) is written as

$$\psi_n = \sqrt{\frac{2}{a}}.\sin\left(\sqrt{\frac{8\pi^2 mE}{h^2}}.x\right)$$

$$\psi_n = \sqrt{\frac{2}{a}}.\sin\left[\left(\frac{8\pi^2 mE}{h^2}\right)^{1/2}.x\right]$$

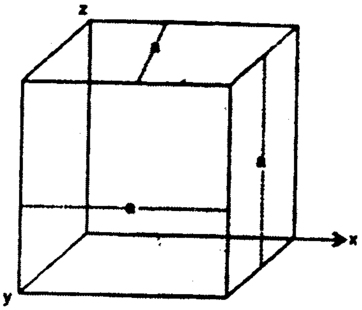
The mathematical process described above is called normalization and value of constant A is called normalization factor. In equation (16)

Normalization factor = $\sqrt{2/a}$

The wave function ψ_n is now said to be normalized. In other words, equation (15) and (16) are the expressions for the normalized wave function or normalized solution of Schrodinger's wave equation for a particle in a one dimensional box.

WAVE MECHANICAL TREATMENTN OF A PARTICLE IN A THREE - DIMENSIONAL POTENTIAL BOX

Consider a microscopic particle (e.g., electron) of mass m moving in a three-dimensional cubic potential box having sides a, b and c; in length along x, y and z axes respectively. The potential energy of the particle is zero within box ($V = 0$) but infinite everywhere outside the box ($V = \infty$) (Fig .2)



With these assumptions, the Schrodiñger's wave equation for the particle inside the box will be

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2}\frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 mE}{h^2}\psi = 0 \qquad \text{......(1)}$$

Dividing through out by ψ

$$\frac{1}{\psi}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\frac{\partial^2\psi}{\partial z^2}\right)+\frac{8\pi^2 mE}{h^2}=0 \qquad \ldots\ldots(2)$$

The wave function ψ depends upon three coordinates x, y and z. Hence can be written as the product of three wave functions, one each for x, y and z

Hence $$\psi=\psi_x.\psi_y.\psi_z \qquad \ldots\ldots(3)$$

The total energy (E) of the particle may be taken to be the sum of three components E_x, E_y and E_z along three axes x, y and z respectively. Hence

$$E=E_x+E_y+E_z \qquad \ldots\ldots(4)$$

Substituting equ (2) in equ (4), we get

$$\frac{1}{\psi_x\psi_y\psi_z}\left[\frac{\partial^2(\psi_x\psi_y\psi_z)}{\partial x^2}+\frac{\partial^2(\psi_x\psi_y\psi_z)}{\partial y^2}+\frac{\partial^2(\psi_x\psi_y\psi_z)}{\partial z^2}\right]-\frac{8\pi^2 m}{h^2}(E_x+E_y+E_z)=0$$

On simplification

$$\left(\frac{1}{\psi_x}.\frac{\partial^2\psi_x}{\partial x^2}+\frac{1}{\psi_y}.\frac{\partial^2\psi_y}{\partial y^2}+\frac{1}{\psi_z}.\frac{\partial^2\psi_z}{\partial z^2}\right)+\frac{8\pi^2 m}{h^2}(E_x+E_y+{}_z)=0 \qquad \ldots\ldots(6)$$

That is equation (6) consists of three independent terms (differential equations), each term is the function of one variable only, hence

$$\frac{1}{\psi_x}.\frac{\partial^2\psi_x}{\partial x^2}+\frac{8\pi^2 mE_x}{h^2}=0 \qquad \ldots\ldots(7)$$

$$\frac{1}{\psi_y}.\frac{\partial^2\psi_y}{\partial y^2}+\frac{8\pi^2 mE_y}{h^2}=0 \qquad \ldots\ldots(8)$$

$$\frac{1}{\psi_z}.\frac{\partial^2\psi_z}{\partial z^2}+\frac{8\pi^2 mE_z}{h^2}=0 \qquad \ldots\ldots(9)$$

Each of the above three equations (7), (8) and (9) is similar to Schrodinger's wave equation for the particle moving in a one – dimensional box only, hence their solutions for energy are,

$$\left.\begin{aligned} E_x &= \frac{n_x^2 h^2}{8ma^2} \\ E_y &= \frac{n_y^2 h^2}{8mb^2} \\ E_z &= \frac{n_z^2 h^2}{8mc^2} \end{aligned}\right\} \qquad \text{......(10)}$$

and the solutions for wave function are

$$\left.\begin{aligned} \psi_x &= \sqrt{2/a}\,.\sin\left(\frac{n_x \pi x}{a}\right) \\ \psi_y &= \sqrt{2/b}\,.\sin\left(\frac{n_y \pi y}{b}\right) \\ \psi_z &= \sqrt{2/c}\,.\sin\left(\frac{n_z \pi z}{c}\right) \end{aligned}\right\} \qquad \text{......(11)}$$

Discussion of Equations (10) and (11)

1. The numbers n_x, n_y and n_z are the quantum numbers along x, y and z directions respectively. These are capable of taking up all integral values, i.e., 1,2,3,4, .. that is, these values are quantized. Hence these numbers, n_x, n_y and n_z are given the name quantum numbers . .'

2. The total energy, Eis given by

$$\boxed{E = E_x + E_y + E_z = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)} \qquad \text{..... (12)}$$

Since n_x, n_y and n_z can assume only integral values, it is clear that the particle may have only certain discrete values for E. That is the energy of the particle is quantized.

3. The total wave function ψ is given by

$$\psi = \psi_x \cdot \psi_y \cdot \psi_z$$

or $$\psi = \sqrt{8/abc}\,\sin\left(\frac{n_x \pi x}{a}\right).\sin\left(\frac{n_y \pi y}{b}\right).\sin\left(\frac{n_z \pi z}{c}\right) \quad \text{..... (13)}$$

$$\boxed{\psi = \sqrt{8/V}\,\sin\left(\frac{n_x \pi x}{a}\right).\sin\left(\frac{n_y \pi y}{b}\right).\sin\left(\frac{n_z \pi z}{c}\right)}$$

Hence equation (13) gives the value of normalized wave function. The factor $\sqrt{8/V}$ is called the normalized factor.

Normalization factor = $\sqrt{8/V}$

Where V =Volume of the three-dimensional box.

In equation (13), the quantum number n_x, n_y and n_z can have only integral values, this equation gives a family of acceptable wave functions.

Hydrogen atom

The hydrogen like atom is a two-particle system consisting of an electron with change -e and an atomic nucleus with charge $+^{ze}$. Since the electron is very much faster than the nucleus particles, it is assumed that the nucleus is stationery as compared to electron. The Schrodinger equation for the hydrogen like atom will then be the equation for a single electron moving around the nucleus.

$$\left[-\frac{h^2}{8\pi^2 me}\nabla^2 + V\right]\Psi(x,y,z) = E\Psi(x,y,z) \quad \text{..... (1)}$$

Where $\Psi(x,y,z)$ is a function of the Cartesian coordinates x,y,z of the electron. In order to solve this equation, the Caresian coordinates are converted to spherical coordinates r, θ and Φ which are defined as follows

$x = r\sin\theta\ \mathrm{Cos}\phi$

$y = r\sin\theta\ \sin\phi$

$z = r\ \mathrm{Cos}\phi$

$x^2 + y^2 + z^2 = r^2$ and the ranges of the coordinates are $0 \leq r\ r \leq \infty; 0 \leq \theta \leq \pi$ and $0 \leq 2\pi$

The transformation of coordinates in equation (1) in terms of spherical polar coordinates, gives rise to the following equation.

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial\psi}{\partial r}\right]+\frac{1}{r^2\sin}\cdot\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\psi}{\partial\theta}\right]+\frac{1}{r^2\sin^2\theta}\cdot\frac{\partial^2\psi}{\partial\psi^2}+\frac{8\pi^2me}{h^2}\left[E+\frac{ze^2}{4\pi\varepsilon_0 r}\right]\Psi=0$$

Since potential energy is a function of only r the wave function ψ in equation (2) may be written as the product of three functions each one dependent an one spherical polar coordinates

$$\psi(r,\theta,\phi) = R(r)\theta\ (\theta)\phi\ (\phi) \qquad .....(3)$$

This is substituted in equation (2) and multiplied by $r^2\sin^2\theta / R\theta\phi$ and we obtain,

$$\frac{\mathrm{Sin}^2\theta}{R}\cdot\frac{d}{dr}\left(r^2+\frac{dR}{dr}\right)+\frac{\mathrm{Sin}\theta}{\theta}\cdot\frac{d}{d\theta}\left(\mathrm{Sin}\theta\frac{d\theta}{d\theta}\right)$$

$$+\frac{1}{\phi}\frac{d^2\phi}{d\phi^2}+\frac{8\pi^2m}{h^2}\ r^2\mathrm{Sin}^2\theta\left(E+\frac{Ze^2}{4\pi\varepsilon r}\right)=0 \qquad .....(4)$$

This leads to a situation that is analogous to that which arise for the particle in three dimensional box.

$$\frac{d^2\phi}{d\phi^2}+m^2\phi=0 \qquad .....(5)$$

and

$$\frac{\mathrm{Sin}^2\theta}{R}\cdot\frac{d}{dr}\left(r^2+\frac{dR}{dr}\right)+\frac{\mathrm{Sin}\theta}{\theta}\cdot\frac{d}{d\theta}\left(\mathrm{Sin}\theta\frac{d\theta}{d\theta}\right)-$$

$$=m^2+\frac{8\pi^2m}{h^2}\ r^2\mathrm{Sin}^2\theta\left(E+\frac{Ze^2}{4\pi\varepsilon r}\right)=0 \qquad ......(6)$$

dividing equ. (6) by $\mathrm{Sin}^2\theta$ and rearranging to obtain

$$\frac{1}{R}.\frac{d}{dr}\left(r^2.\frac{dR}{dr}\right)+\frac{8\pi^2 m}{h^2}r^2\left(E+\frac{Ze^2}{4\pi\varepsilon r}\right)$$

$$=\frac{m^2}{\mathrm{Sin}^2\theta}-\frac{1}{\theta\,\mathrm{sin}}.\frac{d}{d\theta}\left(\mathrm{Sin}^2\theta\frac{d\theta}{d\theta}\right) \quad .....(7)$$

In this equation the left side is a situation of r only, while the right side is only on θ.

Two separate equation there become.

$$\frac{1}{\mathrm{Sin}\theta}.\frac{d}{dr}\left(\mathrm{Sin}\theta.\frac{d\theta}{d\theta}\right)+\left(e(e+1)-\frac{m^2}{\mathrm{Sin}^2\theta}\right)\theta=0$$

and

$$\frac{1}{r^2}.\frac{d}{dr}\left(r^2.\frac{dR}{dr}\right)+\frac{8\pi^2 m}{h^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}-\frac{e(e+1)}{r^2}\right)R=0$$

The solution of the radial equation (9) is the equation of atomic for a

$$E=-\frac{2\pi^2 Z^2 me^4}{n^2h^2(4\pi\varepsilon_0)^2}$$

$$E=\frac{-Z^2e^2}{4\pi\varepsilon_0\,a_0 n^2}$$

where $a_0=\dfrac{h^2}{4\pi^2 me\,e^2}$

a_0 is called the Bohr radius.

UNIT III

Approximation method

Quantum mechanics gives an exact solution for the hydrogen atom. But when we consider the helium atom, the quantum mechanical solution is not possible. Hence, it is apparent that we must resort to approximation methods when treating a many electron system. There are two common methods of obtaining approximate solutions to the wave equation they are

1. The variation method
2. The perturbation method.

The variation method:

Let us consider Ψ in a many electron wave function of a system, then the Schrodinger equation in operator form is

$$\hat{H}\psi = E\psi \qquad .....(1)$$

where $\hat{H}$ is the complete Hamiltonian operator and E is the total electronic energy of the system.

The average energy is written as

$$E = \int \psi^{*} \hat{H} \psi \, dy$$

where Ψ is any normalized well behaved wave function. In this equation wave function Ψ is not known accurately even for a two-electron system. So the wave function Ψ is chosen arbitrarily. If the chosen wave function is the correct wave function, then it is possible to calculate the accurate energy E_0 of the lowest state of the system with equ. (2). On the other hand if we choose an inferior wave function, we could expect to get a poor agreement of the calculated energy value with the experimental one.

According to the variation principle, if Ψ_0 is the correct wave function for a system, i.e one that will give the correct energy E_0 of the system. then any other chosen wave function Ψ_1 will give an energy E_1 greater then E_0 i.e.,

$$\int \psi_i^* \hat{H} \psi_i \, d\tau \geq E_0 \qquad .....(3)$$

The advantage of this method is that if we choose a trial function containing several parameters and then minimize the energy given by Equation 3 with respect to these parameters, the corresponding wave function and energy available will be very close to the actual state of the system.

Example. Let us consider the case of helium atom in the ground state. Our trial function for two electrons is the hydrogen like one electron wave function.

$$\psi(1) = \left(\frac{Z^{1^3}}{\Pi}\right)^{1/2} e^{-z^1 r_1}$$

$$\psi(2) = \left(\frac{Z^{1^3}}{\Pi}\right)^{1/2} e^{-z^1 r_2}$$

where Z is effective nuclear charge. The complete wave function for the helium atom is then given by

$$\Psi_{(1,2)} = \left(\frac{Z^{1^3}}{\Pi}\right)^{1/2} e^{-z^1(r_1 + r_2)}$$

2. The Perturbation method

Perturbation method is another technique of arriving at energy and wave function for a system for which schrordinger equation cannot be solved. The perturbation theory, therefore, involves determination of the eigen functions (ψ_n) and eigen values (E_n) of the perturbed Hamiltonian $\hat{H}$ in term of those $\left(\psi_n^0 \text{ and } E_n^0\right)$ of the unperturbed Hamiltonian $\hat{H}^0$

It is imagined that the perturbation is being applied continuously in small steps this amounts to

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}^1 \qquad ......(1)$$

where λ is a parameter which can vary from 0 to 1 when A = 0, the system is unperturbed and when $\lambda = 1$ the perturbation is complete.

The Schrodinger equation for the unperturbed and perturbed system can be written as

$$\hat{H}^0 \psi_n^0 = E_n^0 + \psi_n^0 \qquad \text{.....(2)}$$

$$\hat{H}\psi_n = E_n + \psi_n \qquad \text{.....(3)}$$

$$\left(\hat{H}_0 + \lambda\hat{H}^1\right)\psi_n = E_n\psi_n \qquad \text{.....(4)}$$

where the subscript n denotes the state of a system. If $\hat{H}$ depends on λ, both ψ_n and E_n will depend on λ. So as a first step, we expand these functions as Taylor series assuming that $\lambda\hat{H}^1 << \hat{H}$

$$\psi_n = E_n^0 + \lambda\psi_n^{(1)} + \lambda^2\psi_n^2 \text{.............} \qquad \text{.....(5)}$$

$$E_n = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^2 \text{.............} \qquad \text{.....(6)}$$

where $\psi_n^{(k)}$ and $E_n^{(k)}$ are k^th^ order correction term to the ψ_n^0 and E_n^0 respectively and given us

$$\psi_n^{(k)} = \frac{1}{k_0^1}\left(\frac{\partial^k\psi_n}{\partial\lambda^k}\right)_{\lambda=0} \qquad \text{.....(7)}$$

$$E_n^{(k)} = \frac{1}{k_0^1}\left(\frac{\partial^k E_n}{\partial\lambda^k}\right)_{\lambda=0} \qquad \text{.....(8)}$$

substituting (5) and (6) in (4) and rearranging (7) and (8)

$$\left(\hat{H}^0\psi_n^0 - E_n^0\psi_n^0\right) + \lambda\hat{H}^0\psi_n^{(1)} + \hat{H}^0\psi_n - E_n^0\psi_n^{(1)} - E_n^0\psi_n^0$$

$$+ \lambda^2\left(\hat{H}^0\psi_n^{(2)} + \hat{H}^1\psi_n^{(1)} - E_n^0\psi_n^{(2)} - - E_n^{(1)}\psi_n^{(1)} - E_n^{(2)}\psi_n^0\right) = 0 \qquad \text{.....(9)}$$

the equation (9) may be written

$$\lambda^1 = \left(\hat{H}^0 E_n^0\right)\Psi_n^{(1)} = -\hat{H}\psi_n^0 + E_n^{(1)}\psi_n^0 = 0 \qquad \text{.....(10)}$$

First order correction

$$\psi_n^{(1)} = \sum_{m \neq n}\left(\frac{\int\psi_m^0 H^1 \psi_n^0 d\tau}{E_n^0 - E_m^0}\right)\psi_m^0 \qquad \text{......(11)}$$

The above. equation says that the first order correction $\psi_n^{(1)}$ to the wave function can be determined from the eigen function and eigen values of the unperturbed system.

Application of wave mechanics to Helium atom

The helium atom has two electrons moving in a field of a nucleus of charge +2e. Let us consider the nucleus to be at rest and will place the origin of the co. ordinate system at the nucleus (Fig. 1). The Hamiltonian operator of the helium atom in terms of atomic units are written as,

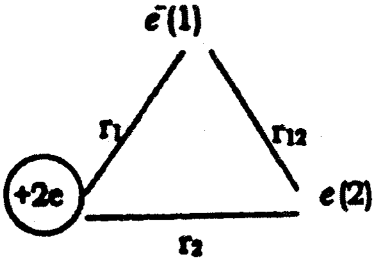


Fig. (1)

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \qquad .....(1)$$

(OR)

$$\hat{H} = \left(\frac{1}{2}\nabla_1^2 - \frac{2}{r_1}\right) - \left(\frac{1}{2}\nabla_2^2 - \frac{2}{r_2}\right) + \frac{1}{r_{12}} \qquad .....(2)$$

The expression with in two brackets may be identified at the Hamiltonian $\hat{H}(1)$ and $\hat{H}(2)$ two separate He$^+$ ions (z =2) i.e.,

$$\hat{H} = \hat{H}(1) + \hat{H}(2) + \frac{1}{r_{12}} \qquad .....(3)$$

Let us consider the two electron Hamiltonian $\hat{H}$ as a sum of two one electron Hamiltonians $\hat{H}$ (1) and $\hat{H}$ (2) which may, therefore, be considered as the unperturbed Hamiltonians $\hat{H}^0$ of the He$^+$ atom

$$\hat{H}^0 = \hat{H}(1) + \hat{H}(2) \qquad .....(4)$$

Where $\hat{H}$ (1) and $\hat{H}$ (2) have hydrogen like eigen functions (orbital) ϕ (1) and ϕ (2) respectively.

$$\hat{H}(1)\phi(1) = E(1)\ \phi(1)$$

$$\hat{H}(2)\phi(2) = E(2)\ \phi(2)$$

E (1) and E (2), the eigen values, represent the orbital energies

$$\psi^0 = \phi(1) \text{ and } \phi(2) \qquad .....(5)$$

$$E^0 = E(1) + E(2)$$

$$H^{0}\psi^{0} = \left[\hat{H}(1)+\hat{H}(2)\right]\phi(1)\phi(2)$$

$$= \hat{H}(1)\left[\phi(1)\phi(2)\right]+\hat{H}(2)\left[\phi(1)\phi(2)\right]$$

$$H^{0}\psi^{0} = \left[\hat{H}(1)\phi(1)\right]\phi(2)+\left[\hat{H}(2)\,\phi(2)\right]\phi(1)$$

$$= \left[E(1)\phi(1)\right]\phi(2)+\left[E(2)\,\phi(2)\right]\phi(1)$$

$$H^{0}\psi^{0} = \left[E(1)+E(2)\right]\left[\phi(1)\phi(2)\right] \qquad .....(6)$$

$\hat{H}(1)$ operates on $\phi(1)$ and H(2) on $\phi(2)$ only and

$$\phi(1)\,\phi(2) = \phi(2)\,\phi(1)$$

The independent electron approximation says that the function $\psi^{0} = \phi(1)\,\phi(2)$ which is true eigen function of may be $\hat{H}^{0}$ may be used as an approximate eigen function of $\hat{H}$ in other words, the atomic orbital $\phi(1)$ and $\phi(2)$ that are eigen function of one electron Hamiltonian $\hat{H}(1)$ and $\hat{H}(2)$ respectively may serve as a basis of the description of the two electron atom. Therefore the two-electron problem is thus reduced to two one-electron hydrogen like problems. In the ground state of He atom, for example both the electron has the same orbital function 1 S given as

$$IS(1) = \sqrt{\frac{Z^{3}}{r}}\exp(-Zr_{1}) \qquad .....(7)$$

$$IS(2) = \sqrt{\frac{Z^{2}}{r}}\exp(-Zr_{2}) \qquad .....(8)$$

Under this approximation

$$\psi(1,2)\text{ or }\psi = IS(1)IS(2) = \sqrt{\frac{Z^{3}}{r}}\exp\left(-Z(r_{1}+r_{2})\right) \qquad .....(79)$$

where atomic units are used

The presence of one electron effectively reduces the nuclear charge for the other electron. The value of Z in the equation (9) should be less than Z; Z may be used as a variable parameter the value of which can be determined by minimizing the energy i.e.; by setting

$$\frac{dEIs^2}{dz} = 0$$

Where as

$$E_{1S}2 = \int \psi\, \hat{H}\, \psi\, d\psi$$

substitute $\hat{H}$ and ψ and writing IS for φ ,we get

$$E_{IS}^2 = \int\int IS(1)IS(2)\left[\hat{H}(1)+\hat{H}(2)+\frac{1}{r_{12}}\right]IS(1)IS(2)d\tau_1 d\tau_2$$

$$= \int\int IS(1)IS(2)\hat{H}(1)IS(1)IS(2)d\tau_1 d\tau_2 +$$
$$\int\int IS(1)IS(2)\hat{H}(2)IS(1)IS(2)d\tau_1 d\tau_2 +$$
$$\int\int IS(1)IS(2)\left(\frac{1}{r_{12}}\right)IS(1)IS(2)d\tau_1 d\tau_2 +$$

$\hat{H}(1)$ and $\hat{H}(2)$ the Hamiltonian of the He^+ which operate an electron (1) and (2) respectively

$$\therefore E_{IS}^2 = \int\int IS(1)IS(2)E^{He+}_{(1)}IS2(1)IS(2)d\tau_1 d\tau_2$$
$$+\int\int IS(1)IS(2)E^{He+}_{(1)}IS2(1)IS(2)d\tau_1 d\tau_2 + J$$
$$E^{He+}_{IS}(1) = E^{He+}_{IS}(2) = E_{1S}\ (say)$$

Equation (9) can be written as I1,I 2

$$E_{1S}2 = 2E_{1S}\ \int\int[IS(1)\ IS(2)]^2\, d\tau_1 d\tau_2\ J$$
$$E_{1S}2 = 2E_{1S} + J$$

(Because 1S function are normalized

E_{1s} the energy of a He+ in 1S state, is known to be given by

$$E_{1S} = \int IS\left(-\frac{1}{2}\nabla^2 - \frac{z}{r}\right) 1s\, d\tau \qquad ....(1)$$

In the present case, however, 1S is the eigen function of

$-\frac{1}{2}\nabla^2 - \frac{z}{r}$ with ≤ 2, and the eigen value is $-\frac{Z^2}{2}$

Equation (11) can be written as

$$E_{1S} = \int IS\left(-\frac{1}{2}\nabla^2 - \frac{z}{r} - \frac{2-Z}{r}\right) 1Sd\tau$$
$$= \int IS\left(-\frac{1}{2}\nabla^2 - \frac{z}{r}\right)1sd\tau - \int IS\left(\frac{2-Z}{r}\right)1sd\tau$$

$$= -\frac{Z^2}{2}\int 1S2\,d\tau - (2-Z)\int 1S\frac{1}{r}1S\,d\tau$$

$$E_{1s} = -\frac{Z^2}{2} - (2-Z)\int 1S\frac{1}{r}1S\,d\tau \qquad .....(12)$$

The evaluation of second term in the above equation

$$1S = \frac{Z^3}{\pi}\exp - Zr \text{ and } d\tau = r^2\,dr\sin\theta\,d\varphi\,d\phi$$

$$\int 1S\frac{1}{r}1S\,d\psi = \frac{Z^3}{\pi}\int_0^{\infty}\frac{1}{r}\exp(-2Zr)r^2\,d\tau r$$

$$= \frac{Z^3}{\pi}4\pi\int_0^{\alpha} r\exp(-2Zr)\,d\tau r$$

$$= 4z^3\frac{1}{(2Z)^2} = Z$$

$$E_{1S} = -\frac{Z^2}{2} - (2-Z)Z$$

$$E_{1S2} = 2\left(-\frac{Z^2}{2} - (2-Z)Z\right) + J \qquad ......(13)$$

$$E_{1S2} = -Z^2 - 2Z(2-Z) + \frac{5}{8}Z$$

By the Principle of minimization

$$\frac{dE_{1S}^2}{dZ} = 2Z - \frac{27}{8} = 0$$

$$Z = \frac{27}{16} \qquad .....(14)$$

$$E1S^2 = \left(\frac{27}{16}\right)^2 - \frac{27}{8}\times\frac{27}{16} = -2.849 \text{ a.u}$$

$$= -77.28\text{eV or}$$

$$= -1.24\times10^{-17}\text{J}$$

The value of $Z = \frac{27}{16}$ represents the effective nuclear charge, i.e., the charge of the nucleus that one electron feels due to the partial screening by the other electron, the difference

$2-\frac{27}{16}=\frac{5}{16}$ represents the screening effect.

The Pauli Anti symmetry Principle

Let us consider the case of the two-electron system. If $\psi(1,2)$ re resents the wave function corresponding to the electrons (1,2) $\psi_b(1)$ and $\psi_b(2)$ be the wave functions representing the states of individual electrons then

$$\psi(1,2)=\psi\ a(1)\ \psi\ b(2) \qquad .....(1)$$

where each wave function on the right hand side is completely independent of the other. Since the electrons are indistinguishable particles we cannot specify the positions of the electrons exactly. Therefore an exactly good wave function will be

$$\psi(2,1)=\psi\ a(2)\ \psi\ b(1) \qquad .....(2)$$

As the particles are identical there should not be any difference in the probability $|\Psi|^2$ of the system when electrons are interchanged, i.e.,

$$|\Psi(1,2)|^2=|\Psi(2,1)|^2$$

$$\Psi(1,2)=\pm\Psi(2,1) \qquad .....(3)$$

When $\psi(1,2)=\psi(2,1)$, the wave function is a symmetric. A wave function is said to be symmetric if the interchanged of a pair of particles leaves the sign of the wave function unchanged.

When $\psi(1,2)=-\psi(2,1)$ the wave function is antisymmetric. The function is antisymmetrical if the interchange of a pair of particles changes the sign of ψ. Taking into account the indistinguishable of the electrons, the best representation for two electrons can be attained by taking the linear combination of equation 1 and equation 2.

$$\psi=\psi_a(1)\,\psi_b(2)\pm\psi_a(2)\,\psi_b(1) \qquad .....(4)$$

The symmetric wave function.(Ψ_s) will be given by

$$\psi=\psi_a(1)\,\psi_b(2)+\psi_a(2)\,\psi_b(1) \qquad .....(5)$$

and the anti symmetric wave function

$$\psi_A=\psi_a(1)\,\psi_b(2)-\psi_a(2)\,\psi_b(1) \qquad .....(6)$$

If the electron 1 and 2 arc interchanged in these function, it is obvious that Ψ_s is unaltered but Ψ_A changes its sign as shown below.

$$\begin{aligned}\psi_{A1} &= \psi_a(2)\,\psi_b(1)-\psi_a(1)\,\psi_b(2)\\ &=\left[\psi_a(1)\,\psi_b(2)-\psi_a(2)\,\psi_b(1)\right]\\ \psi_{A1} &= -\psi_A(2)\end{aligned}$$

When the two electrons have the same set of orbital quantum numbers n, 1, m.

Example: The ground state helium atom ($1S^2$) then $\psi_a = \psi_b$ so that $\psi(1,2) = \psi\,1S(1)\psi\,1S(2)$. If the electrons are interchanged, the functions $\psi(1,2)$ will be symmetric and will represent the same state of the system i.e.,

$$\psi_{1S}(1)\psi_{1S}(2)= \psi_{1S}(2)\psi_{1S}(1) \qquad .....(7)$$

For the two-electron system, there are four possible ways in which the spin function can be written

$$\alpha(1)\alpha(2),\beta(1)\beta(2),\ \alpha(1)\beta(2)\ \text{and}\ \alpha(2)\beta(1) \qquad .....(8)$$

Out of these four spin functions, the last two are not acceptable because they distinguish between the electrons. Electrons are identical to one another and there is no way of experimentally determining which electron has spin + 1/2 and which has spin $-\frac{1}{2}$. Hence, the third and fourth spin functions replaced by their linear combination which will overcome the problem of distinguish ability of electrons are given by

$$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)\pm\alpha(2)\beta(1)\right], \qquad ....(9)$$

Thus, the proper spin function for the two-electron system becomes

$$\alpha(1)\alpha(2),\beta(1)\beta(2),\ \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)+\alpha(2)\beta(1)\right],$$

$$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\alpha(2)\beta(1)\right] \qquad .....(10)$$

The first three spin functions are symmetric and the last one is anti symmetric with respect to interchange of electrons.

The complete wave function for the ground state helium atom will be a product of the orbital wave functions given by Equation (7) and the spin functions equation (10) i.e..

$$\psi = \alpha(1)\alpha(2)\ \psi_{1s}(1)\psi_{1s}(2)$$

$$\psi = \beta(1)\beta(2)\ \psi_{1s}(1)\psi_{1s}(2)$$

$$\psi = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \alpha(2)\beta(1)\right]\psi_{1s}(1)\psi_{1s}(2)$$

$$\psi = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]\psi_{1s}(1)\psi_{1s}(2)$$

the question now arises as to whether all these combinations are allowed answer lies with the Pauli's exclusion principle. According to this principle "A wave function representing the state of a system containing more than one electron must be anti-symmetric in the exchange of pairs of electron coordinates, including spin coordinates. Realizing that symmetric (+) x symmetric (+) or anti symmetric (-) x anti symmetric (-) is symmetric (+) but symmetric (+) x anti symmetric is anti-symmetric (-).

Now, in equation (11), the first three relations are symmetric a d the last one is anti symmetric with respect to the interchange of a pair of electrons. Hence, . by the Pauli's exclusion principle, the only state which in acceptable is

$$\psi = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]\psi_{1s}(1)\psi_{1s}(2) \qquad \text{..... (12)}$$

spectroscopic and chemical experiments indicate that in the case of he ground state helium atom, only one state is available. Thus the results confirm he validity of the Pauli's exclusion principle.

Slater determinants

The anti symmetric wave functions for a many electron atoms are constructed by following the general procedures. But with increase in the number of electrons, the number of terms increases in such large proportions (or example 5! i.e., 120 terms for an atom with 5 electron only) that we must find an abbreviated form to represent a wave function. A short hand form is determinant in which the spin orbital the elements; each row in this determinant, is labeled with an electron and each column with a spin - orbital. The normalized wave function for a three-electron atom example

The Born - oppenheiner approximation

The exact solution of the Schrodinge: equation is not possible even for light atom. Therefore, the Schrodinger equation $\hat{H}\psi = E\psi$ in extremely complicated and its exact solution is not possible.

The Hamiltonian operator for a molecule is

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} + \hat{V}_{NN} \qquad \text{.....(1)}$$

Where $\hat{T}_N$ - kinetic energy operators for the nuclei

$\hat{T}_e$ - Kinetic energy operators for the electrons

$\hat{V}_{ee}$ - the electron - electron repulsion term

$\hat{V}_{eN}$ - the electron-nuclei repulsion term

$\hat{V}_{NN}$ - the nuclear - nuclear repulsion term

Since the electrons are much lighter than the nuclei, they move much faster in a molecule. The electron carry out many cycles of motion in the time it takes the nucleus to move a short distance. The calculations shows that the nuclei move only about 1 m while in the same time, electron speeds through distance of about 1 m. Therefore, we can consider the nuclei to be fixed while the electron moves, through the whole volume of the molecule. We can now separate the Schrodinger equation for a molecule into two separate equations which are depending for the electronic motion and the other on the static nucleus position. This approximation in known as the Bom-Oppenheiner approximation. In the above equation the $\hat{T}_N$ operator is not affected by the electronic motion. Since potential energy V_{NN} due to the nuclei-nuclear repulsion is a constant quantity for a fixed 'inter nuclear distance. The electronic Hamiltonian can be written as

$$\hat{H}_e = \hat{T}_e \ \hat{V}_{eN} + \hat{V}_{ee} \qquad \text{.....(2)}$$

The Shrodinger equation for only electronic motion is given by

$$\left(\hat{H}_2 + \hat{V}_{NN}\right)\psi_e = \left(E_e + \hat{V}_{NN}\right)\psi_e \qquad \text{.....(1)}$$
$$= U\psi_e$$

where = $U = E_e + V_{NN}$

Since V_{NN} is a constant quantity

$$\hat{H}_e \psi_e = E_e \psi_0$$

where E_e is the electronic energy, ψ_e is the corresponding wave function and U is the total energy of the nuclei and electrons.

HARTREE -FOCK SELF CONSISTENT FIELD THEORY

Hartree's functions are only orbital functions. Fock included corresponding spin function also

$$\psi = [\phi, \alpha(1)], [\phi_2, \alpha(2)] \ldots\ldots\ldots\ldots \phi_n, \alpha_n \qquad \ldots..(1)$$

Where $\alpha(1)$, $\alpha(2)$, $\alpha(3)$ ...... $\alpha(n)$ are spin functions. This is the best method of finding out the eigen function for many electron system. In Hartree SCF method the orbital product is not anti-symmetric, where as Fock used anti-symmetric wave function and followed same procedure as describe by Hartree.

Fock introduced a new operator $\hat{F}$ the Fock operator to include the electron exchange and obtained pseudo schrodinger equations in which each orbital is an eigen function of $\hat{F}$

$$\hat{F} \phi i = E_i \phi i \qquad \ldots..(2)$$

The eigen value E_i is the orbital energy of ϕ_i The Fock equation are difficult to derive but easy to interpret. For an atom with closed shell configuration the Fock operator (in atomic units) for electron is

$$\hat{F} = -1/2 \nabla_1^2 - \frac{Z}{\gamma_1} + \sum_{j=1}^{n/2} \left(2\hat{J}_i - \hat{K}_j \right) \qquad \ldots..(3)$$

The first two terms constitute the hydrogen like (core) Hamiltonian for the electron (1). The symbols $\hat{j}$ and $\hat{K}$ with single subscript are coulomb operator and exchange operator respectively. These are defined as

$$\hat{J}_j \phi(1) = \left[\int \phi_j(2) \frac{1}{\gamma_{12}} \phi_j(2) d\tau_2 \right] \phi_i(1) \qquad \ldots..(4)$$

$$\hat{K}_j\phi_i(1) = \left[\int\phi_j(2)\frac{1}{\gamma_{12}}\phi_i(2)d\tau_2\right]\phi_j(1) \qquad .....(5)$$

In the above equation ϕ_i (1) is not an eigen function of $\hat{K}_j$; the effect of $\hat{K}_j$ is to charge $\phi_i(1)$ to $\phi_j(1)$. These operators are to named as they yield the average coulomb and exchange energies as

$$\int\phi_i(1)\hat{J}_i(1)d\tau = \int\int\phi_i(1)\phi_j(2)\frac{1}{\gamma_{12}}\phi_j(2)\phi_i(1)d\tau_1 d\tau_2 = Jij \qquad ......(6)$$

$$\int\phi_i(1)\hat{K}_i(1)d\tau = \int\int\phi_i(1)\phi_j(2)\frac{1}{\gamma_{12}}\phi_j(2)\phi_i(1)d\tau_1 d\tau_2 = Kij \qquad ......(7)$$

The exchange term have appeared due to the anti-symmetry of the wave function.

Fock operator is different from Hamiltonian operator of the electron 1 which is given as

$$\hat{H}(1) = -\frac{1}{2}\nabla_1^2 - \frac{Z}{\gamma_1} + \frac{1}{2}\sum\frac{1}{\gamma_{ii}} \qquad .....(8)$$

The Fock operator the summation term $\sum\left(2\hat{J}_i - \hat{K}_j\right)$ includes $\hat{j}_i$ and $\hat{K}_i$ which must be known before we write down the expression for $\hat{F}$ explicity.

But $\hat{j}_i$ and $\hat{K}_i$ involve in the above equation and ϕ_i are eigen function of $\hat{F}_0$. Thus to know ϕ_i we need $\hat{F}$ and to know $\hat{F}$ we need ϕ_i So we have to take to interactive procedure. We start with a reasonable set of orbital and apply the Hantree's method repeated interaction as described of finally obtain HFSCF atom.

$$E_i = \int\phi_i\hat{F}\phi_i d\tau$$

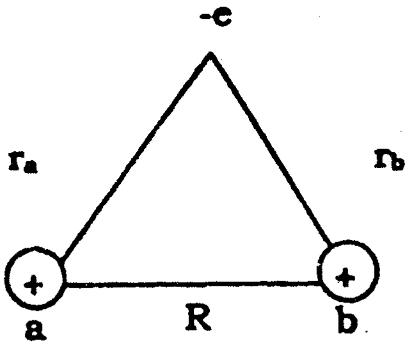
$$= \int\phi_i\left(-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1}\right)\phi\phi_i d\tau +$$

$$= \int\phi_i\left(\sum 2\hat{J}_i - k\hat{j}_i\right)\phi_i d\tau$$

$$Ei = E_i + \sum 2J_{ij} - K_{ij}$$

MO treatment of the hydrogen molecule in $\left(H_2^+\right)$

This simplest molecule consists of two protons and one electrons. Adopting the Born-oppenheimer approximation, the electronic Schrodinger equation for the hydrogen molecule ion is considerably separately. The electronic Hamiltonian operator for H_2^+



where r_a and r_b are the distances from the electron to nuclei a and b respectively and R is the internuclear distance.

$$\hat{H} = -\frac{h^2}{8\Pi^2 m}\nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R} \qquad \text{.....(1)}$$

In atomic units m = e = h/2π = 1

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \qquad \text{.....(2)}$$

$H_{AA} = \int \psi_A \hat{H} \psi_A d\tau$ Columbic integral

$H_{AA} = \int \psi_A \hat{H} \psi_B d\tau$ exchanged orbital

$H_{AA} = \int \psi_A \psi_B \, d\tau$ Overlap interactions

$$H_{AA} = \int \psi_{ISA}\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}\right)\psi_{ISA} d\tau$$

$$H_{AA} = \int \psi_{ISA}\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_A}\right)\psi_{ISA} d\tau - \int \psi_{ISA}\frac{1}{r_B}\psi_{ISA}\, d\tau + \int \psi_{ISA}\frac{1}{R}\psi_{ISA}\, dz$$

$$H_{AA} = \int \psi_{ISA}\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_A}\right)\psi_{ISA} d\tau - \int \psi_{ISA}\frac{1}{r_B}\psi_{ISA}\, d\tau + \int \psi_{ISA}\frac{1}{R}\psi_{ISA}\, d\tau \text{....(3)}$$

the operator Within the brackets in the first integral of equation (3) can be identified as the Hamiltonian of an H atom.

$$\therefore \int \psi_{ISA}\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_A}\right)\psi_{ISA} d\tau$$

$$= \int_{ISA} E_H \, 1S_A \, d\tau \, E_H = E_H \qquad \text{.....(4)}$$

because IS_A is normalized E_H is the energy of a single H atom which is known to be - 0.5 a.u. In the second integral, l/r_B is the energy (in a.u) of attraction between the electron and the nucleus B at a distance of r_B; so the integral gives the total energy of columbic attraction (1) between the electron and that nucleus.

$$J = \int 1SA \frac{1}{r_B} 1SA \, d\tau$$

The 3rd integral

$$\int 1SA \frac{1}{R} 1SA \, d\tau = \frac{1}{R} \int 1SA.1SA \, d\tau = \frac{1}{R} \text{ (for a fixed value of R)}$$

is the energy of repulsion between the two nuclei at a distance R from each other thus substitute the value of equation (4), (5) and (6) in equation (3)

$$H_{AA} = E_H - J + \frac{1}{2} \quad \text{......(7)}$$

$$H_{AA} = \int \psi_{1SA} \hat{H} \psi_{1SB} \, d\tau$$

$$\langle 1SA | \hat{H} | 1SB \rangle$$

$$H_{AB} = \int \psi_{1SA} \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_A} + \frac{1}{r_B} - \frac{1}{R} \right) \psi_{1SB} \, d\tau$$

$$= \int 1SA \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_B} + \right) \psi_{1SB} \, d\tau - \int 1SA \frac{1}{r_A} 1SB \, d\tau + \int \psi_{1SB} \frac{1}{R} 1SB \, d\tau \quad \text{.....(8)}$$

$$\int 1SA \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_B} \right) 1SB \, d\tau$$

since

$$\left[-\frac{1}{2}\nabla^2 - \frac{1}{r_B} \right] 1SB = E_H.1S_B$$

Multiply both sides by 1SA we get

$$\int 1SA \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_B} \right) 1SB = E_H \int 1SA \, \psi 1S_B \, d\tau$$

$$\int 1SA \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_B} \right) 1SB = E_H S \quad \text{.....(9)}$$

$$\int 1SA \ \frac{1}{r_A} 1SB \ d\tau = K \qquad .....(10)$$

This energy K arises due to exchange of electron's position between the two nuclei A and B and hence is called the exchange energy.

$$\int 1SA \ \frac{1}{R} \ 1SB \ d\tau = \frac{1}{R} \int \psi_{SA} \psi_{1SB} \ d\tau \qquad .....(11)$$

$$= \frac{S}{R}$$

Substitute the value of (9), (10), (11) in equ. (8) we get.,

$$H_{AB} = E_H.S - K + \frac{S}{R} \qquad .....(12)$$

The symmetric and anti symmetric energy states are

$$E_S = \frac{H_{AA} + H_{AB}}{1+S} \qquad .....(13)$$

$$E_A = \frac{H_{AA} + H_{AB}}{1-S} \qquad .....(14)$$

(7) and (12) value
substitute the value of H_{AA} and H_{AB} in equ. (13) and (14) we get.

$$E_S = \frac{E_H - J + \frac{1}{R} + E_H.S - K + \frac{S}{R}}{1+S} \qquad .....(4)$$

$$= \frac{EH}{1+S} - \frac{J}{1+S} + \frac{1}{R(1+S)} + \frac{E_H.S}{1+S} - \frac{k}{1+S} \frac{S}{R(1+S)}$$

$$= \frac{EH}{1+S} - \frac{J}{1+S} + \frac{1}{R+SR} + \frac{E_H.S}{1+S} - \frac{k}{1+S} \frac{S}{R+SR}$$

$$E_s = \frac{E_H - J + \frac{1}{R} + E_H S - K + \frac{1}{R}}{1+S}$$

$$E_s = E_H + \frac{1}{R} - \frac{J+K}{1+S} \qquad .....(15)$$

$$E_A = E_H + \frac{1}{R} - \frac{J-K}{1-S} \qquad .....(16)$$

The evaluation of E_s therefore, evaluation of the three integrals J, K and S. The results of evaluation are expressed as function of R as follows

$$J = \frac{1}{R}\left[1-(1+R)e^{-2R}\right] \qquad .....(17)$$

$$K = (1+R)e^{-R} \qquad .....(18)$$

$$S = \left(1+R+\frac{R^2}{3}\right)e^{-2R} \qquad .....(19)$$

substitute the value of (17), (18), (15) in equ (19) and (16) we get symmetric energy state and anti symmetric energy state. The results of such calculation for several values of R, relative to the energy of H atom (i.e E_H) taken as zero.

Energy of H_2^+ for various value of R

R (a.u)	E_s (a.u)	E_A (a.u)
0.5	1.079	2.35
1.0	0.212	1.019
1.5	0.005	0.572
2.0	-0.054	0.338

. The value of E_s or E_A plotted against

These calculations and plotting brings out certain very interesting features.

1. For any value of R, E_s is less than E_A. Beyond a certain value of R, E_s becomes negative (i.e., $<E_H$), but E_A is always greater than E_H i.e., it is always positive.
2. The curve for E_s shown a minimum corresponding to R=2.5 a.u were E_{SA} = -0.0165a.u but that for E_A decreases continuously with increase in R always remaining above the E_A side.

This means that in the ground state the energy of H_2^+ is 0.065a.u less than that H^0 - H^+ separate infinity, this value (0.065 a.u = 1.77 e.v) therefore, represents the dissociation energy. Similarly, the position of minimum i.e., R = 2.5 a.u = 1.32A ° represents the equilibrium and enough (R) in H_2^+.

MO treatment of the Hydrogen molecule

The treatment of a H_2 molecule, within the framework of the MO theory and the Born-Oppenheimer approximation is essentially the same as that of H_2^+, exerts that there is an extra $1/r_{12}$ term. The hydrogen molecule consists of two protons (a and b) and two electrons (1 and 2), the electronic Hamiltonian is given by

$$\hat{H} = -\frac{1}{2}\left(\nabla_1^2+\nabla_2^2\right)-\left[\frac{1}{ra_1}-\frac{1}{ra_2}+\frac{1}{rb_1}-\frac{1}{r_{12}}+\frac{1}{rab}\right]$$

The corresponding Molecular orbitals are

$$\psi_1 = C_1 1S_a(1) + C_2 1S_a(1) \qquad \text{.....(1)}$$

$$\psi_1 = C_1 1S_a(2) + C_2 1S_b(2) \qquad \text{.....(2)}$$

The normalized solution of these equations

$$\psi_1 = \frac{1}{(2+2Sab)^{1/2}}\left[1Sa(1)-1Sb(1)\right]$$

$$\psi_2 = \frac{1}{(2+2Sab)^{1/2}}\left[1Sa(2)-1Sb(2)\right]$$

Where ψ_1 is the bonding MO and ψ_2 is anti bonding MO, and corresponding equations are

$$E_1 = \frac{Haa+Hab}{(1+Sab)^{1/2}}$$

$$E_2 = \frac{Haa+Hab}{(1-Sab)^{1/2}}$$

Where Haa, Hbb are the coulomb integrals, Hab the exchange integral and Sab in the overlap integral. Hence the molecular wave function that would describe the electron distribution of a hydrogen molecule can be written as

$$\psi_{Mo} = \psi_1(1)\psi_1(2)$$

where two electrons are placed in the bonding MO

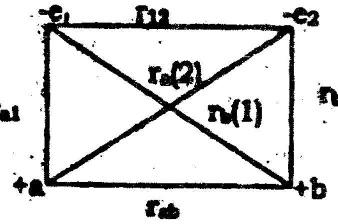
$$\psi_{Mo} = \frac{1}{2+2Sab}\left[1S_a(1)+1S_b(1)\right]\left[1S_a(2)+1S_b(2)\right]$$

$$= \frac{1}{2+2Sab}\left[1S_a(1)+1S_a(2)+1S_b(1)+1S_b(2)+1S_a(1)+1S_b(2)+1S_a(2)+1S_b(1)\right]$$

The first two forms in this expression correspond to situation in which both electrons 1 and 2 are associated with the same proton. Therefore, the first term corresponds to the ionic structure H_a^+ H_b^+ and the second term corresponds to the ionic structure H_a^+ H_b^+.On the other hand the third and the fourth terms correspond to situation in which electrons shared equally by both the protons and therefore, they correspond to the covalent structure of the hydrogen molecule.

Valence Bond Theory fot H_2 molecule

Hydrogen molecule contains 2 electrons and 2 nucleus



There are two possible structures of H_2 molecules

1. When electron 1 is associated with molecules a and electron 2 with nucleus b

$$H_a(1)H_b(2) \qquad .....(I)$$

Hence the orbital wave function for Ha (1) and Hb (2) will be $\psi_a(1)$ and $\psi_b(2)$. Hence wave function for structure I is

$$\psi_I = \psi_a(1).\psi_a(2) \qquad .....(1)$$

2. When electron 2 is associates with nucleus a and electron 1 is associated with nucleus b

$H_a(2)\ H_b(1)$
II

$$\psi_{II} = \psi_a(2).\psi_a(1) \qquad .....(1)$$

The two electrons are distinguishable. As the atom approach, one another the atomic orbitals overlap and it is impossible to distinguish the two electrons (1) and (2). When two electrons are indistinguishable in the H_2 molecule, the wave function ψ_I must be equal to ψ_{II}.

$$\psi_I = \psi_{II}$$

(or)

$$\psi_a(1).\psi_b(2) = \psi_I = \psi_a(2).\psi_b(1) \ .... (3)$$

True wave function is likely to be some contribution of the two -wave functions ψ_I and ψ_{II}

$$\psi = C_1\psi_I + C_2\psi_{II} \qquad .....(4)$$

$$\psi = C_1\psi_a(1)\psi_a(2) + C_2\psi_a(2)\psi_b(1) \qquad .....(5)$$

Since H_2 molecule is symmetrical, the two wave function ψ_I and ψ_{II} contribute equally, therefore $C_1 = \pm C_2$ The co-efficient C_1 and C_2 are relative quantities, we can put $C_I = 1$ and $C_2 = \pm 1$. Putting these values ofC_I and C_2 in equations (5). We get two possible wave functions.

$$\psi_S = \psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1) \qquad .....(6)$$

$$\psi_A = \psi_a(1).\psi_b(2) - \psi_a(2)\psi_b(1) \qquad .....(7)$$

ψ_S = symmetric wave function and does not change if initials (1) and (2) are interchanged.

ψ_A=Anti symmetric wave function. The wave function ψ_A changes to $-\psi_A$ it the initials (i.e.; electron) are interchanged.

• Since H_2 molecule contains two electrons there should be two Laplacian's operator ∇_1^1 and ∇_2^2.

Schrodinger's wave equation for the two electron system.

$$(\nabla_1^2 + \nabla_2^2)\psi + \frac{8\Pi^2 m}{h^2}(E - V)\psi = 0 \qquad .....(8)$$

$\hat{H}$ for H_2 molecule

$$\hat{H} = \frac{-h^2}{8\pi^2 m}\left[\nabla_1^2 + \nabla_1^2\right] - \ell^2\left[\frac{1}{r_a(1)} + \frac{1}{r_b(1)} + \frac{1}{r_a(2)} + \frac{1}{r_b(2)}\right] + h^2\left[\frac{1}{r_{12}} + \frac{1}{r_{ab}}\right] \qquad .....(9)$$

the integral H_{11} may be defined as

$$H_{II} = \int\int \psi_I\, \hat{H}\, .\psi_I .d\tau_1 d\tau_2 \qquad .....(10)$$

Substitute k values such as $\hat{H}$ and ψ_1 we get

$$H_{II} = \int\int \psi_a(1)\psi_b(2)\left[\frac{-\ell^2}{8\Pi^2 m}\left[\nabla_1^2 + \nabla_2^2\right]\right] - e^2\left[\frac{1}{r_a(1)} + \frac{1}{r_b(2)} + \frac{1}{r_b(1)} + \frac{1}{r_b(2)}\right] + e^2\left[\frac{1}{r_{12}} + \frac{1}{r_{ab}}\right]\Bigg]\psi_a(1)\psi_b(2)d\tau_1 d\tau_2$$

.....(11)

$$\left[\frac{-h^2}{8\pi^2 m}\nabla_1^2 \frac{-e^2}{r_a(1)}\right]\psi_a(1) = E_o\psi_a(1)$$

$$\frac{-e^2}{8\pi^2 m}\nabla_2^2 \frac{-e^2}{r_b(2)}\psi_b(2) = E_0\psi_b(2)$$

$$H_{II} = \iint \psi_a(1)\psi_b(2)\left[2E_0 = \frac{e^2}{r_{ab}} + \frac{e^2}{r_{12}} + \frac{e^2}{r_a^{(12)}} + \frac{e^2}{r_b^{(1)}}\right]\psi_a(1)\psi_b(2)\,d\tau_1 d\tau_2 \quad .....(12)$$

If two atom 'a' and 'b' are far apart, their mutual potential energy is nil i.e., $V = 0$. Thus the system H_2 molecule under consideration is equivalent to two separate hydrogen atoms, and if these atoms are in their normal state, the approximate wave function (including spin) will be similar to two hydrogen wave functions. If it is assumed that is wave functions are normalized, then equation (12).

$$H_{II} = 2E_0 + \frac{e^2}{r_{ab}} + J_1 - 2J_2 \quad ..... (13)$$

$$J_1 = e^2 \iint \frac{1}{r_{12}}\left(\psi_a(1)\psi_b(2)\right)^2 d\tau_1 d\tau_2 \quad ..... (14)$$

and because of the equivalents of two electrons

$$J_2 = e^2 \iint \frac{1}{r_b(1)}\left(\psi_a(1)\psi_b(2)\right)^2 d\tau_1 d\tau_2 \quad ..... (15)$$

same general treatment for H_{12}

$$H_{12} = 2E_0 S_{12} + \frac{e^2}{r_{ab}} + k_1 - 2k_2$$

$$k_1 = e^2 \iint \frac{1}{r_{12}}\left(\psi_a(1)\psi_b(2)\psi_a(2)\psi_b(2)\right)d\tau_1 d\tau_2$$

$$k_2 = e^2 \iint \frac{1}{r_a(1)}\left(\psi_a(1)\psi_b(2)\psi_a(2)\psi_b(1)\right)d\tau_1 d\tau_2 \quad ..... (16)$$

$$k_2 = e^2 \iint \frac{1}{r_a(2)}\left(\psi_a(1)\psi_b(2)\psi_a(2)\psi_b(2)\right)d\tau_1 d\tau_2$$

If these results are now substituted the equation for the ,energy states of the H_2 molecule.

For symmetric state $E_s - 2E_0 = \frac{e^2}{r_{ab}}\left[\frac{(J_1 - 2J_2) + (k_1 - 2k_2)}{1 + S_{12}}\right]$

Anti symmetric state = $E_A - 2E_0 = \frac{e^2}{r_{ab}}\left[\frac{(J_1 - 2J_2) - (k_1 - 2k_2)}{1 - S_{12}}\right]$

$$E_+ = \frac{H_{11} + H_{12}}{1 + S^2}$$

$$E_- = \frac{H_{11} - H_{12}}{1 - S^2}$$

$$E = 2E_H + \frac{1}{R} + \frac{J + K}{1 + S^2}$$

$$E = 2E_H + \frac{1}{R} + \frac{J + K}{1 + S^2}$$

Hybridization

The linear combination of the orbitals of the same atom is aclled hybridization. The combination of n atomic orbitals generates 'n' hybrid orbitals of an atom. It can be shown that the hybrid orbitals have better directional and properties and form stronger bends.

Example: sp, Sp^2 and Sp^3 hybridization

S - p Hybridization

The combination of a, s and b orbital, giving two hybrid orbitals ψ_1 and ψ_2 may be expressed as

$$\psi_1 = a_1\psi_s + b_1\psi_p \qquad .....(1)$$

$$\psi_2 = a_2\psi_s + b_2\psi_p \qquad .....(1)$$

The values of the linear combination co-efficient a_1, b_1, a_2 and b_2 may be determined by the following consideration.

1. ψ_1 and ψ_2 are normalized

i.e., $\int \psi_s^2 \, d\Psi = 1$

$$\int \psi_p^2 \, d\Psi = 1$$

2. ψ_1 and ψ_2 are orthogonal

i.e., $\int \psi_S \psi_p \, d\Psi = 1$

3. ψ_1 and ψ_2 are equivalent

Square the equation (1) and integrated with $d\psi$

$$\int \psi_1^2 \, d\Psi = \int a_1^2 \psi_1^2 \, d\Psi + \int b_1^2 \psi_1^2 \, d\Psi + \int 2\psi_{1S} \psi_{1P} \, d\Psi = 1$$

$$a_1^2 + b_1^2 = 1 \qquad .....(3)$$

from equation (2)

$$a_2^2+b_2^2=1 \qquad \text{.....(4)}$$

$$(a_1\psi_S+b_1\psi_P)(a_2\psi_S+b_2\psi_P)=\psi_1\,\psi_2$$

$$a_1a_2\int\psi_S\psi_P\,d\Psi+b_1\,a_2\int\psi_S\psi_P\,d\Psi+a_1\,b_2\int\psi_S\psi_P\,d\Psi+b_1\,b_2\int\psi_P\psi_P\,d\Psi=\psi_1\,\psi_2 d\Psi=0$$

$$a_1a_2+b_1b_2=0$$

Since the s atomic orbital is spherically symmetrical and the two hybrid orbitals ψ_1 and ψ_2 are equivalent, the share of S functions is equal in both ψ_1 and ψ_2 i.e.,

$$a_1^2=a_2^2\frac{1}{2}$$

or

$$a_1=a_2\frac{1}{\sqrt{2}}$$

substitute this in equ (3) we get

$$\frac{1}{2}+b_1^2=1$$

$$b_1^2=\frac{1}{2}$$

$$b_1=\frac{1}{\sqrt{2}} \qquad \text{.....(7)}$$

substitute the value of equ (5) and (6) in (1) 1

$$\psi_1=\frac{1}{\sqrt{2}}(\psi_s+\psi_P)$$

substitute value of equ (6) and (7) in equ (5)

$$\frac{1}{2}+\frac{1}{\sqrt{2}}b_2=0 \qquad b_2=-\frac{1}{\sqrt{2}} \qquad \text{.....(8)}$$

substitute the value of equ (5) and 8 in equ (2) we get

$$\psi_2=\frac{1}{\sqrt{2}}(\psi_S+\psi_P) \qquad \text{.....(9)}$$

Substitute the value of equation (6) and (7) in equ. (5)

$$\frac{1}{2}=\frac{1}{\sqrt{2}}b_2=0 \qquad b_2=-\frac{1}{5^2}$$

Substitute the value equation (5) and (8) in equ. (2)

$$\psi_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$$

For Example:-.

$$\psi_2 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$$

At carbon atom 1, the electron density $a_1^2 = \frac{1}{2}$

At carbon atom 2, the electron density $a_2^2 = \frac{1}{2}$ since we have two π electron in ϕ_1, the total electron density at C_1 and C_2 each is $qr = 2$.

$x \frac{1}{2} = 1$

$$\left.\begin{matrix}\varepsilon \text{ charge} \\ \text{density}\end{matrix}\right\} = 1 - 1 = 0$$

at carbon 1
charge density
at carbon 2 = 1-1 =0

Butadiene:-

$C_1 = C_2 - C_3 = C_4$ There are four 2 p_z atomic orbitals to be combine and four π -electrons in the molecule. The HMO's are of the form

$$\psi = C_1\phi_1 + C_2\phi_2 + C_3\phi_3 + C_4\phi_4 \qquad \text{.....(1)}$$

and the secular determinant is

$$\begin{array}{c|cccc|} & \phi_1 & \phi_2 & \phi_3 & \phi_4 \\ \phi_1 & x & 1 & 0 & 0 \\ \phi_2 & 1 & x & 1 & 0 \\ \phi_3 & 0 & 1 & x & 1 \\ \phi_4 & 0 & 0 & 1 & x \end{array} = 0$$

where, $x = \frac{\alpha - E}{\beta}$

This determinant upon expansion gives the polynomial equation

$x^4 - 3x^2 + 1 = 0$

(or)

$(x^2 - x - 1)(x^2 - x - 1) = 0$

Hence

The three Sp² hybrid orbitals formed by combination of a S orbital with two p-orbitals are expressed as

$$\psi_1 = a_1S + b_1P_x + C_1P_y \qquad .....(1)$$

$$\psi_2 = a_2S + b_2P_x + C_2P_y \qquad .....(2)$$

$$\psi_3 = a_3S + b_3P_x + C_3P_y \qquad .....(3)$$

The co-efficient can be determined as follows :

Since the three hybrids are equivalent, the single S orbital is considered to divide itself equally among them i.e.,

$$a_1^2 = a_2^2 = a_3^2 = \frac{1}{3} \text{ or}$$

$$a_1 = a_2 = a_3 = \frac{1}{\sqrt{3}} \qquad .....(4)$$

One of the three hybrids, say ψ_1 may be assigned any direction; let it be the X-axis. Then, there will be no contribution from p_y i.e., $C_1 = O$. The normalization condition requires that

$$a_1^2 + b_1^2 + C_1^2 = 1; a_1^2 + b_1^2 = 1$$

$$\frac{1}{3} + b_1^2 = 1 \text{ or } b_1 = \sqrt{2/3}$$

Thus

$$\psi_1 = \frac{1}{\sqrt{3}}S + \sqrt{\frac{2}{3}}\,Px \qquad .....(5)$$

By orthogonality of ψ_1 and ψ_2

$$[a_1a_2 + b_1b_2 + C_1C_2 = 0]$$

where $C_1 = 0\ C_2 = 0$

$$[a_1a_2 + b_1b_2 = 0]$$

$$\frac{1}{3} + \sqrt{\frac{3}{2}}b_2 = 0$$

$$b_2 = -\frac{1}{\sqrt{6}}$$

and by normalization of ψ_2

$$a_2^2 + b_2^2 + C_2^2 = 1$$

$$\frac{1}{3} + \frac{1}{6} + C_2^2 = 1$$

$$C_2 = \frac{1}{\sqrt{2}}$$

$$\psi_2 = \frac{1}{\sqrt{3}} S - \frac{1}{\sqrt{6}} Px + \frac{1}{\sqrt{2}} Py \qquad ..... (6)$$

similarly Orthogonality of ψ_1 and ψ_3

$$a_1 a_3 + b_1 b_3 + C_1 C_3 = 0$$
$$a_1 a_3 + b_1 b_3 = 0$$

$$\frac{1}{3} + \sqrt{\frac{2}{3}} b_3 = 0 \qquad \text{or} \qquad b_3 = -\frac{1}{\sqrt{6}}$$

and by orthogomility of ψ_2 and ψ_3

$$a_2 a_3 + b_2 b_3 + C_2 C_3 = 0$$

$$\frac{1}{3} + \frac{1}{6} + \frac{1}{\sqrt{2}} \sqrt{3} = 0$$

$$\sqrt{3} = -\frac{1}{\sqrt{2}}$$

$$\text{Thus } \psi_3 = \frac{1}{\sqrt{3}} S - \frac{1}{\sqrt{6}} p_x - \frac{1}{\sqrt{2}} p_y \qquad ..... (7)$$

The directional properties of these hybrid orbitals and their bonding power can be determined by making the following substitution in equ (5), (6) and (7) we get

$$s = 1$$

$$P_x = \sqrt{3} \sin\theta \cos\phi$$
$$P_y = \sqrt{3} \sin\theta \cos\phi$$

The three functions defining the directional properties of the hybrid orbitals are accordingly

$$\psi_1 = \frac{1}{\sqrt{3}} + \sqrt{\frac{2}{3}} \operatorname{Sin}\theta \operatorname{Cos}\phi \qquad ..... (8)$$

$$\psi_1 = \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{6}}\sqrt{3}\ \mathrm{Sin}\,\theta\,\mathrm{Cos}\,\phi + \frac{1}{\sqrt{2}}\sqrt{3}\,\mathrm{Sin}\,\theta\,\mathrm{Sin}\,\phi$$

$$\psi_2 = \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}}\sqrt{3}\ \mathrm{Sin}\,\theta\,\mathrm{Cos}\,\phi + \sqrt{\frac{3}{2}}\ \phi\mathrm{Sin}\,\theta\,\mathrm{Sin}\,\phi \qquad \text{..... (9)}$$

$$\psi_3 = \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}}\ \mathrm{Sin}\,\theta\,\mathrm{Cos}\,\phi - + \sqrt{\frac{3}{2}}\ \mathrm{Sin}\,\theta\,\mathrm{Sin}\,\phi \qquad \text{..... (10)}$$

If two of the hybridization functions f_1 and f_2 indicate directions in the xy- plane, for which $\theta = 90°$ or $\sin\theta = 1$ the above equ (8), (9) became

$$f_1 = \frac{1}{\sqrt{3}} + \sqrt{2}\ \mathrm{Cos}\,\phi \qquad \text{..... (11)}$$

$$f_1 = \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}}\mathrm{Cos}\,\phi + \frac{1}{\sqrt{3}}\ \mathrm{Sin}\,\phi \qquad \text{..... (12)}$$

The maximum value of f_1 will be

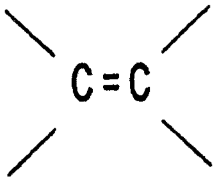
$$f_1 = \frac{1}{\sqrt{3}} + \sqrt{2} = 1.992$$

Huckel Molecular orbital Theory(HMO)

Ethylene:

The ethylene molecule contains twelve valence electrons. Among the twelve valence electron ten form σ bonds and the remaining two π - electrons which forms a single π bond between the two carbon atom of ethylene.

According to HMO, the σ electron should be ignored while calculating the energies.



The wave function for the π electron in the LCAO- MO approximation

$$\psi = C_1\,\phi_1 + C_2\,\phi_2 \qquad \text{..... (1)}$$

Where ϕ_1 and ϕ_2 represent the $2p_z$ atomic orbitals of carbon atom C_1 and carbon atoms C_2.

Using the rules for setting up the Huckel secular determinant

$$\begin{vmatrix} x & I \\ I & x \end{vmatrix} = \cap$$

Where $x = (\alpha - E)/\beta$

The determinant, upon expansion such gives

$$x^2 - 1 = 0$$

$$x = \pm 1$$

Thus, the energy levels are

$$E = \alpha - x\beta$$

For $x = -1 \quad \frac{\alpha - E}{\beta} = -1 \quad E_1 = \alpha + \beta$ **(Bonding)**

$x = +1 \quad \frac{\alpha - E}{\beta} = +1 \quad E_2 = \alpha - \beta$ **(Antibonding)**

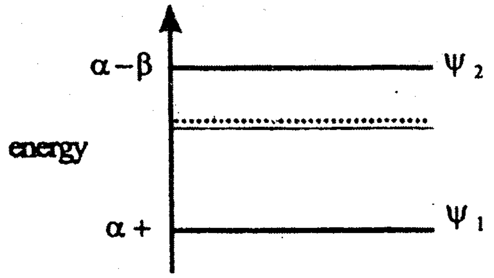
The two HMO energies are

$$E_1 = \alpha + \beta$$

$$E_2 = \alpha - \beta$$

Thus we get two energy levels E_1 and E_2 corresponding to the two molecular orbitals ψ_1 and ψ_2

The resonance integral, β is a negative quantity, being approximately the energy of the probability density of the electron in the field of the nuclei screened by the sigma electrons. Thus $E_1 < E_2$. ψ_1 has energy less than an isolated cabon atom and is therefore, a bonding MO. ψ_2 has greater energy than an isolated carbon atom and is therefore, an antibonding molecule.



$$E \text{ total} = 2E_1 = 2(\alpha+\beta)$$

In the absence of bonding, the total energy of the two electrons lying in the two p_z atomic orbital would be 2α.

The π bond energy is

$$E_\pi = 2(\alpha+\beta) - 2\alpha = 2\beta$$

Determination of the MOS

The two linear equations corresponding to the secular equation (2) are

$$C_1 x + C_2 = 0$$

$$C_1 + C_2 x = 0$$

For $x = -1$ $C_1 - C_2 = 0$ or $C_1 = C_2$

Since the MOs are exrmalised

$$\int \psi^* \psi d\tau = 1$$

$$C_1^2 \int \phi_1^2 d\tau + C_2^2 \int \phi_2^2 d\tau. + 2C_1C_2 \int \phi_1\phi_2 d\tau = 1$$

$$2C_1^2 = 1$$

$$C_1^2 + C_2^2 = 1 \qquad \text{where } C_2 = C_1$$

$$C_1 = C_2 = \frac{1}{\sqrt{2}}$$

Hence $\Psi_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$

$$E_1 = \alpha+\beta$$

For x = + 1

$$\psi_2 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$$

$$E_2 = \alpha - \beta$$

Bond Order:

The partial bond order p_{12} associated with the molecular orbital

$\psi_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$ is given by

$$P_{12}^1 = \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2}} = \frac{1}{2}$$

The partial bond order associated with the antibonding orbital is given by

$$P_{12}^1 = \frac{1}{\sqrt{2}}\left(-\frac{1}{\sqrt{2}}\right) = -\frac{1}{2}$$

It follows that a positive value of partial bond order strengthens the π -bond while a negtive value weakens it

In the ground state of ethylene two π - electron bond to ϕ , 1 the total π - bond order $P_{12} = 2\,P_{12}^1 = 2x\,{}^1\!/_2 = 1$

Charge density:-

The total electron density q_r at an atom r is the sum of electron densities contributed to different electrons in each HMO

$$q_r = \sum nj\, a_{jr}^2$$

where a_{jr} is the coefficient of the atom r in the jth HMO, and nj is the number of electrons in that HMO,

In a π system, a neutral carbon is associated with an electron density of 1.00 and the net charge density is defmed as

$$\varepsilon_r = 1 - qr$$

$$\psi_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$$

For Example:- .

$$\psi_2 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$$

At carbon atom 1, the electron density $a_1^2 = \frac{1}{2}$

At carbon atom 2, the electron density $a_2^2 = \frac{1}{2}$ since we have two π electron in ϕ_1, the total electron density at C_1 and C_2 each is qr = 2.

$x \frac{1}{2} = 1$

$$\left.\begin{matrix}\varepsilon \text{ charge} \\ \text{density}\end{matrix}\right\} = 1 - 1 = 0$$

at carbon 1
charge density
at carbon 2 = 1-1 =0

Butadiene:-

$C_1 = C_2 - C_3 = C_4$ There are four $2p_z$ atomic orbitals to be combine and four π -electrons in the molecule. The HMO's are of the form

$$\psi = C_1\phi_1 + C_2\phi_2 + C_3\phi_3 + C_4\phi_4 \qquad \text{.....(1)}$$

and the secular determinant is

$$\begin{array}{c|cccc|} & \phi_1 & \phi_2 & \phi_3 & \phi_4 \\ \phi_1 & x & 1 & 0 & 0 \\ \phi_2 & 1 & x & 1 & 0 \\ \phi_3 & 0 & 1 & x & 1 \\ \phi_4 & 0 & 0 & 1 & x \end{array} = 0$$

where, $x = \frac{\alpha - E}{\beta}$

This determinant upon expansion gives the polynomial equation

$x^4 - 3x^2 + 1 = 0$

(or)

$(x^2 - x - 1)(x^2 - x - 1) = 0$

Hence

$x^2 + x - 1 = 0$

$x^2 - x - 1 = 0$

The roots of these quadratic equations are

$$x = \frac{-1 + \sqrt{5}}{2} = +0.618$$

$$x = \frac{-1 - \sqrt{5}}{2} = -1.618$$

$$x = \frac{1 + \sqrt{5}}{2} = +1.618$$

$$x = \frac{1 - \sqrt{5}}{2} = -0.618$$

Hence the energy levels are $E = \alpha - x\beta$

$E = \alpha - x\beta$

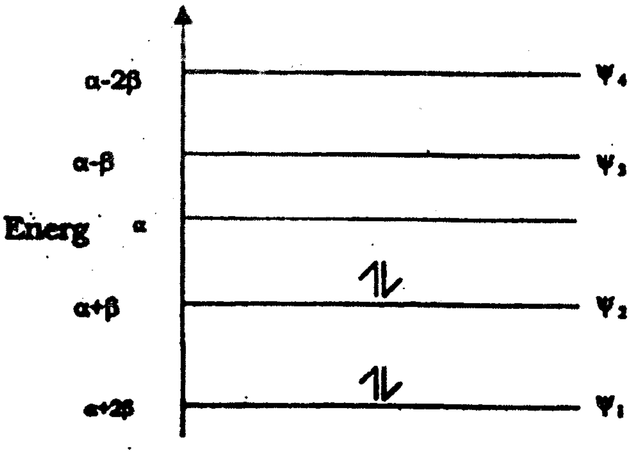
$X = -1.618;\quad E_1 = \alpha + 1.618\beta\ (\text{BMO})$

$X = -0.618;\quad E_2 = \alpha + 0.618\beta\ (\text{BMO})$

$X = +0.618;\quad E_3 = \alpha - 1.618\beta\ (\text{ABMO})$

$X = +1.618;\quad E_4 = \alpha - 1.618\beta\ (\text{ABMO})$

Since the resonance integral β is a negative quantity, we can construct the molecular diagram for the butadiene molecule is



in accordance with the Paulis exclusion principle the four π -electrons of butadiene are accommodated in the BMO.'s ψ_1 and ψ_2

Giving the total π electron energy as $E_\pi = 2(\alpha+1.618\beta)+2(\alpha+0.618\beta)$

$E\pi = 4\alpha + 4.472\beta$

π bond energy $= 4\alpha + 4.472\beta - 4\alpha$

$= 4.472\beta$

The total π -electron energy of the four π -electrons in butadiene is $4\alpha + 4.472\beta$

The energy of two π - electron in ethylene is $2\alpha + 2\beta$

The Delocalisation energy is defined as the difference in energy of the π - electrons in a molecule and sum of the energies of the isolated double bonds present in the classical structure of the same molecule.

Classical structure	Delocalised structure
$H_2C=CH-CH=CH_2$	$C-C-C-C$
$2(\alpha+\beta)\ 2(\alpha+\beta)$	$4\alpha+4.472\beta$

$$\left.\begin{matrix}\text{Delocalisation}\\ \text{Energy}\end{matrix}\right\} = (4\alpha+4.472\beta)-2(2\alpha+2\beta)$$

$DE = 0.472\beta$

The DE is a measure of the stability of the molecule. The higher the energy, the more stable is the molecule. Thus butadiene is more stable than two ethylene molecular by an energy of 0.472β.

The HMO Coefficient:-

In term of x, the secular equation are

$$a_1x + a_2 = 0 \qquad .....(1)$$

$$a_1 + a_2x + a_3 = 0 \qquad .....(2)$$

$$a_2 + a_3x + a_4 = 0 \qquad .....(3)$$

$$a_3 + a_4x = 0 \qquad .....(4)$$

Using $x = -1.618$ corresponding to the contest enerty HMO ψ_1 we get

$a_2 = -a_1 x = 1.618\,a$

$a_3 = -a_1 - a_2 x = -a_1 - (1.61891)(-1.618)$

$a_3 = 1.618\,a_1$

Hence $a_2 = a_3$

$a_3 = -a_4 x = 1.618\,a_4$

Hence $a_1 = a_4$

From the condition of normalisation $a_1^2 + a_2^2 + a_3^2 + a_4^2 = 1$

$$a_1^2 + (1.618 a_1)^2 + (1.618 a_1) + a_1^2 = 1$$

$$a_1 = \frac{1}{\sqrt{7.24}} = 0.372 = a_4$$

$a_2 = 1.618 \times 0.372 = 0.602 = a_3$

$$\psi_1 = 0.372 p_1 + 0.602 p_2 + 0.602 p_3 + 0.372 p_4$$

Similarly, the confiners for ψ_2, ψ_3 and ψ_4 and can be found by using the values x: -0.618, +0.618 and 1.618 receptively. The four HMO's of butadiene one that found to be as follows

$$\psi_1 = 0.372 p_1 + 0.602 p_2 + 0.602 p_3 + 0.372 p_4$$

$$\psi_2 = 0.602 p_1 + 0.372 p_2 - 0.372 p_3 - 0.602 p_4$$

$$\psi_3 = 0.602 p_1 - 0.372 p_2 - 0.372 p_3 - 0.602 p_4$$

$$\psi_4 = 0.372 p_1 - 0.602 p_2 + 0.602 p_3 - 0.372 p_4$$

Butadiene:-

Bond order:

The four π - electrons involved in butadiene occupy the two bonding orbitals.

$$\psi_1 = 0.372 p_1 + 0.602 p_2 + 0.602 p_3 + 0.372 p_4$$

$$\psi_2 = 0.602 p_1 + 0.372 p_2 - 0.372 p_3 - 0.602 p_4$$

Accordingly we get the following values for the partial bond orders between different carbon atoms .

$$P_{12}^{1} = 0.372 \times 0.602 = 0.224$$

$P_{23}^1 = 0.602 \times 0.602 = 0.367$

$P_{34}^1 = 0.602 \times 0.372 = 0.224$

$P_{23}^1 > P_{12}^1 = {}_{14}^{1} > 0$. This shows that the contribution of the electron belonging to ϕ, strengthens the central bond.

Similarly, the partial bond order for ψ_2

$P_{12}^1 = 0.372 \times 0.602 = 0.224$

0.894 0.447 0.894

H_2C - CH- CH- CH_2

The sum of π bond orders is given by

$$\int = p_{12} + p_{23} + p_{34}$$

$= 0.894 + 0.447 + 0.894$

$= 2.236$

Thus, the total π bond order is greater than two by 0.236.

electron density: (Butadiene)

$q_1 = 2 \times (0.372)^2 + 2 \times (0.602)^2 = 1.0$

$q_2 = 2 \times (0.602)^2 + 2 \times (0.372)^2 = 1.0$

$q_3 = 2 \times (0.602)^2 + 2 \times (-0.372)^2 = 1.0$

$q_4 = 2 \times (0.372)^2 + 2 \times (-0.602)^2 = 1.0$

Charge density $\xi = 1 - 1 = 0$

Total electron density = 4.0 in agreement with the fact that these are 4 π electrons in the molecule.

UNIT - IV

INTRODUCTION

1. It deals with the application of statistical mechanics to thermodynamics.
2. It has been used successfully to relate the microscopic properties of the individual molecules (moment of inertia, dipole moment, etc.,) with macroscopic properties (molar heat entropy, polarization etc.,) of a system which is having a large number of molecules.
3. It should be possible to calculate macroscopic properties of a system from a suitable summation of the properties of microscopic constituents. This is precisely the aim of statistical mechanics.
4. Even in the absence of any information about specific individual particles in a large assembly of particles, the properties can be predicted by using the laws of probability.
5. In a system containing a collection of particles or molecules each can be in any of the various available energy levels and spatial distributions. The macroscopic properties of the system depend on how many molecules are occupying the different states. It has now been possible to develop statistical methods to obtain information of the distribution of molecules among the possible states. This enables one to evaluate the various properties of the bulk system. In fact, there are now three different equations for the thermodynamic probability (W) which are required to meet different physical system. The three statistics as they are called, are those of

   Maxwell-Boltzmann, Bose Einstein and Fermi-Dirac statistics

System, assembly and ensemble

If there is a collection of particles, a single particle is referred to as a s stem and collection of particles as a whole as an assembly.

An ensemble may be defined as a collection of a very large number of assemblies which are independent of each other but which have been made macroscopically as identical as possible.

Different types of ensembles

Uniform ensemble: In an uniform ensemble, the density in phase space is a constant.

$$\underset{N \to \alpha}{Lt} \frac{\Delta N}{N} = \text{cons tan t}$$

where ΔN denotes the number of systems in an element of volume ΔV and N total number of systems in the ensemble.

Micro canonical ensemble

When the units are separated by impermeable adiabatic walls, the ener of every system is the same and the ensemble is said to be microcanonical. For example, the number of molecules N, the volume V and the energy of the units E will be the same in all the units.

E,V,N	E,V,N	E,V,N
E,V,N	E,V,N	E,V,N
E,V,N	E,V,N	E,V,N

Canonical ensemble

On the other hand, if the units are separated by a diathermic wall letting the energy fluctuate about some average value E, while the temperature T remains the same the ensemble is called a canonical ensemble.

T,V,N	T,V,N	T,V,N
T,V,N	T,V,N	T,V,N
T,V,N	T,V,N	T,V,N

Grand - canonical ensemble

The third type of ensemble is based on open systems where the number of molecules in a unit is not kept constant while V and T and the chemical potential μ are the same in all the units. These ensembles are called grand canonical ensembles.

T,V, μ	T,V, μ	T,V, μ
T,V, μ	T,V, μ	T,V, μ
T,V, μ	T,V, μ	T,V, μ

Maxwell-Boltzmann Distribution Law

1. Maxwell-Boltzmann statistics assumed that the particles ate independent but distinguishable.
2. This statistics was therefore quite suitable in dealing with solid systems where particles have distinct positions in the crystal lattice.
3. But for gases where identical indistinguishable particles are concerned, this statistics would be unsatisfactory. It has to be appropriately modified in its application to gases.

Let us consider N molecules being grouped into i levels such that the first level contains n_1 molecules, second level n_2 molecules and so on.

The number of non-equivalent arrangements (thermodynamic probability)

$$W = \frac{N!}{n_1!n_2!n_3!...n_i!} \qquad ......(1)$$

Taking ln on both sides

$$\ln W = \ln N! - (\ln n_1! + \ln n_2! + ... + \ln n_j!)$$

$$\ln W = \ln N! - \sum_{1}^{i} n_i \ln n_i - \sum_{1}^{i} n_i$$

when 'N' is large, Striling's approximation can be used to evaluate the factorials

$$\ln N! = N \ln N - N$$

$$\sum_{1}^{i} \ln n_i! = -\sum_{1}^{i} n_i \ln n_i - \sum_{1}^{i} n_i$$

$$= -\sum_{1}^{i} n_i \ln n_i - N$$

$$\ln W = N \ln N - \sum_{1}^{i} n_i \ln n_i$$

N and E are constants, any small variation in these must be zero.

$$\sum_{1}^{i} \delta n_i = 0 \qquad .....(2)$$

consider, total energy of the system is also constant

$$\sum_{1}^{i} \varepsilon_i \delta n_i = 0 \qquad .....(3)$$

Mathematical probability 'P' is proportional to W

$$P \alpha W$$

$$P = C^1 W (C^1 \text{ constant})$$

$$\ln P = \ln C^1 + \ln W$$

$$\ln P = \ln C^1 + N \ln N - \sum_{1}^{i} n_i \ln n_i$$

N and C^1 are constants and the condition for a maximum probability is

$$\delta(\ln p) = 0$$

$$\delta(-\ln p) = \delta\left(\sum_{1}^{i} n_i \ln n_i\right) = 0$$

$$\delta \sum_{1}^{i} (\delta n_i) \ln n_i + \sum_{1}^{i} \delta n_i = 0 \qquad .....(4)$$

So, eqn. (4) becomes

$$\sum_{1}^{i} \ln n_i \delta n_i = 0 \left(\because \sum_{1}^{i} \delta n_i = 0 \right) \qquad ....(5)$$

Equ 2 multiplied by α^1

$$\sum_{1}^{i} \alpha^{1}\,\delta n_i = 0 \qquad \text{.....(6)}$$

Equ 3 multiplied by β

$$\sum_{1}^{i} \beta\varepsilon_i\,\delta n_i = 0 \qquad \text{.....(7)}$$

combine equ 6, 7 and 5

$$\sum_{1}^{i} \left(\ln n_i + \alpha^{1} + \beta\varepsilon_i\right)\delta n_i = 0$$

$$\ln n_i = -\alpha^{1} - \beta\varepsilon_i$$

$$n_i = e^{-\alpha}\, e^{-\beta\varepsilon_i} \qquad \text{.....(8)}$$

$$\ln n_i = -\alpha^{1} - \beta\varepsilon_i \quad (g_i = \text{Degeneracy number}) \qquad \text{.....(9)}$$

$$n_i = \frac{g_i}{e^{\alpha^{1} + \beta\varepsilon_i}} \qquad \text{.....(10)}$$

Equ 8, 9 and 10 are the various forms of Maxwell Boltzmann distribution law.

Bose-Einstein statistics (Quantum statistics)

1. Bose-Einstein statistics applicable to systems consisting of identical and indistinguishable particles, there being no limit to the number of particles in any level.
2. Light quanta (photons), alpha particles, deuteron and all atoms and molecules composed of an even number of elementary particles like ^{12}C, ^{14}N, $^{16}0$ fall in this category. The spin of the nucleus is either zero or an integral number. Such particles are called Bosons.

For this statistics, the total number of different and distinguishable ways of arranging N particles among all energy level. (the thermodynamic probability).

$$W = \pi_{1}^{i} \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!} \qquad \text{.....(1)}$$

Taking natural logarithms of equation (1) and applying Stirling's approximation and on simplification, we get

$$d\ln W = \sum_{1}^{i}\left[\ln\left(n_i + g_i - 1\right)dn_i - \ln n_i\, dn_i\right] = 0$$

$$\sum_{1}^{i}\left[-\ln n_i + g_i - 1) + \ln n_i\,\right]dn_i = 0 \qquad .....(2)$$

We know

$$\sum_{1}^{i} dn_i = 0.....(A) \qquad \text{and} \qquad \sum_{1}^{i} \varepsilon_i dn_i = 0.....(B)$$

Multiplying equation (A) by α^1 and equation (B) by β and adding to equation (2) and simplified, we get

$$\boxed{n_i = \frac{g_i}{e^{\left(\alpha^1 + \beta\varepsilon_i\right)} - 1}} \qquad .....(3)$$

Equation (3) is Bose-Einstein distribution Law.

Fermi - Dirac statistics

1. It is also deals with indistinguishable particles of integral half spin
2. In the Boltmann or in the Bose -Einstein statistics, there was no restriction to number of particles present in any energy state.
3. When fermi-Dirac statistics is applied to particles like electrons the pauli-Exclusion principle is also taken into consideration (i.e.,) two electrons (particles) in an atom cannot have the same energy state. In simple words it means that not more than one particle could be assigned to a particular energy state. Here this particle is known Fermions.

   In this statistics, the total number of different and distinguishable ways of arranging n_1, n_2, n_3 .... etc., particles among the energy levels $\varepsilon_1, \varepsilon_2, \varepsilon_3$ is given

$$W^1 = \prod_{1}^{i} \frac{g_i!}{n_i!\left(g_i - n_i\right)!} \qquad ....(1)$$

Taking natural logarithms of both sides of equation (1), applying Stirling's approximations and consider the condition for the maximum probability and simplified, we get

$$\sum_{1}^{i} \ln n_i - \ln(g_i - n_i) dn_i = 0 \qquad ..... (2)$$

But $\sum_{1}^{i} dn_i = 0 .....(A)$ and $\sum_{1}^{i} \varepsilon_i dn_i = 0 .....(B)$

Multiplying equation (A) by α^1, equation (B) by β and adding with equation (2)

$$\sum_{1}^{i} \left[\ln n_i - \ln(g_i - n_i) + \alpha^1 + \beta\varepsilon_i) dn_i\right] = 0 \qquad ..... (3)$$

Equ (3) is simplified

$$n_i = \frac{g_i}{e^{\alpha^1 + \beta\varepsilon_i} + 1} \qquad ..... (4)$$

The equation (4) is known as Fermi-Dirac distribution Law.

PARTITION FUNCTION

Statistical thermodynamics analysis has been facilitated by usirtg the partition function. The partition function may be defined as follows

$$f = \sum g_i . e^{-\varepsilon_i/kT} \qquad ..... (1)$$

For general purposes, it is essential to measure energy levels relative to the ground state. It, therefore, follows that equation.

$$f = \sum_{0}^{\alpha} g_i . e^{-\varepsilon_i/kT} \qquad ..... (2)$$

The term partition function is given by Fowler. It is a dimensionless quantity. Its value has been found to depend on the molecular weight, molecular volume, temperature etc. Thus the partition function may be defined as thd sum of the probability factors for different energy states or more conveniently i' can be stated as the way in which the energy of a system is partitioned among the molecules which are constituting the system.

$$\frac{n_0}{N}=\frac{1}{f}\text{ (or) } f=\frac{1}{\frac{n_0}{N}} \qquad \text{......(3)}$$

Thus the partition function may be defined as the reciprocal of the mole fraction of e molecules occupying the ground state. It is also the ratio of the total number of molecules the number of molecules in the ground state.

artition function and thermodynamics function

Internal energy

The internal energy 'U' of a system of N molecules is given by

$$U=\sum_1^i n_i\varepsilon_i$$

We know $n_i=\frac{N}{f}g_i.e^{-\varepsilon_i/kT}$

$$U=\frac{N}{f}\sum_1^i \varepsilon_i g_i.e^{-\varepsilon_i/kT} \qquad \text{.....(1)}$$

Since $f=\sum_1^i g_i.e^{-\varepsilon_i/kT}$

$$\frac{df}{dt}=\sum_1^i g_i\left(\frac{-\varepsilon_i}{k}\right).e^{-\varepsilon_i/kT}-\frac{1}{T^2}$$

$$kT^2.\frac{df}{dt}=\sum_1^i g_i\varepsilon_i.e^{-\varepsilon_i/kT} \qquad \text{..... (2)}$$

quation (2) and (1)

$$U=NkT^2.\frac{1}{f}.\frac{df}{dT}\text{ (or) } U=NkT^2\left[\frac{d\ln f}{dT}\right]$$

. Entropy in terms of partition function

Consider a system of N indentical molecules distributed among the quantum levels in ccordance with the Maxwell - Boltzmann distribution law

The Thermodynamic probability of distribution of N particles a such that n_1,n_2,n_3........ re in the energy levels ε_1 , ε_2 , ε_3 is given by

$$W = \frac{N!}{\prod_{1}^{i} n_i!}$$

Taking ln and applying Stirling's approximation

$$\ln W = N \ln N - \sum_{1}^{i} n_i \ln n_i$$

We know $n_i = \frac{N}{f} g_i . e^{-\varepsilon_i/kT} \left(g_i = 1\right)$

$$n_i = \frac{N}{f} . e^{-\varepsilon_i/kT}$$

$$\ln W = N \ln N - \sum_{1}^{i} n_i \ln\left(\frac{N}{f} . e^{-\varepsilon_i/kT}\right)$$

$$\ln W = N \ln f + \frac{U}{kT}$$

According to Boltzmann Planck equation

$S = k \ln W$

$S = k (N \ln f + U/kT) = Nk \ln f + U/T$

3. Heat capacity at constant volume (C_v)

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v$$

$$C_v = Nk . \frac{\partial}{\partial T}\left(T^2 . \frac{\partial \ln f}{\partial T}\right)_v$$

4. Enthalpy

$H = U + PV$

Substitution of U Value and P Value; $P = NkT\left(\frac{\partial \ln f}{\partial V}\right)_T$

$$H = NkT^2\left(\frac{d\ln f}{\partial T}\right) + NkT\left(\frac{\partial \ln f}{\partial V}\right)_T .V$$

$$H = NkT\left[T.\left(\frac{d\ln f}{\partial T}\right) + V\left(\frac{\partial \ln f}{\partial V}\right)_T\right]$$

5. Free Energy

$$G = H - TS = U + PV - TS = A + PV$$

$$A = -NkT \ln f$$

$$G = -NkT\ln f + NkT\left(\frac{\partial \ln f}{\partial V}\right)_T V$$

6. Work function (A)

$$A = U - TS$$

$$A = U - T\,[Nk \ln f + U/T]$$

$$A = -NkT \ln f$$

Translational Partition function

The partition function f_t for a translation motion in one direction is given as follows

$$f_1(x) = \sum g_t .e^{-\varepsilon_i/kT} \qquad .....(1)$$

Where ε_t → translational energy of a molecule in 'x' direction

k → Boltzmann constant

g_t → Statistical weight of each traslational level

The statistical weight of each level is unity ($g_i = 1$). Therefore, partition function $f_t^{(x)}$ becomes as follows

$$f_t^{(x)} = \sum e^{-\varepsilon_i/kT} \qquad .....(2)$$

The translational energy is also quatified and for a particle in a one dimensional box, the translational energy levels are given by

$$\varepsilon_t = \frac{n^2h^2}{8\,ml^2} \text{ erg molecule}^{-1} \qquad \text{.....(3)}$$

combining equation (2) and (3)

$$f_t(x) = \sum e \frac{n^2h^2}{8\,m\,l_x^2\,kT}$$

As the energy levels are so closely spaced, the variation of energy may be taken to be continuous and summation will be replaced by integration.

$$f_t(x) = \int_0^{\alpha} e \frac{n^2h^2}{8ml_x^2\,kT}.dn$$

$$f_t(x) = \left(\frac{2\pi m\,kT}{h}\right)^{\frac{1}{2}}.l_x$$

Similarly, the translational partition function for a molecule in three directions x, y and z at right angles to each other is obtained is as follows

$$f_t = f_t(x).f_t(y).f_t(z)$$

$$f_t = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} l_xl_yl_z = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

Where V represents the volume accessible to a molecule

Rotational partition function

The partition function for rotational energy of a diatomic molecules is given as follows

$$f_r = \sum g_r.e^{-\varepsilon_r/kT} \qquad \text{.....(1)}$$

From quantum mechanical principles it follows that the rotational energy (ε_r) for a diatomic molecule in the jth state is given as follows

$$\varepsilon_r = J(J+1)\frac{h^2}{8\pi^2 I} \qquad \text{.....(2)}$$

J = rotational quantum number J = 0,1,2,3, ...

I = moment of inertia

As the rotational energy at the Jth level is degenerate in (2J+ 1) ways, the value of statistical weight is given as follows

$$g_r = (2J+1) \qquad \text{.... (3)}$$

combining equ (1), (2) and (3)

$$f_{(r)} = \sum (2J+1) e^{-J(J+1)h^2/8\Pi^2 IkT} \qquad \text{..... (4)}$$

As the levels are closely spaced, it means that the summation can be replaced by integration. Thus, we obtain

$$f_{(r)} = \int_0^{\alpha} (2J+1) e^{-J(J+1)h^2/8\Pi^2 IkT} .dj \qquad \text{..... (5)}$$

$$= \int_0^{\alpha} (2J+1) e^{-J(J+1)\beta} .dj \qquad \text{..... (6)}$$

$$\text{Where } \beta = \frac{h^2}{8\pi^2 IkT} \qquad \text{..... (7)}$$

Again put Z = J(J+ 1)which on differentiation becomes as follows

$$dZ = (2J+1).dJ \qquad \text{.... (8)}$$

on combining equation (6) and (7), we have

$$\boxed{f_r = \frac{8\pi^2 IkT}{h^2}}$$

$$f_r = \int_0^{\alpha} \left(e^{-\beta z}\right).dz = \frac{1}{\beta} \qquad \text{..... (9)}$$

on combining equation (7) and (9), we obtain

..... (10)

The result has been found to be only true for heteronuclear molecules such as NO, HCl etc., But in the case of homonuclear molecules such as O_2, N_2, etc., only half of the rotational terms will be present.

In order to avoid complications a symmetry number σ is introduced. Thus equation (10) becomes

$$\boxed{f_r = \frac{8\pi^2 IkT}{\sigma h^2}}$$

Heteronuclear molecule HCl, NO $\sigma = 1$

For homonuclear diatomic molecule $\sigma = 2$.

Vibrational partition function

The partition function for vibrational energy of a diatomic molecule is given as follows·

$$f_v = \sum g_v e^{-\varepsilon v/kT} \qquad \text{..... (1)}$$

The statistical weight of each vibrational level is unity. Hence the equation (1) becomes as follows

$$f_v = \sum e^{-\varepsilon v/kT} \qquad \text{..... (2)}$$

The vibrational energy levels are given by the equation

$$\varepsilon_v = (V + 1/2)h\nu$$

V → vibrational quantum number can be 0, 1,2, etc.,

ν → Frequency of vibration

h → Planck's constant

For the lowest energy level V = 0, the vibrational energy (i.e.,) the zero point energy is equal to h ν /2. The vibrational energy of any level referred t the zero point energy is given by

$$\varepsilon_v = (V+1/2)h\nu - h\nu/2 = vh\nu$$

$$f_v = \sum e^{-vh\nu/kT} = \left(1-e^{-h\nu/kT}\right)^{-1} \qquad \text{.... (3)}$$

Theories or Heat Capacities or Solids

The quantum theory explains the variation of heat capacity with temperature. Specific heat is the heat capacity referring to 1 gm of material . The variation of heat capacity with temperature for several solid elements is shown in Fig. 1.

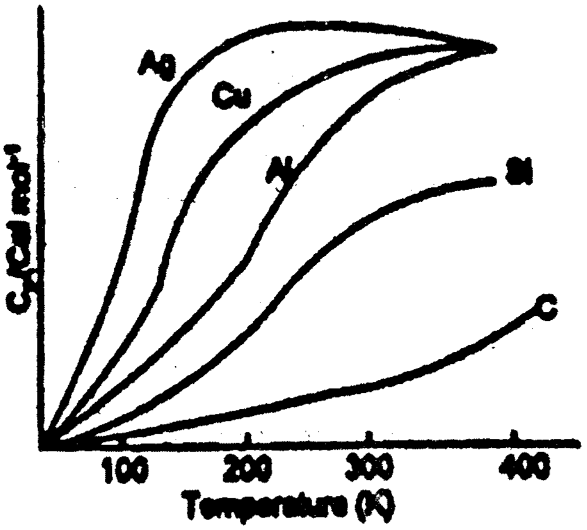


Fig 1. Variation of heat capacity with temperature

The heat capacities for elements like aluminium, copper and zinc increase very rapidly with temperature, approaching a value of 3R = 5.97 cal mole^{-1}) at or near room temperature. carbon and silicon, on the other hand, show a much gradual increase in heat capacity with temperature and do not attain the 3R value until very much higher temperatures. In fact, the heat capacity of carbon does not become 3R until above 1300°C.

Einstein Theory

Albert Einstein applied quantum theory to determine the allowable energy

levels $E_v = (V + \frac{1}{2})h\nu$

$V = 0, 1, 2, ...$

He has assumed only one quantum state per energy level. He has postulated that all atoms do oscillate same frequency of vibration, ν . According to Einstein absorption of energy by the oscillators do not take place continuously, but discontinuously in line with Plank's quantum theory. With these above assumptions, the capacity per mole at constant volume C_v at any temp. is given by the expression,

$$C_v = 3R\left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{\left(e^{h\nu/kT}-1\right)^2} \qquad .....(1)$$

Q_E the characteristic Einstein temperature is defined as

$$Q_E = \frac{h\nu}{k} \qquad ....(2)$$

Equation (1) indicates that C_v is the same function of Q_E/T for all mono atomic solids. Further thisequation predicts that C_v will approach zero at T=O, an that at high temperatures C_v will approach asymptotically the value of 3R. In both these respects the equation is in general agreement with the facts.

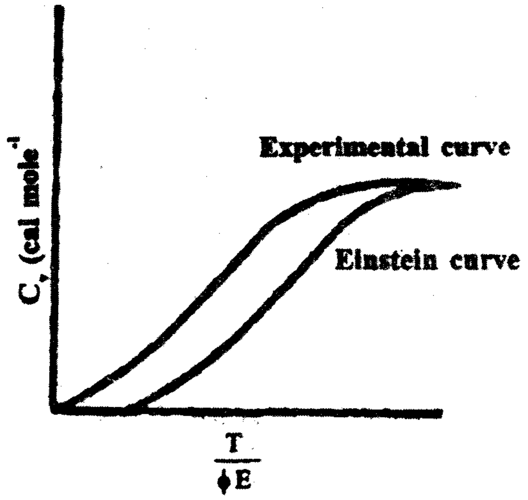


Fig 2

The shape of the curves predicts a low value for C_v at low temperatures.

Debye Theory

A more successful theory of heat capacity of solids was proposed by Peter Debye in 1912. He has assumed a continuous distribution of frequencies i.e.,) a solid may vibrate with any frequency ranging from zero up to limiting frequency, ν_m

Debye has derived an expression for C_v as a function of temperature based on the principles of theory of elasticity and by employing quantum theory. Debye has treated the atomic structure of solid as a homogeneous elastic medium and vibrations can be considered to be equivalent to elastic waves.

$$Cv = 3R\left[1 - \frac{1}{20}\left(\frac{\theta_D}{T}\right)^2 + \frac{1}{560}\left(\frac{\theta_D}{T}\right)^4 + \ldots\right] \qquad \ldots. (3)$$

Q_D the characteristic Debye temperature is defined as

$$Q_D = \frac{h\nu_m}{k}$$

The Debye curve is in excellent accord with experiment for a large group of crystalline solids. The theory predicts that C_V will be zero at T = 0, an will approach the limit of 3R at higher temperatures.

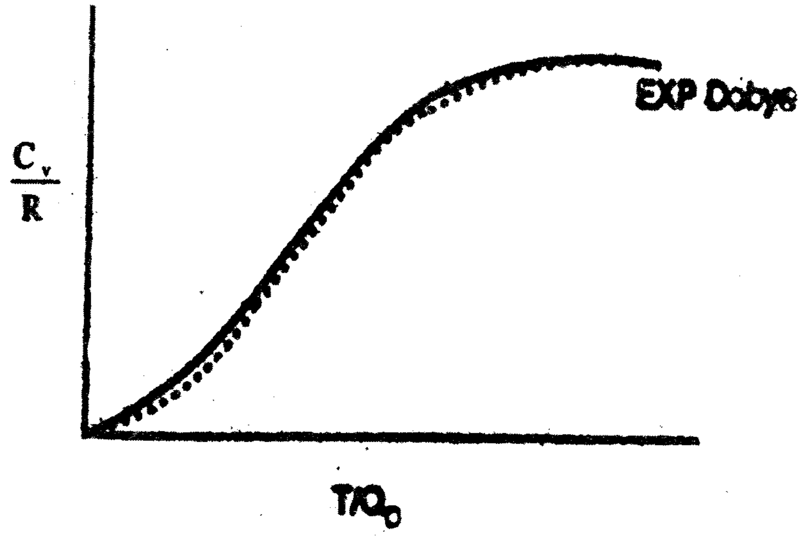


Fig 3.

Another valuable contribution of the Debye theory is that it predicts at very low temperatures a linear relation between C_v and T^3, namely

$$C_v = 464.4\left(\frac{T}{\theta_D}\right)^3 \text{cal deg}^{-1}\text{g atom}^{-1} \quad \text{.... (4)}$$

or $C_V \alpha T^3$

Note $T < \theta_D / 10$

Eqn. (4) is known as the Debye Third Power Law

Limitation of the Debye theory is that it accounts only for heat capacities up to 3R. Yet certain elements, particularly the alkali metals reach values of C_v considerably above this limit at higher temperatures. The excess absorption of energy is usually ascribed to electrons, of whose displacement by the thermal means the Debye theory takes no account.

UNIT - V

THEORY OF STRONG ELECTROLYTES

Debye and Huckel derived a quantitative relationship between the attractive forces of the ions in an electrolyte and the electrolytic conductance. Later Onsager developed the relationship.

Accounting to Debye Huckel theory every ion in solution is surrounded by an ionic atmosphere of opposite sign. This atmosphere arises in the following manner. Imagine a positive ion A and consider a small volume element dv at the end of radius vector Y (Figure - I).

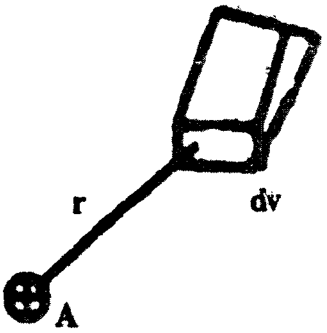


Fig.I. Ionic atmosphere

As a result of thermal movements of the ions, there will be sometimes an excess of positive and sometimes on excess of negative ions in the volume element dv. If a time average is taken dv will be found to have, as a consequence of electrostatic attraction by the positive charge at A, a negative charge density, i.e., the probability of finding ions of opposite sign in the space surrounding a given ion is greater than the probability of finding ions of the same sign.

Every ion may thus be regarded as being associated with ionic atmosphere of opposite sign. The net charge of the atmosphere is equal in magnitude but opposite sign to that of the central ion. The charge density will be greater in the immediate vicinity of the latter and will fall off with increasing distance.

Suppose the time - average of the electrical potential in the centre of the volume element dv is ψ The work required to bring a positive ion from infinity up to this positive is $Z+ \in\psi$ and to bring up a negative ion is $-Z - \in\psi$, where Z+ and Z- are the numerical values of the valencies of the positive and negative ions respectively and $\in$ is the unit charge, ie., the electronic charge . Applying the Boltzmann law of distribution of particles in a field of varying potential energy, the time-average number of positive ions (dn_+) and of negative ions (dn_-) present in the volume element dv are given by

$$dn_+ = n_+ e^{-(Z+\in\psi/kT)} dv$$

$$dn_- = n_- e^{-(-Z-\in\psi/kT)} dv$$

Where n_+ and n_- are the total, numbers of positive and negative ions, respectively, in unit volume of the, solution; k is the Boltzmann constant and T is the absolute temperature. The electrical density i.e., the net charge per unit volume, in the given volume element is therefore given by

$$\rho = \frac{\in\left(Z_+ dn_+ - Z_{-dn}\right)}{dv}$$

$$\rho = \left(n_+ z_+ e^{-(z+\in\psi/kT)} - n - z_{-e}^{(Z-\in\psi/kT)}\right) \qquad .....(1)$$

with the assumption that ($Z^{+\in\psi/kT}$) is much less than unity, the expression for the electrical density (equation 1) becomes:

$$\rho = \frac{-\in^2 \psi}{kT} \sum n_i Z_i^2$$

where n_i and z_i represent the number (per unit volume) and valence of the ions of the ith kind.

Applying poissons's equation and converting rectangular coordinates to polar coordinates, since the distribution of potential about any Point in the electrolyte must be spherically symmetrical, a relationship between ρ and ψ can be recognized as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial T}\right)=-\frac{4\pi\rho}{D} \quad .....(3)$$

Inserting the value of ρ given by equation (2)

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial T}\right)=\left(\frac{4\pi\epsilon^2\psi}{DkT}\sum n_i Z_i^2\right)=k^2\psi \quad .....(4)$$

where the quantity k (not to be confused with specific conductance) is defined by

$$k=\left[\frac{4\pi\epsilon^2}{DkT}\sum n_i Z_i^2\right]^{1/2} \quad .....(5)$$

The differential equation (4) can be solved, and the solution has the general form

$$\psi=\frac{Ae^{-kr}}{r}+\frac{A'e^{kr}}{r} \quad .....(6)$$

Where A and A' are constants which can be evaluated in the following manner, Since must approach zero as r increases, because the potential at an infinite distance from a given point in the solution must be zero, it follows that the constant A' must be zero.

Hence, $$\psi=\frac{Ae^{-kr}}{r} \quad ....(7)$$

For a very dilute solution $\sum n_i Z_i^2$ is almost zero. and hence is k (from equation), the value of the potential at the point under consideration will be A/r (according to equation (7). In such a dilute solution the potential in the neighbourhood of any ion will be due to that ion alone, since other ions are too far away to have any influence. If the ion is regarded as point charge the potential at small distances will be Zi ϵ/Dr. Therefore

$$\frac{A}{r}=\frac{Z_1\epsilon}{Dr}$$

$$A=\frac{Z_1 \in}{D}$$

Insertion of this result in equation (7) yeilds

$$\psi=\frac{Z_1 \in}{D}.\frac{e^{-Kr}}{r} \qquad .....(8)$$

This equation may be written in the form

$$\psi=\frac{Z_1 \in}{Dr}-\frac{Z_i \in}{Dr}\left(1-e^{-kr}\right)$$

For dilute solutions k is small and $1-e^{-kr}$ is equal to kr. Hence

$$\psi=\frac{Z_1 \in}{Dr}-\frac{Z_i \in k}{D} \qquad .....(9)$$

The first term on the right of equation (9) is the potential at a distance r due to a given point ion when there are no surrounding ions. The second term must therefore, represent the potential arising from the ionic atmosphere. Therefore, the potential due to the ionic atmosphere is given by

$$\psi=-\frac{Z_i \in k}{D} \qquad ....(10)$$

If the whole of the charge of the ionic atmosphere which is $-Z_1 \in$, since it is equal in magnitude and opposite in sign to that of the central ion itself, were placed at a distance 1/k from the ion the potential produced at it would be $-Z_1 \in k/D$ Which is identical with the value given by equation (10). So, the effect or ion atmosphere is equivalent to that of a single charge, of the same magnitude, placed at a distance $1/k$ from the ion; this quantity $1/k$ is regarded as a measure of the thickness of the ion atmosphere in a given solution.

According to the definition of k, i.e., equation (5), the thickness of the ionic atmosphere depends on the number of ions of each kind present in unit volume and on their valence. If C_i is the concentration (of the ions of ith kind) in gram-ions per litre, then

$$n_i = c_i \frac{N}{1000}$$ Where

N is the Avogadro number. Hence from equation (5)

$$\frac{1}{k} = \left[\frac{DT}{\sum c_i Z_i^2} \frac{1000k}{4\pi\varepsilon^2 N} \right]^{1/2} \qquad \text{..... (11)}$$

Substituting the values of the constants ($k=1.38 \times 10^{-16}$ erg per degree)

$\varepsilon = 4.802 \times 10^{-10}$ e.s. unit., and $N= 6.023 \times 10^{23}$

$$1/k = 2.81 \times 10^{-10} \left[\frac{DT}{\sum c_i Z_i^2} \right]^{1/2} \text{cm} \qquad \text{..... (12)}$$

The thickness of the ionic atmosphere decreases with increasing concentration and increasing valence of the ions; it increases with increasing dielectric constant of the solvent and with increasing temperature.

TIME OF RELAXATION

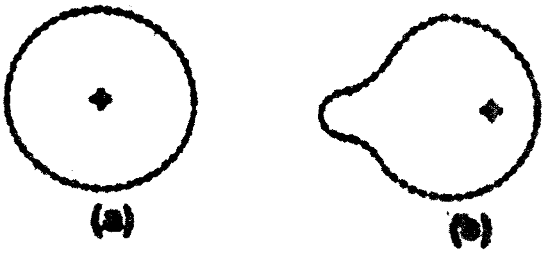


Figure - 2: Asymmetry effect (a) Field off, (b) Field on

As long as the ionic atmosphere is stationary it has spherical symmetry. When the ion is made to move under the influence of an applied electric field, the symmetry is disturbed. If a particular kind of ion; moves to the right each ion has to constantly buildup its ionic atmosphere to the right, while the charge density to the left gradually decays (figure 2). The rate at which the atmosphere to the right forms and that to the left dies away is expressed in terms of a quantity called the time of relaxation of the ionic atmosphere. The decay of the ionic atmosphere occurs exponentially, and so return to random distribution is asymptotic and theoretically only at infinite time it will fall to zero. The ionic atmosphere will fall virtually to zero in the time $4 q \theta$, where θ is the relaxation time and q is defined by

$$q = \frac{Z_+Z_-}{Z_+ + Z_-} \frac{\lambda_+\lambda_-}{Z_+\lambda_- + Z_-\lambda_+}$$

Z is the valence (numerical) and A is the ion conductance of the respective ions. For a binary electrolyte z+ and z. are equal and q is 0.5 and the relaxation time is 2 θ

Suppose an ion of valence z is moving with a steady velocity under the influence of an electrical force εzV, where V is the applied potential gradient. But this force is opposite to the force due to resistance represented by Ku, where K is the coefficient of frictional resistance and u is the steady velocity of the ion. To maintain uniform velocity, both the forces must be equal.

$$\varepsilon zV = Ku$$

$$K = \frac{\varepsilon zV}{u} \qquad \text{.....(14)}$$

Relaxation effect (Asymmetry effect) and electrophoretic effect

Due to the finite time of relaxation, the charge density behind the moving ion is greater than in front. Thus there will be an excess charge of opposite sign behind the moving ion. This will retard the moving ion and this retarding effect is called relaxation effect or asymmetry effect.

Another factor which retards the moving ion is the tendency of the applied field to move the ionic atmosphere, with its associated solvent molecules, in a direction opposite to that of the central ion. This will exert an additional resistance on the central moving ion. This is similar to the effect in colloids and is called as electrophoretic effect'.

Debye and Huckel applying Stokes' law gave an expression for the electrophoretic force of an ion of the ith kind.

$$\text{Electrophoretic force} = \frac{\varepsilon z_i k}{6\Pi \eta} K_i V \qquad \text{..... (15)}$$

where ε, Z_1 and K have their usual significance, η is the viscosity of the medium, K_1 is the coefficient of frictional resistance of the solvent and V is the applied potential.

Onsagar deduced an equation for the relaxation force

$$\text{Relaxation force } \frac{\varepsilon^3 z_i k}{6DkT} \omega V \qquad \text{..... (16)}$$

where D is the dielectric constant of the medium and ω is defined by

$$\omega = Z_+ Z_- \frac{2q}{1+\sqrt{q}} \qquad \text{..... (17)}$$

the value of q is given by equation (13). Equating the forces acting on anion of ith kind moving with a steady velocity.

Applied electrical force = Frictional force of the solvent
+ Electrophoretic force + Relaxation force

$$\text{i.e., } \varepsilon Z_i V = K_i u_i + \frac{\varepsilon Z_i K}{6\Pi \eta} K_1 V + \frac{\varepsilon^3 z_1 k}{6DkT} \omega V \qquad \text{..... (18)}$$

on dividing the equation by $K_i V$ and rearranging

$$\frac{u_i}{V} = \frac{\varepsilon z_1}{K_i} - \frac{\varepsilon z_i K}{6\Pi \eta} - \frac{\varepsilon^3 z_1 k}{6DkT} \frac{\omega}{K_1}$$

If the field strength is 1 volt cm-^{1}, i.e., v is 1/300, then

$$u_i = \frac{\varepsilon z_i}{300K_i} - \frac{\varepsilon k}{300}\left[\frac{z_i}{6\Pi\eta} + \frac{\varepsilon^2 z_1}{6DkT}\,\frac{\omega}{K_i}\right] \qquad \text{.....(19)}$$

An infinite dilution k is zero and hence

$$u^0 i = \frac{\varepsilon z_i}{300K_i} \qquad \text{.....(20)}$$

Since $F u^0 i = \lambda^0 i$

$$\frac{\varepsilon z_i}{300K_i} = \frac{\lambda^0 i}{F}$$

Further $u_i = \lambda_i / \alpha F$ where α is the degree of dissociation. If this result and equation (20) are introduced into equation (19) we get

$$\frac{\lambda_i}{\alpha F} = \frac{\lambda^0 i}{F} - \frac{\varepsilon k}{300}\left[\frac{z_i}{6\Pi\eta} + \frac{\varepsilon}{6DkT}\cdot\frac{\varepsilon z_i \omega}{K_i}\right] \qquad \text{.....(21)}$$

with the assumption that the electrolyte is completely dissociated ($\alpha = 1$) and making use of equation (20), equation (21) modifies to

$$\lambda_i = \lambda^0 i - \frac{\varepsilon k}{300}\left[\frac{z_i F}{6\Pi\eta} + \frac{300\,\varepsilon\,\lambda^0\,\omega}{6DkT}\right] \qquad \text{.....(22)}$$

Introducing the expression for k and the values of ε, k and n equation (22) becomes

$$\lambda_i = \lambda^\circ i - \left[\frac{29.15 z_i}{(DT)^{1/2}\eta} + \frac{9.90 \times 10^5 \lambda^\circ i\omega}{(DT)^{3/2}}\right]\sqrt{C_+Z_+^2 + C_-z_-^2} \quad \text{..... (23)}$$

ince $C = C_+z_+ = C_-z_-$. (C in equivalents per liter and C_+ and C_- in gram ions per liter)

$$\lambda_i = \lambda_i^\circ - \left[\frac{29.15 z_i}{(DT)^{1/2}\eta} + \frac{9.90 \times 10^5 \lambda^\circ i\omega}{(DT)^{3/2}}\right]\sqrt{\alpha\,(z_i + z)} \quad \text{..... (24)}$$

The equivalent conductance of an electrolyte is equal to the sum of the conductances f the constitutent ions and hence.

$$\frac{\lambda_1}{\lambda_i} = \frac{\lambda^\circ i}{\lambda_i^\circ} - \left[\frac{29.15(z_+ + z_-)}{(DT)^{1/2}\eta} + \frac{9.90 \times 10^5 \lambda_i^\circ \omega}{(DT)^{3/2}}\right]\sqrt{C(z_+ + z_-)} \quad \text{.... (25)}$$

For uni-univalent electrolytes Z+ = Z- = 1 and $\omega = 2 - \sqrt{2}$ and, equation (25) educes to

$$\Lambda = \Lambda_o - \left[\frac{82.4}{(DT)^{1/2}\eta} + \frac{8.20 \times 10^5}{(DT)^{3/2}}\Lambda_o\right]\sqrt{C} \quad \text{..... (26)}$$

This equation is known as Debye-Huckel - Onsager conductance equation

The Debye:-Huckel Onsager conductance equation explains the decrease of the quivalent conductance with increase in concentration as due to decrease of ionic velocity esulting from interionic forces. . The first term in the brackets gives the effect of lectrophoretic force and the second term represents the influence of the relaxation or asymmetry force. The magnitude of the interionic forces increases with increase of the valence of the ions (Z_+ and Z_-) and concentration of the electrolyte.

VERIFICATION OF DEBYE-HUCKEL-ONSAGER EQUATION

For a uni-univalent electrolyte, assuming complete dissociation, the Debye-Huckel-Onsager equation may be written as

$$\lambda = \lambda_\circ - (A + B\lambda_\circ)\sqrt{C} \qquad \text{.... (27)}$$

where A and B are constants characteristic of the solvent and the temperature and are given by equation (28) and (29)

$$A = \frac{82.4}{(DT)^{1/2}\,\eta} \qquad \text{.... (28)}$$

$$B = \frac{8.2 \times 10^5}{(DT)^{3/2}} \qquad \text{.... (29)}$$

AQUEOUS SOLUTIONS

Verification of equation is to show that the equivalent conductance is a linear function of the square root of the concentration and the slope of the line is numerically equal to $A + B\Lambda_0$; the values of A and B may be calculated from equations (28) and (29).

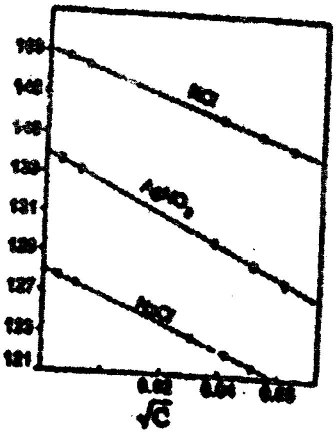


Figure - 3

In figure - 3 the experimentally determined equivalent conductances of aqueous solutions of a few uni-univalent electrolytes are plotted against the square roots of the corresponding concentrations. The slope of the line is found to be numerically equal to $A + B\Lambda_0$, and the intercept to the estimated equivalent conductance at infinite dilution (Λ_0). The DHO equation is strictly obeyed at concentrations upto about 2 x 10^{-3} equivalent per liter.

For electrolytes of unsymmetrical valence type, i.e., Z+ and Z_ are different, the verification of the DHO equation is difficult since the evaluation of the factor in equation (25) requires the mobilities of the ions at infinite dilution; for this transference numbers of the ions are needed. The higher the valence type of the electrolyte the lower is the limit of concentration at which the DHO equation is applicable.

Further bi-valent electrolytes such as copper sulphate the plot of the equivalent conductance against the square root of the concentration is not a straight line, but is concave to the $\sqrt{C}$ axis (Figure - 4). The slopes at appreciable concentrations are much greater than those calculated theoretically. This may be due to the incomplete dissociation at the experimental concentration. The shapes of the curves indicated that in very dilute solutions the slopes approach the theoretical values.

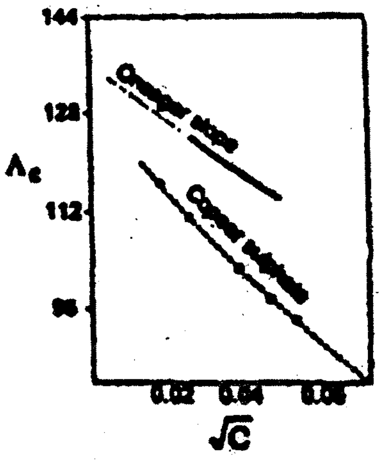


Figure – 4 Deviation from DHO equation

Electrolytes like chlorides and thiocyanates of alkali metals of methanol obey DHO equation. Salts of higher valence types exhibit appreciable deviations. These discrepancies become more marked the lower the dielectric constant of the medium. Especially if the latter is non-hydroxylic solvent. Substances, which are strong electrolytes and almost completely dissociate in water behave as weak, incompletely dissociated electrolytes in solvents of low dielectric constant. Hence deviation from DHO equation is observed.

DISPERSION OF CONDUCTANCE AT HIGH FREQUENCIES: DEBYE-FALKENHAGEN EFFECT

An important consequence of the existence of the ionic atmosphere, with a finite time of relaxation is the variation of conductance with frequency at high. frequencies, referred to as the dispersion of conductance or the Debye Falkenhagen effect. If an alternating potential of high frequency is applied to an ion with the relaxation time of the ionic atmosphere, the unsymmetrical charge distribution formed around an ion in motion will not have time to form completely. If the oscillation frequency is high enough, the ion will be virtually stationary and its ionic atmosphere will be symmetrical. Therefore the retarding force due to the relaxation or asymmetry effect will disappear partially or entirely as the frequency of the oscillations, of the current is increased. Hence at sufficiently high frequencies the conductance of a solution. should be greater than that observed with low frequency alternating current or with direct current. The frequency at which the increase of conductance is expected is approximately $1/\theta$, where θ is the relaxation time. The relaxation time for a binary electrolyte.

$$\theta = \frac{71.3 \times 10^{-10}}{Cz\lambda} \text{sec.}$$

And the limiting frequency ν above which abnormal conductance is expected is

$$v \approx \frac{CZ\Lambda}{71.3} \times 10^{10} \text{ oscillations per second}$$

The corresponding wave length

$$\lambda \approx \frac{2.14}{CZ\Lambda} \text{ meters}$$

For most electrolytes other than acids and bases, in aqueous solutions, Λ is about 120 at 25°C and hence

$$\lambda \approx \frac{2 \times 10^{-2}}{CZ} \text{ meters}$$

For uni-univalent electrolyte of 0.001 molar concentration the Debye-Falkenhagen effect should be observed with high frequency oscillations of wave length of about 20 meters or less.

$$\lambda \approx \frac{2 \times 10^{-2}}{0.001 \times 1} = 20 \text{ meters}$$

The higher the valence of the ions and the more concentrated the solution the shorter the wave length (higher the frequency) of the oscillations required for the effect to become evident.

The calculated ratio of the decrease of conductance due to relaxation effect at a, short wave length λ, i.e., $\Lambda_R(\lambda)$, to that at long wave length Λ_R, i.e., at low frequency, is plotted as ordinate against the wave length as abscissa (Figures 5 and 6).

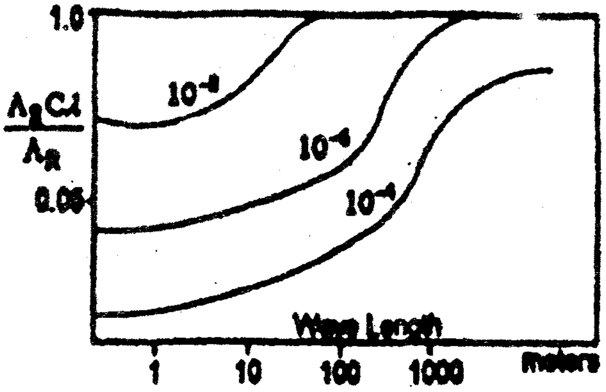


Figure 5 : High Frequency conductance dispersion of potassium chloride

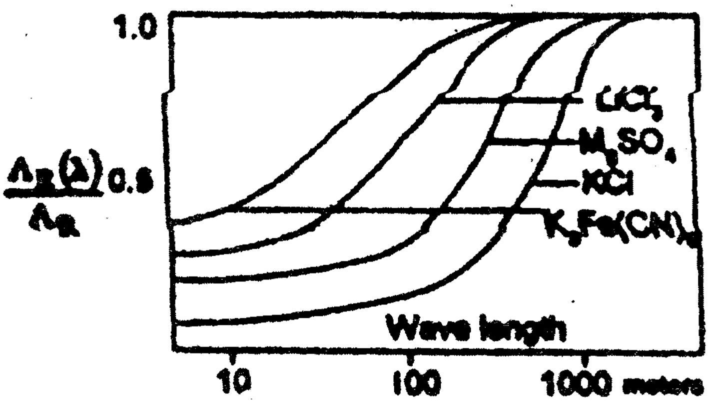


Figure 6 : High Frequency conductance dispersion of salts at 10^{-4} mole per litre.

It is seen that the decrease of conductance due to reduction or asymmetry effect decreases with decreasing wavelength or increasing frequency.

CONDUCTANCE WITH HIGH POTENTIAL GRADIENTS: WIEN EFFECT

When the applied potential is of the order of 20,000 volts per cm., anion will move at a speed of about 1 meter per sec., and it will travel several times the thickness of the ionic atmosphere in the time of relaxation. As a result there is no time for the ion to build up the ionic atmosphere and hence the moving ion is virtually free from an oppositely charged ion atmosphere. In these circumstances both asymmetry and electrophoretic effects will diminish and at sufficiently high voltage will disappear. The equivalent conductance at any appreciable concentration will be greater than the value at low voltage. This is known as wien effect. The wien effect is most marked where there is large interionic attraction, i.e., in concentrated solutions of high valence ions. The Wien effect for potassium ferricyanide is depicted in figure 7. The quantity Δ/λ is the increase of equivalent conductance due to the application of a. potential gradient represented in X- axis. At very high potential the relaxation and electrophoretic effects are completely eliminated and hence and $\Delta\lambda$ values tend towards a limit.

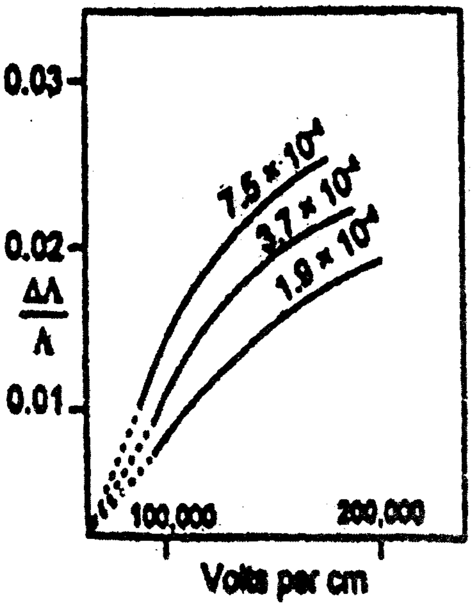


Figure 7. Wien effect for potassium ferricyanide

For an incompletely dissociated electrolyte the measured equivalent conductance should be $\alpha\Delta_0$ where α is the degree of dissociation. The Wien effect for weak acids and bases is several times greater than expected. This is more so as the voltage is raised. The powerful electric fields produce a temporary dissociation of the weak electrolyte into ions. This phenomenon is called as dissociation field effect.

To conclude, the conductance with very high frequency currents and at high potential gradients provide clear evidence for the theory of electrolytic conductance based on the existence of ionic atmosphere.

ACTIVITY AND ACTIVITY COEFFICIENT

When a pure liquid or a mixture is in equilibrium with its vapour the chemical potential of any constituent in the liquid must be equal to that in the vapour.

$$\mu_i = \mu_i^o + RT \text{ In } p_i$$

Since the partial vapour pressure of any constituent of an ideal solution is proportional to its mole fraction (X_i) in the solution the above equation is modified.

$$\mu = \mu_x^o + RT \text{ In } X_i$$

The above equation is true for ideal solutions. If the solution is not, ideal the equation is further modified

$$\mu_i = \mu_x^o + RT \text{ In } x_i f_i$$

The correction factor f_i is called as the activity coefficient of the constitutent i in the given solution. Activity coefficient is a measure of the deviation from ideal behaviour. For an ideal solution the activity coefficient 'f' is unity.

$$\mu_i = \mu_x^o + RT \text{ In } x_i f_i$$

The product of activity coefficient and mole fraction is called the activity.

$$X_i f_i = a_i$$

$$\mu_i = \mu_m^o + RT \text{ In } a_i$$

The mole fraction of the solute is proportional to its concentration. The concentration may be expressed in terms of molarity (c) or molality (m)

$$\mu = \mu_x^o + RT \text{ In } xfx$$

$$\mu = \mu_c^o + RT \text{ In } x\ Cf_c$$

$$\mu = \mu_x^o + RT \text{ In } x\ mf_m$$

f_c ,is normally written as f and f_m is given the symbol y

ACTIVITY AND MEAN ACTIVITY

If a_+ and a_- are the activities of the ions produced by the electrolyte and v_+ and v. are the number of positive and negative ions respectively, the mean activity $a_\pm$ is calculated by the following equation.

$$a_\pm \equiv \left(a_+^{v+} a_-^{v-}\right)^{1/v}$$

Where v is the total number of ions

Activity a_2 of the electrolyte is given below

$$a_+^{v+} a_-^{v-} = a_2$$

Mean activity = (activity)$^{1/v}$

Similarly mean activity coefficient is explained

$$\gamma_\pm = \left(\gamma_+^{v+} \gamma_-^{v-}\right)^{1/v}$$

ACTIVITY COEFFICIENT

The activity coefficients of dilute solutions of uni-univalent electrolytes are almost equal to 1. The deviation is very less. Irrespective of the electrolyte the activity coefficients of uni-univalent electrolytes at dilute solutions are almost equal. For the same concentration when we move from uni-unibalent to uni-bivalent the deviation increases. The activity coefficient depends upon the ionic strength of the solution are almost equal. For the same concentration when we move from uni-univalent to uni-bivalent the deviation increases. The activity coefficient depends upon the strength of the solutions.

THE DEBYE-HUCKEL LIMITING LAW

The thickness of the ionic atmosphere is given by equation

$$1/k = \left(\frac{DT}{\sum c_i z_i^2} \frac{1000R}{2\pi\varepsilon^2 N}\right)^{1/2} \qquad .....(30)$$

since ionic strength, $\mu = 1/2 \sum c_i z_i$

$$k = \left[\frac{8\pi\varepsilon^2 N^2}{1000DRT} \mu\right]^{1/2} \qquad .....(31)$$

Activity coefficient of an electrolyte is related to the thickness of the ionic atmosphere by the expression.

$$l_e f_i = \frac{-Z_i^2 \varepsilon^2 N}{2DkT} \qquad .....(32)$$

Introducing equation (31) into equation (32) and dividing the right - hand side by 2.303 to convert natural to common logarithms

$$\log f_i = -\frac{N^2 \varepsilon^2}{2.303 R^{3/2}} \left[\frac{2\pi}{1000}\right]^{1/2} \frac{Z_i^2}{(DT)^{3/2}} \sqrt{\mu} \qquad .....(33)$$

Substitution of numerical values of universal constants we get

$$\log f_i = -1.823 \times 10^6 \frac{Z_i^2}{(DT)^{3/2}} \sqrt{\mu} \qquad .....(34)$$

For a given solvent and temperature D and T are constants and hence

$$\log f_i = -AZ_i^2 \sqrt{\mu} \qquad .....(35)$$

where A is a constant for the solvent at the specified temperature. This equation is known as the Debye-Huckel limiting law. It expresses the variation of the activity coefficient of an ion with the ionic strength of the medium. It is called the limiting law because the approximation made in the derivation of the potential at an ion due to its ionic atmosphere is applicable only at infinite dilution. This law holds good for electrolytes in very dilute solution. The general conclusion drawn from the limiting law equation (35) is that the activity coefficient of an ion should decrease with increasing ionic strength of the solution. The decrease is greater the higher the valence of the ion and the lower the dielectric constant of the solvent. The mean activity coefficient of an electrolyte may be written as

$$\log f_\pm = -AZ + Z_- \sqrt{\mu} \qquad .....(36)$$

where Z_+ and Z_- are the valences of the ions.

ELECTRODE KINETICS

A reaction-taking place on the surface of an electrode involves the following steps;

1. Diffusion of the reactants to the surface of the electrode
2. Absorption of reactants on the surface of the electrode
3. Transfer of electrons or to the adsorbed reactant species
4. Description of products from the surface
5. Diffusion of products away from the surface of the electrode.

The necessary activation energy for the ions and electrons involved in a reaction is produced by the electric field. Since the reactions are investigated at temperatures more than zero degree centigrade, thermal energy in addition to electrical energy also contribute to activation energy.

For each ionic species at equilibrium, the rate of electron transfer in the cathodic direction is exactly balanced, by the electron transfer in the anodic direction so that the current density (current per unit area)

$$jc = ja = jo$$

It is this condition, which determines the equilibrium difference in electric potential, $\Delta\phi eq$. The currrent density jo at equilibrium is called the exchange current density. The rate r of the chemical reaction at the surface of an electrode is given by

$$r = j/zF$$

where z is the charge on the ionic species and F is the faraday. We see that in an electrochemical reaction $r \alpha j$, it may be mentioned that while the rate of the chemical reaction at the electrode is expressed in units of mol $m^{-2}S^{-1}$, the rate of the change transfer at the electrode is expressed in units of A m^{-2}

For a given electrochemical reaction, the electrodes are said to be nonpolarisable if they have high exchange - current density. Application of potential difference across a non polarisable electrode results in an increased flow of charge between the electrode and the solution, though the potential difference across the electrical double layer does not change. Thus the charge moves rapidly to and from the electrode with the result that no charge density is built up in the surface layers. Calomel electrode furnishes an example if non polarisable electrode.

If the applied potential difference across a polarisable electrode is increased, there is a little flow of charge into the solution. The charges remain in the electrical double layer and increase the potential difference across it. Mercury electrode in KI solution is an example of a polarisable electrode.

When an electrochemical cell operates under non-equilibrium conditions, $jc \neq ja$. In such case the potential difference between the cell terminals departs from the equilibrium value $\Delta\phi = E$, the cell EMF. If the cell is converting chemical free energy into electrical energy, $\Delta\phi < E$ If, on the other hand, the cell is using an external source of energy to cause chemical reaction, $\Delta\phi <$ The actual value of $\Delta\phi$ depends upon the current density j at the electrodes. It is customary to define the quantity over potential of the cells as

$$\Delta\phi - \Delta\phi eq = \eta$$

The value of η id determined in part by the potential difference (iR) required to overcome the resistance R in the electrolyte and the leads. The corresponding electrical energy id dissipated as heat; it is analogous to the frictional losses in irreversible mechanical process. The remaining part of η, which is of a particular theoretical interest, arises from the rate limiting process at the electrodes. The corresponding electrical energy is being used for providing part of the activation energy in one or more steps of the electrode reaction.

THEORETICAL INVESTIGATION OF KINETICS OF AN ELECTRODE REACTION

Butler - Volmer Equation

Consider the electrode reaction

$$M^{2+}(aq) + ze \rightarrow M(s)$$

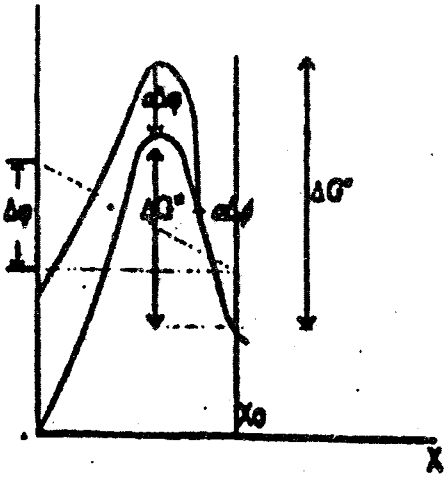


Fig. 8. Gibbs function curve for the electrode reaction

Which will occur when the reaction ion M^{2+} is in the vicinity of an electrode surface so that the electrons are transferred from the electrode to the ion.

Now according to the Eyring activated complex theory (ACT), the rate constant k_2 of the chemical reaction is given by

$$k_2 = B \exp(-\Delta G^{o\neq}/RT) \quad \ldots (37)$$

Where $G^{O\neq}$ is the standard Gibbs free energy of activation and B is some constant. Figure (12) shows the reaction paths along the free energy surfaces between he reactants and the products. The "reaction coordinate" is normal to the electrode surface. The electrochemical reaction involving electron transfer occurs in a region near the electrode that coincides with the region of the electrical double layer. It may be mentioned that the double layer has very high electric field or the order of 10 G G^9 Vm G^{-1}, assuming that a potential difference of one volt exists across a typical double layer of thickness 1 nm. . Such fantastically high electric field can literally tear the ions from the solid metal surface, dragging them into the solution. Assuming the Helmholtz model of the double layer, we may assume that the potential varies linearly with X (figure). The position of the outer Helmholtz plane is at X_o where the reactant molecule can be located.$M^{2+}(aq) + ze \rightarrow M(s)$ in the vicinity of the electrode surface showing the lowering of $\Delta G^{\neq}$ by the electric potential.

We shall consider a reaction at the electrode in which particular species is reduced by the transfer of a single electron in a rate-determining step. Let (Ox) and (Red) be the concentrations of the oxidized and reduced forms of the species, respectively, outside the double layer. Clearly, the net current at the electrode is the difference of the currents resulting from the reduction [Ox] and oxidation of (Red). The rates of these processes are $k_c[Ox]$ an $k_a[Red]$, respectively. In a reduction process, the magnitude of charge transferred per mole of reactin events is $F = eN_A$ where F is the Faraday constant. Hence, the cathodic current density j_c, arising from the reduction is given by

$$j_c = Fk_c[Ox] \qquad \text{..... (38)}$$

An opposing anodic current density I_a, arising from oxidation is,

$$j_c = Fk_c[Red] \qquad \text{..... (39)}$$

Where the k_c s are the corresponding rate constants. Hence, the net current density at the electrode is given by

$$J = j_a - j_c = Fk_a[Red] - Fk_c[Ox] \qquad \text{..... (40)}$$

$$= FB_a[Red]\exp(-\Delta Ga^{\neq}/RT) - FB_c[Ox]\exp(-\Delta G_a^{\neq}/RT \qquad \text{..... (41)}$$

where we have made use of Eq. (37) and assumed that Gibbs free energy of activation is different for the cathodic and anodic processes. When $j_a > j_c$ so that $j > 0$, the current is anodic and when $j_a > j_c$ so that $j = 0$, the current is cathodic.

Let us consider a reduction reaction. As an electron is transferred from one electrode to another, the electrical work done is $e\Delta\phi$, where e is the electronic charge and $\Delta\phi$ is the potential difference between the electrodes. Hence, the Gibbs free energy of activation is changed from $\Delta G^{\neq}$ to $+F\Delta\phi$, if the transition state corresponds to .Ox being very close to the electrode. Thus, if $\Delta\phi > 0$, more work has to be. done to bring Ox to its transition state, with the result hat Gibbs free energy of a activation is increased. On the other hand, if the transition state corresponds to Ox being far from the electrode (i.e., close to the outer pane of the double layer), then. $AG^{\neq}$ is independent of $\Delta\phi$. In practice, however, the situation is midway between the two extremes. Hence, we can write the Gibbs free energy of activation for reduction as $\Delta G^{\#} + \alpha F \Delta\phi$ where α, called the transfer coefficient or symmetry factor, lies between 0 and 1, i.e., $0 < \alpha < 1$.

Let us next consider the oxidation of Red. Here Red discards an electron to the electrode with the result that the extra work needed for reaching the transition state is zero if this state lies close to the electrode and if that state lies away from the electrode (i.e, close to the outer plane of the double layer), the work needed is $-F\Delta\phi$, so that $\Delta G^{\#} - (1-\alpha)F\Delta\phi$ Substituting for the two Gibbs, free energies of activation in eq. 41, we obtain the following expression for the current density:

$$j=\left\{FB_a\left[Red\right]\exp\left(-\Delta G_a^{\#}/RT\right)\right\}e^{(1-\alpha)F\Delta\phi RT}-FB_c\left[Ox\right]\exp\left(-\Delta G_c^{\#}/RT\right)e^{-\alpha F\Delta\phi RT} \quad \text{..... (42)}$$

$$= j_a - j_c$$

At equilibrium $\Delta\phi - \Delta\phi_{eq}$ and the net current is zero and the equlibrium current densities are equal. Thus, if the potential difference differs from its equilibrium value by; the overpotential, so that

$$\eta = \Delta\phi -. \Delta\phi_{eq} \quad \text{..... (43)}$$

the two current densities are,

$$j=\left\{FB_a\left[Red\right]\exp\left(-\Delta G_a^{\#}/RT\right)\right\}e^{(1-\alpha)F\Delta\phi}\,eq^{/RTt}\,e^{(1-\alpha)}\eta^{F/RT} = j_{a,e}\,e^{(1-\alpha)}\eta^{F/RT} \quad \text{..... (44)}$$

$$j_c=\left\{FB_c\left[Ox\right]\exp\left(-\Delta G_c^{\#}/RT\right)\right\}e^{-\alpha F\Delta\phi}\,eq/RT\,e_{\eta}^{\alpha}\backslash RT = j_{c,e}\,e_{\eta}^{-\alpha}F/RT \quad \text{..... (45)}$$

Since the two equilibrium current densities, $j_{a,e}$ and $j_{c,e}$ are equal, we can drop the subscripts and designate each of them as J_o, the exchange current density, and write.

$$j = j_o = \left\{e^{(1-\alpha)}\eta^{F/RT} - e^{-\alpha\eta}F/RT\right\} \quad \text{..... (46)}$$

Eq.46 is the well known Butler - Volmer equation, Let us examine the exponentials in Eq.46. When the overpotential η is very small so that $\eta F / RT << 1$, we can use the series expansion.

$$x = 1 + x + \frac{X_2}{2!} + ...$$

to obtain

$$j = J_o \{[1 + (1-\alpha)\eta F/RT + ...] - [\alpha\eta F/RT) + ...]\} \qquad .....(47)$$

$$j = J_o \eta F / RT \qquad .....(48)$$

From Eq. 48 we see that the current density is proportional to the overpotential.

From Eq. 48, we see that,

$$\eta = (RT/F)(i/j_o)$$

When η is small and positive, the current is anodic ($j > 0$, when $\eta < 0$) and when η is small and negative, the current is cathodic ($j < 0$, when $\eta < 0$).

When the overpotential is large and positive (which is the case of an electrode being an anode in electrolysis), the second exponential in Eq.46 is much smaller than the first and may be neglected, giving.

$$j = j_o e^{(1-\alpha)\eta F/RT} \qquad ...(49)$$

Hence, taking logs of both sides

$$\ln j = \ln jo + (1-\alpha)\ \eta F/RT \qquad ...(50)$$

When the overpotential is large but negative (corresponding to the cathode in electrolysis), the first exponential in Eq. 46 is much smaller than the second and may be neglected and we have.

$$j = -\ j_o e^{-\alpha\eta F/RT} \qquad .....(51)$$

so that

$$\ln(-j) = \ln j_o - \alpha\eta nF / RT \qquad .....(52)$$

Eq.50 and 51 are called the Tafel Equations

Figure (9) shows the plot of the current density j versus the over potential η is in accordance with the Butler - Volmer equation. We consider two Cases, labeled η as A and B. In case A there are high exchange current densities j_0 at both electrodes. The individual electrode curves are labeled A' and A". In this case even a small over potential will produce appreciable flow through the cell. The other case, B, 'corresponds to very low exchange current density J_0 (We have not shown the individual electrode curves.) In this case, a large value over potential is required to cause appreciable current flow through the cell. Thus, we see that it is the exchange current density J_0 which, according to the Butler Volmer equation, determines the activation over-potential. The Shape of the current density versus over potential curves is evidently determined by the value of the transfer coefficient α, which can be determined by fitting the experimental curve to the Butler - Volmer equation.

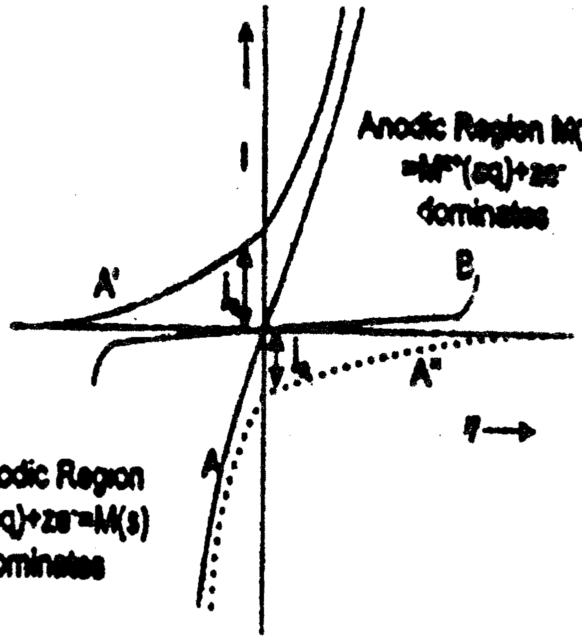


Figure. 9.

Fig (9) Variation of current density with over potential in accordance with the Butler - Volmer equation.

The transfer coefficient can also be determined from the Tafel plot, which is the plot of the logarithm of the current density against the over potential (fig.). The linear portions of the curves in Fig.(10) agree with the Tafel equation. From the slope and the intercept of the Tafel plot, a and i_o can be determiner.

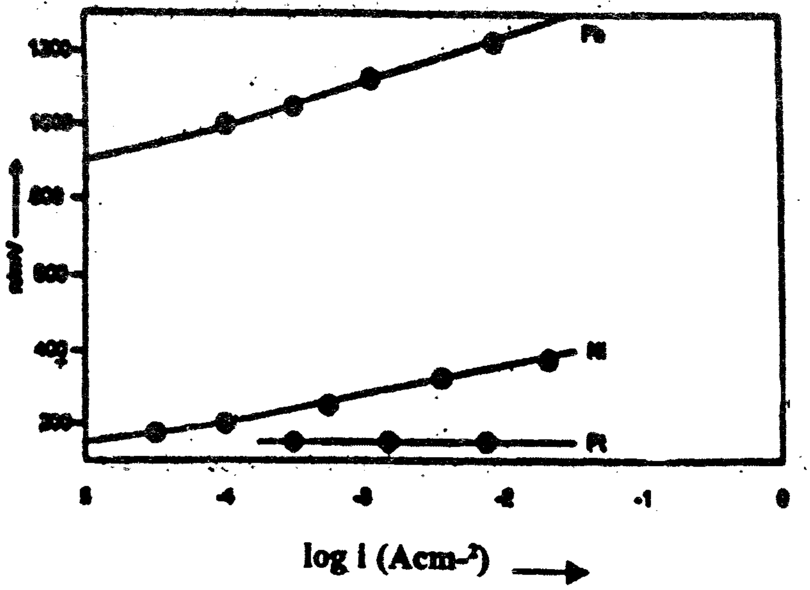


Figure .10.

Fig (10) Variation of over potential for the discharge of H^+ ion on the various metals with current density.

Electrokinetic Phenomena

Electrokinetic phenomena are a relative movement with respect to one another, of a solid and a liquid is accompanied by certain electrical phenomena.

When a liquid is in contact with solid the interface is electrified. When the liquid flows with respect to solid, as the interface is electrified it is accompanied by electrical phenomena. It arises due to the zeta potential present on the diffused layer. This will lie on the solution side - such a phenomenon of movement of one phase with respect to another when the interface is electrified is known as electrokinetic effect. As ions in diffused layer can change and not the ions in the fixed layer. The observed electrokinetic effect is only due to the ions In diffused layer and zeta potential lies on the diffused layer.

The theoretical treatment of electrokinetic phenomena is based on the concept of the existence of an electrical double layer at the solid liquid boundary.

The Electrical Double Layer

According to Helmholtz, the double layer consists of two oppositely charged layers at a fixed distance apart, so that it could be regarded equivalent to an electrical condenser of constant capacity, with parallel plates separated by a distance of the order of a molecular diameters. If the electrical double layer at the interface of motion between a solid and a liquid is regarded as a condenser with parallel plates d cm apart each concepts a charge σ per sq. cm.Then according to electrostatistics:

$$\xi = \frac{4\pi o d}{D}$$

Where ξ is the difference in potential between the plates of zetapotential and D in the dielectric constant of the medium.

The conception of Helmholtz of the double layer involving a sharp potential gradient, was modified by Guoy and Chapman, they used diffuse double layers. According to this view the solution side of the double layer is not merely one molecule or so in thickness but extends for some distance in the liquid phase. In this region thermal agitation permits the free movement of the ions present in the solution, but the distribution of positive and negative charges is not uniform since the electrostatic field arising from the change on the solid will result in a preferential attraction of particles of opposite sign. The picture of the diffuse electrical double layer at the surface between a.solid and a-liquid is thus analogous to the Debye - Huckel concept of the oppositely charged ion - atmosphere surrounding a given ion.

Stern Theory

According to Stern, the double layer consists of two parts: one which is approximately of a molecular diameter in thickness, is suppose to remain fixed to the surface, while the other is a diffuse layer extending some distance into the solution. The fall of potential in the fixed layer is short while that in the diffuse layer is gradual, the decrease being exponential in nature; The potential gradient at the solid-liquid boundary may be represented y Fig. (11). The left hand axis represents the solid phase and the vertical dotted line indicates the extent of the fixed part of the double layer; the relative thickness f this layer, probably, somewhat exaggerated in the diagram. If the potential of the solid is indicated by A and that of the bulk of the liquid by B, the fall of potential in between may occur in two general ways depending, to a large extent, 0 the nature of the ions and molecules present in the solution I & II. In each case sharp fall of potential in the fixed portion and CB is the gradual approximately exponential change in the figure portion of the double layer. The total fall of potential, AB between the solid and the solution is equal to the reversible potential in the case of a system that can behave reversibly; this is represented by the symbol E. The electrokinetics of Zeta potential however, which is involved in electro osmosis, electrophoresis and allied phenomena, is that between the fixed and freely mobile parts of the double layer, this is the potential change from C to B, indicated by ξ is each case (Fig. 11)

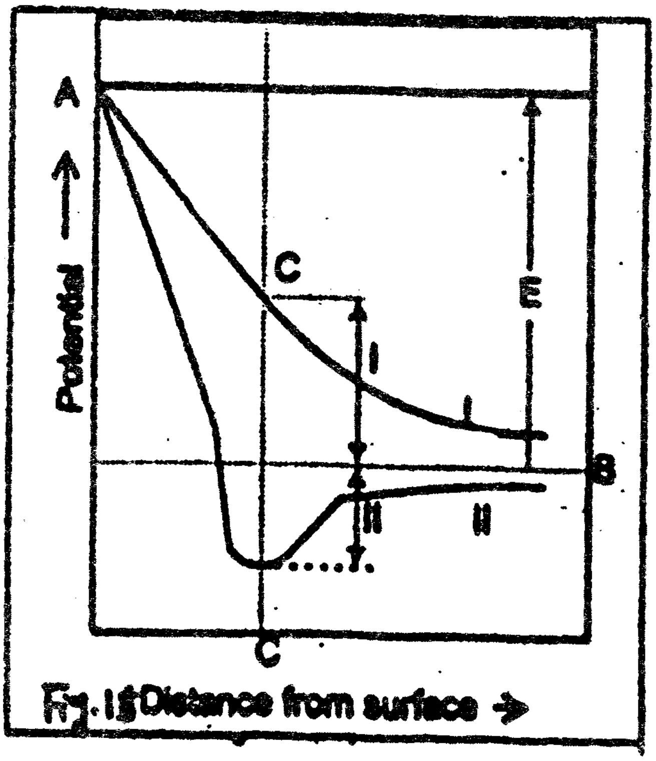


Fig.11

Types of Electrokinetic effects

1. Electro osmosis
2. Streaming potential
3. Electrophoresis

Electro Osmosis

Solid phase is fixed e.g., in the form of a diaphragm, while the liquid is free to move, the liquid will tend to flow through the pores of the diaphragm as a consequence of the applied field. The direction in which the liquid flows should depend on the sign of the charge it carried with respect to that of the solid. This movement of a liquid through the pores of a diaphragm under the influence of an E.M.F. constitutes. This phenomenon is known as electro-osmosis.

Streaming potential

In electrosmosis the difference in potential is responsible for the flow of an electrolyte through a capillary, which is generally expected out of pressure difference (Δ P). Hence, reverse of this process should also be possible i.e., When a liquid (electrolyte) is allowed to flow through a capillary under pressure, it develops potential difference which is known as streaming potential and hence develops a current, known as streaming current.

ELECTROPHORESIS

Electrophoresis involves the movement of charged liquid phase against immobile solid phase. The solid particle with (-)ve charge and size 'a' is surrounded by a diffused layer of thickness K^{-1}. To have the diffuse layer, the particle must be of considerable size. The particle is like a colloidal particle. This arrangement of negatively charged particles surrounded by positively diffused layer is similar to ion surrounded by ionic atmosphere. When the external potential is applied, the negatively charged solid particle (mobile phase) moves in a static liquid phase of positively charge. This phenomena is known as electrophoresis.

VOLTAMMETRY

Voltammetry comprises a group of electro analytical methods that one based upon the potential current behaviour of a polarisable electrode in the solution being analysed. In voltammetry, a measured small potential is impressed across a pair of electrodes, one of which is non polarisable reference electrode and other a polarisable inert electrode. The current which flows depends upon the composition of the solution. In other words, voltammetry and voltammetric analysis are concerned with the study of current voltage, relation at a micro electrode, called working electrode. This electrode may be inert metal, such as Pt or gold. A three electrode cell is however, preferred in general voltammetry. The third anxillary electrode can be a simple wire of P_t. The reference electrode may be of any form.

A variable voltage source is connected in series with a microammeter and the current carrying electrode. Potential at the working electrode, relative to the reference electrode is then measured by a, electrical voltameter. The choice of working electrode in voltammetry depends lengthy on the range of potentials it is desired to interface. Inert Pt electrode is Suitable for potentials more possible them reference electrode calomel electrode (SCE).

POLAROGRAPHY

Polarography involves the study of current - voltage relationships at a dropping mercury electrode under certain controlled conditions. Heyrovsky and Shikata developed an apparatus which increased the applied voltage at a steady rate and simultaneously recorded the current-voltage curve. The apparatus. was called a polarograph and the records obtained are polarograms.

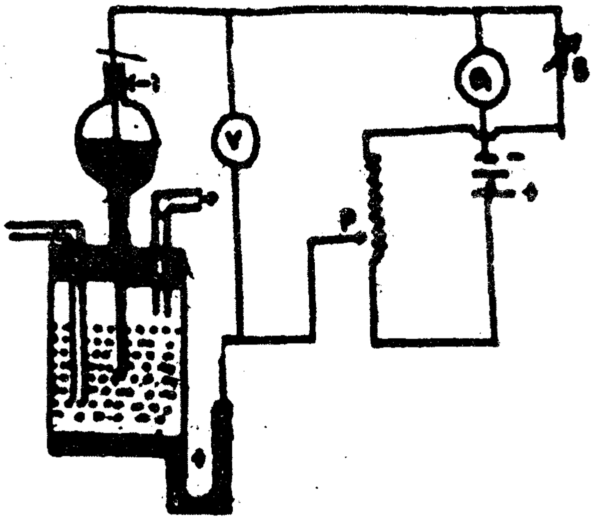


Figure 1. Manual Polarograph

The basic apparatus for polarograpnic analysis is .shown in the figure 1. The dropping mercury electrode here acts as cathode; it is sometimes referred to as indicator or micro-electrode. The anode is a pool of mercury which acts as a reference electrode. Inlet and Outlet tubes, are provided in the cell for expelling the dissolved oxygen from the solution by the passage of an inert gas. P is a potentiometer by which e.m.f. up to 3 volts may be gradually applied to the cell. G is the Galvanometer which measures the current and 'V' is the voltmeter to measure the applied potential.

CURRENT-VOLTAGE CURVE

The cell is filled with an electroactive material eg. $CdCl_2$ solution. A potential is applied between the electrodes and increased in a stepwise manner. From A to B practically no current will pass through the cell. At B, where the potential of the micro-electrode is equal to the decomposition potential of the cadmium ions, the current suddenly begins to increase and the following reaction takes place at DME.

$$Cd^{2+} + 2e^- \rightarrow Cd$$

On further increasing the applied potential, the current continuously increases and reaches a limiting value. After the point 'c' the current no longer increases. (Fig. 2)

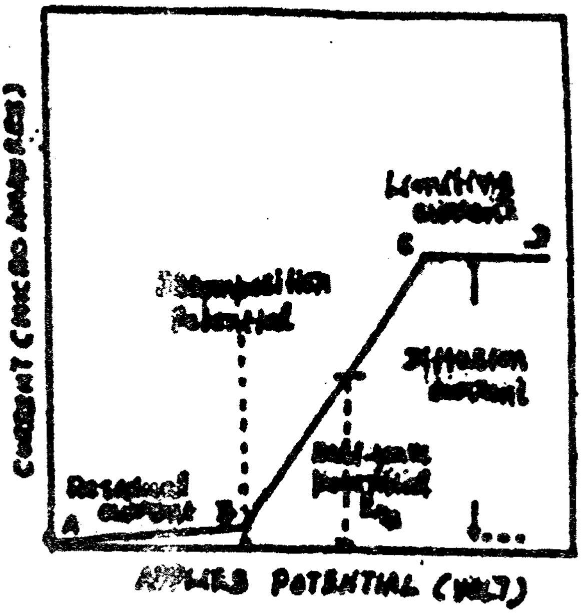


Fig. 2 CURRENT - VOLTAGE CURVE AT DME

Figure . 2

The small current flowing through the solution initially (AB) is called "residual current". At the point 'c' where the current has reached limiting value is called "limiting current". The difference between limiting current and residual current is called "diffusion current"

Diffusion current = Limiting current - Residual current.

THEORY

Electro-active material reaches the surface of the electrode by two processes (I) migration of the charged particles in the electric field caused by the potential difference' existing between the electrode surface and the solution; (2) diffusion of ions under the influence of concentration gradient.

Heyrovsky showed that the migration current can be practically eliminated by adding a supporting electrolyte. The supporting electrolyte must be composed of ions . which are discharged at higher potentials and which will not interfere or react chemically with ions under investigation. If the concentration of supporting electrolyte is very large (at least 100 fold excess), the ions of the added salt practically carry all the current, under these conditions, the limiting current is almost solely a diffusion current. D.ILKOVIC examined the various factors which govern the diffusion current and deduced the following equation:

$$i_d = 607nD^{1/2}Cm^{2/3}t^{1/6} \quad .....(1)$$

i_d = diffusion current in microamperes

D = diffusion coefficient of electroactive species(cm^2S^{-1})

C = its concentration in milimoles per litre

m = rate of flow of mercury from dropping electrode in mg. per second

t = drop time in seconds

n = number of electrons involved in the reduction process.

The ILKOVIC equation is important because it accounts quantitatively for the many factors which influence the diffusion current. Thus, with all the other factors remaining constant, the diffusion current is directly proportional to the concentration of electro-active material. This is of great importance in quantitative polarographic analysis.

ADVANTAGES OF DROPPING MERCURY CATHODE

(1) Its surface area is reproducible with any given capillary (2 The constant renewal of the electrode surface eliminates passivity or poisoning effect (3) The high over potential of hydrogen on mercury renders the electrode useful for electro-active species whose-reduction potential is considerably more negative than the reversible potential of hydrogen discharge (4) Mercury forms amalgams with many metals thereby lowers their reduction potential (5) The diffusion current assumes a steady value immediately and is reproducible.

SALIENT FEATURES OF CURRENT - APPLIED VOLTAGE CURVE

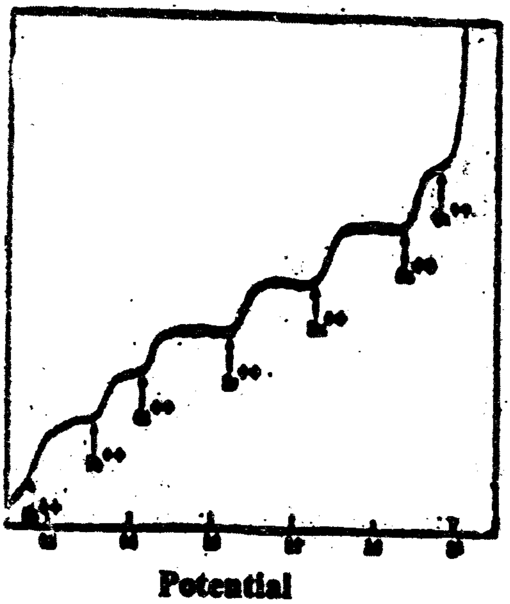


Figure 3. Polarographic waves (Heyrovsky)

The height of the curve is the diffusion current, and is a function of the concentration of the electroactive material. The potential at the point on the polarographic wave where the current is equal to one-half of the diffusion current is termed as the Half-wave potential and is designated as $E_{1/2}$. Half-wave potential is

$$E = E_{1/2} + \frac{0.0591}{n} \log \frac{i_d - i}{i} \qquad \text{.....(2)}$$

Equation (2) gives the relationship between the current at any point i, the diffusion current i_d, the applied voltage E and half-wave potential $E_{1/2}$.

The half-wave potential is also independent of the electrode characteristics and can be used for the qualitative identification of unknown substance present in the solution.

The half wave potential can be evaluated by ploting E versus $\log \frac{i_d - i}{i}$

QUANTITATIVE ANALYSIS

Three methods which are used in practice are :

1. Wave height - concentration plots

Solutions of several different concentrations of the ions under investigation are prepared. The composition of supporting electrolyte is kept same both for unknown and the standard. The heights of the waves are measured and plotted as a function of concentration. The polarogram of the unknown is produced exactly as the standard. By interpolation the concentration of unknown can be found out.

2. Method of Standard Addition

The polarogram of the unknown solution is first recorded. A known volume of standard solution is added to it and a second polarogram is taken . From the height of the two waves, the concentration of unknown can be calculated using Eqn. (3)

$$C_u = \frac{ivc_s}{(i_2 - i_1)(V + v) + i_1 v} \qquad .....(3)$$

C_u = Concn. of unknown

V = Volume of unknown

i_1 = Diffusion current of unknown (wave height)

C_3 = Concn. of standard

v = Volume of standard added

i_2 = diffusion current after the addition of v ml of std.

3. Internal Standard or Pilot Ion Method

A reference ion whose half-wave potential differ atleast by 0.2V is selected. Prepare same concentration of the unknown and pilot ion and record the polarogram separately

Determine the ratio $\frac{(I_d)_s}{(I_d)_x}$

$(I_d)_s$ = Wave height of pilot ion

$(I_d)_x$ = Wave height of unknown

Then the relative wave heights with unknown ion and the known amount of the pilot ion in the unknown solution is measured and compared with the ratio of previously determined Wave-heights. The concn. of unknown can be evaluated from eqn. (4)

$$C_x = \frac{i_x}{i_s} x \frac{(I_d)_s}{(I_d)_x} C_s$$

C_x = Concn. of unknown

C_s = Concn of pilot ion

i_x = Wave height before addition of pilot ion

i_s = Wave height after the addition of pilot ion

APPLICATION TO ORGANIC COMPOUNDS

A large number of organic materials which are polarographically active, such as aromatic hydrocarbons, aromatic and unsaturated aliphatic carboxylic acids, thiols, carbonyl compounds, amines, proteins and amino acids have been investigated since the sensitivity is proportional to no. of electrons, , transferred during reduction or oxidation, organic compounds where six or more electrons are involved in reduction can be determined at very low concentration. Since the half-wave potential varies with structure and substitution, pH, complexing agent etc. the conditions may be suitably selected for determination of a particular compound eg., reduction potential of the disulphide group linked to alkyl group is -1.25V and to a phenyl group is -0.5V.

Some of the functional groups that can be reduced at DME are –CHO.C=O, -C=N, $-NO_2$, -S-S, -C=C-, etc.

STABILITY CONSTANTS OF METAL COMPLEXES

The half-wave potential of a simple metal ion is shifted, almost invariably, in the more negative direction of applied potential and the diffusion current usually becomes smaller when it undergoes complexation with ligands.

For the complex formation

$$M^{n+} + L_j \rightleftharpoons ML_j^{n+}$$

$$\text{the overall stability constant } \beta = \frac{(HL_j^{n+})}{(M^{n+})(L)^j}$$

Where 'j' is the coordination number of the ligand. The shift in half-wave potential due to the presence of complexing agent L is given by equation

$$(E_{1/2})_s - (E_{1/2})_c = \frac{0.0591}{n}\log\beta + j\frac{0.0591}{n}\log(L) \qquad .....(5)$$

Where $(E_{1/2})_s$ is the half-wave potential in absence of ligand and $(E_{1/2})_c$ is the half-wave potential in presence of ligand. The plot of $(E_{1/2})_s$ - $(E_{1/2})_c$ versus log (L) is linear with slope $j = \frac{0.0591}{n}$ and intercept $\frac{0.0591}{n}\log\beta$

Thus the coordination number and stability constants of the complexes can be evaluated.

COULOMETRIC ANALYSIS

When electric current is passed through an electrolyte solution, a chemical reaction takes place and the extent of chemical reaction at an electrode is directly proportional to the quantity of electricity passing through the electrode. The electrolysis is governed by Faraday's two laws of electrolysis.

1. The amounts of substances liberated at the electrode are directly proportional to the quantity of electricity which passes through the solution.

2. The amounts of different substances which are deposited or liberated by the same quantity of electricity are proportional to their chemical equivalent.

- Coulometric analysis is an application of Faraday s Laws of electrolysis. The quantity of electricity is measured in coulombs. If a current of one ampere flows for one second, the quantity of electricity is 1 coulomb in general.

$Q = It$ coulomb

I = current in amperes

If the electrode reaction proceeds with 100 percent efficiency then the quantity of substance reacted may be found by measuring thl quantity of electricity and employing. eqn. (7)

$$W = \frac{W_m Q}{96500n} \qquad .....(7)$$

W = weight of substance produced or consumed in electrolysis

Q = quantity of electricity in coulomb

W_m = gram atomic weight/gram molecular weight of substance being electrolysed

n = no. of electrons involved in the reaction.

Example; If 2650 coulombs of electricity is passed through copper sulphate solution, calculate the amount of copper deposited.

Atomic mass of copper = 63.54

Electrode reaction = $Cu^{2+} + 2e \rightarrow Cu(s) ... n = 2$

$$W = \frac{63.54 \times 2650}{96500 \times 2}$$

$$= 0.8724 \text{ g}$$

Analytical methods based upon the measurement of quantity of electricity and the application of eqn (7) are termed as coulometric methods. If the substance being determined undergoes reaction at one of the electrodes, it is called primary coulometric analysis. If the substance reacts in solution with another substance generated by an electrode reaction, it is called secondary coulometric analysis

Two distinctly different coulometric techniques are available

i) coulometric analysis with controlled potential of the working electrode

ii) coulometric analysis with constant current.

COULOMETRIC ANALYSIS AT CONTROLLED POTENTIAL

i) the substance being determined reacts with 100 percent efficiency at the working electrode

ii) the potential of the working electrode is controlled.

iii) the completion of reaction is indicated by the current decreasing to zero

iv) the quantity of substance reacted is computed by the reading of coulometer or by means by a current - time integrating device.

INSTRUMENTATION

The three instrumental units in controlled potential coulometric analysis are (i) coulometer or other means of measuring the quantity of electricity (ii) D.C. current supply with means for controlling potential (iii) Electrolytic cell.

In controlled potential coulometric analysis, the current decreases exponentially with time according to the equation.

$$i_t = i_o e^{-kt}$$

where i_o is the initial current, it is the current at time t and k is a constant A typical time-current curve is shown in fig.4.

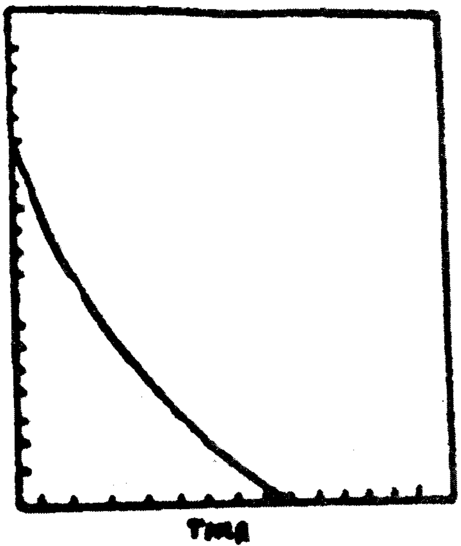


Fig.4 Current versus Time plot for controlled potential coulometric analysis

The current decreases more or less exponentially to zero. The area beneath the curve is a measure of the total quantity of electricity which has passed . A mechanical current-time integrator is available commercially .

A simple circuit to control the electrode potential manually is shown in Fig.3.

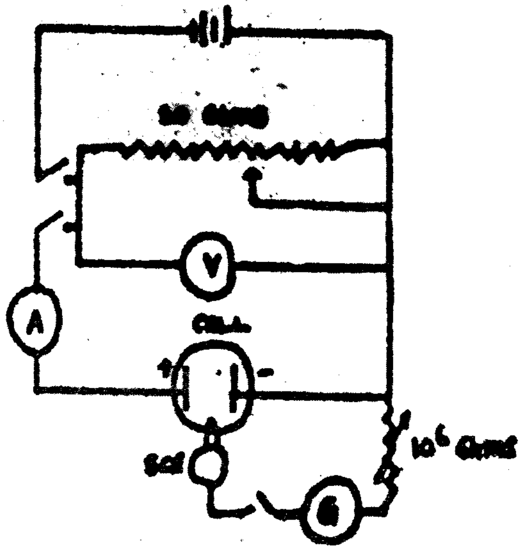


Figure. 5. Circuit to control Electrode Potential

The Ammeter 'A' indicates the electrolysis current. The voltmeter 'v' records the total applied voltage. The potential of the cathode with respect to reference electrode SCE (Saturated calomel electrode) is directly indicated by the high resistance voltmeter 'G'

The resistance is adjusted manually until the potential difference between cathode and SCE attains the desired value as shown by Galvanometer G

As electrolysis proceeds, the cathode tends to become more negative wrt SCE and the rheostat is continuously adjusted to maintain the cathode potential constant at the desired value. The ammeter reading decreases during electrolysis and attains a low current value signalling the completion of reaction. Nowadays 'potentiostats' which automatically maintain the potential of an electrode constant are available.

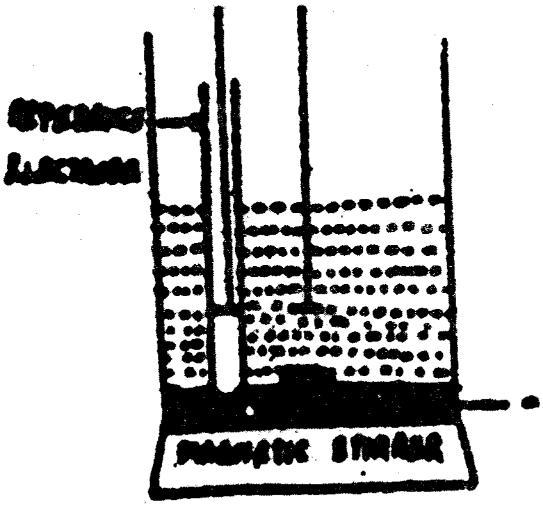


Figure 6 Electrolysis Vessel

A 250 ml pyrex beaker serves as electrolysis vessel, mercury at the bottom of the beaker acts as cathode. The anode is stout platinum wire coiled into a flat spiral. The reference electrode just touches the surface of the mercury cathode.

EXPERIMENTAL PROCEDURE

Supporting electrolyte (50-60ml) is first placed in the cell and the air is removed by passing a rapid stream of nitrogen for 5 minutes. The stirrer is started; the reference electrode is adjusted so that it touches the stirred mercury cathode. The potentiostat is adjusted to maintain desired control potential and the solution is electrolysed until the current drops to a small value. (background current). This preliminary electrolysis removes reducible impurities. Then add 20 ml of sample solution and continue the electrolysis until the current drops to the background current. The quantity of electricity is known from the coulometer or mechanical current-time integrator. The amount of substance is calculated from equation (7).

APPLICATIONS

1. If mercury cathode is used, the optimum control potential for a given separation can be easily determined from polarograms recorded with dropping mercury electrode.

DEPOSITION OF METALS AT CONTROLLED POTENTIAL OF THE MERCURY CATHODE

Elements	Cu	Bi	Pb	Cd	Zn	Ni	Co
E cathode (Volts Vs SCE)	-0.16	-0.40	-0.56	-0.85	-0.45	-0.95	-1.20

By means of controlled cathode potential techniance it is possible to effect such difficult separations as Cu and Bi, Cd and Zn, Ni and Co. If a solution contains Co^{2+} and Ni^{2+} ions, by performing the electrolysis by keeping the potential at -1.20V, Co^{2+} can be estimated; by the keeping the cathode potential at -0.95V Ni^{2+} can be estimated.

2. Sometimes it is possible to reduce a metal to a lower valency state and by controlling a more positive potential, the metal can be oxidised quantitatively to higher valency state. Eg. at -O.15V with a mercury electrode, reduction of U(IV) to U(III) and Cr(III) to Cr(II) occur simultaneously. If electrolysis is carried out at -O.55V, only U (III) is oxidised. When all U (III) has been removed from solution, chromium is determined by oxidation of Cr(II) to Cr (III) at -0.15V.

3. Consider a mixture of antimony (V) and antimony (III) (in supporting electrolyte 6M HCl + O.4M tartaric acid). At -0.2IV, the reduction $Sb^{5+} \rightarrow Sb^{3+}$ occurs and at -0.35V the reduction $Sb^{3+} \rightarrow Sb^{o}$ occurs. Thus it is possible to determine both Sb(III) and Sb(V) in a mixture.

4. Organic compounds such as trichloroacetic acid, and picric acid are quantitatively reduced at mercury cathode whose potential has been controlled.

Coulometry at Constant Current Coulometric Titrations

Constant-current coulometry maintains a constant current during electrolysis. A reagent is generated which reacts stoichiometrically with the substance to be determined. For ego for estimation of Cl^- ion, Ag^+ ion is generated employing silver electrodes. The generated Ag^+ ion reacts with Cl^- to give AgCl.

In coulometric titrations the reagent is generated electrically and its amount is evaluated from the knowledge of current and generating time. Since a small quantity of electricity can be readily measured with high degree of accuracy, the method has high sensitivity.

Advantages of Coulometric Titrations

1. Standard solutions are not required. The coulomb becomes the primary standard.
2. Unstable reagents such as bromine, chlorine can be generated and consumed immediately.
3. Small amount of titrants are prepared.
4. The sample solution is not diluted ,
5. This method is readily adopted to remote control. Therefore radioactive and other dangerous materials can be titrated.
6. This method is particularly useful and accurate in the range from milligram quantities down to microgram quantities and can be used in trace analysis.

Detection of End Point

Various methods are used for detection of the end point. It can be found by means of normal coloured indicators, or by instrumental methods such as potentiometry, amperometry and photometry. Potentiometric and photometric indication find use· in acid-base and redox titrations, while amperometric procedures are applicable to redox and precipitation. reactions.

Instrumentation

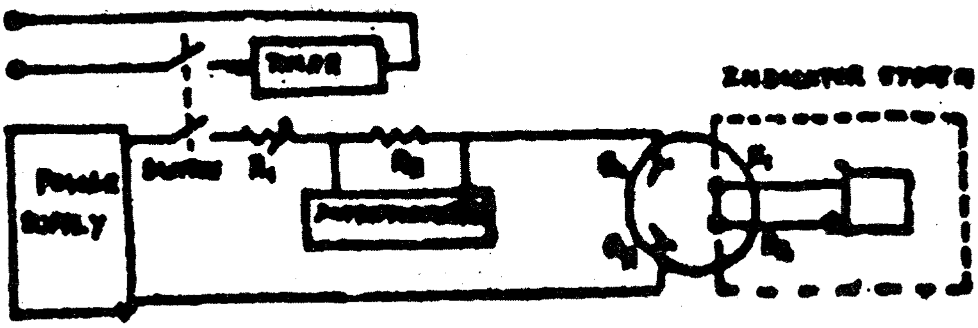


Figure 7. Coulometery at constant current

The schematic diagram for constant current coulometric methods is shown in Fig.7. The power supply provide a D.C. voltage of about 300V. The current passes, through a series - regulating tube (R_1) and a precision resistor (R_2) to the electrolytic cell. G_1 and G_2 are the generator electrodes and E_1 and E_2 are electrodes for the end-point detector system.

The voltage drop across the resistor R_2 can be measured very precisely with a manual or recording potentiometer and hence 'i' can be calculated, time measurements are normally made with a precision electric stop clock. A single switch control actuates both the timer and electrolysis current.

PRIMARY COULOMETRIC TITRATIONS

In primary coulometric titrations at constant current, the substance to be determined reacts directly at the electrode. One major area of application involves the electrode material itself participating in an anodic process. eg., During electrolysis, Ag^+ ions are generated at the anode and diffuses in solution. The Ag^+. ion readily reacts Cl^- (to be determined) to form AgCl. The end point may be detected amperometrically. By this method mercaptans, sulfhydryl groups can be titrated. Since the potential of working electrode is not controlled, this class of titrations is limited to reactants which are non-diffusible.

SECONDARY COLOMETRIC TITRATION

In secondary coulometric titrations an active intermediate is first generated quantitatively by the electrode process, and this then reacts directly with the substance to be determined.

For example for the coulometric determination of Fe^{2+}, excess of Ce^{3+} is added to the solution. Anodically Ce^{3+} is oxidised to Ce^{4+} and the liberated . Ce^{4+} instaneously reacts with Fe^{2+} ion in solution.

$$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$$

As long as Fe^{2+} ion is present in the solution, Ce^{4+} will be consumed. When all Fe^{2+} has been exhausted, the end point is signalled by the first peristance of excess of Ce^{4+} in the solution and may be detected photometrically at a wavelength at which Ce^{4+} absorbs strongly.

AMPEROMETRIC TITRATIONS

Let us consider the electrolysis of an electro-active substance between dropping mercury electrode (DME) functioning as cathode and some reference electrode acting as anode.

A potential is applied between these electrodes and increased in a stepwise manner (Fig. 2). At first only small current follows - the so called residual current and this continues upto decomposition potential. At this point, the following reaction takes place.

$$M^{n+} + ne \longrightarrow M_{(s)}$$

and hence a steep rise in current is observed (Fig. 2). The current will continue to rise with increasing potential and then reaches a limiting value. If sufficient supporting electrolyte is present in the solution, the diffusion current (limiting current - residual current) is proportional to the concentration of electroactive material in the solution. If some of the electroactive material is removed by interaction with another reagent, the diffusion current will decrease. This is the fundamental principle of amperometric titrations. The diffusion current at a suitable applied voltage is measured as a function of the volume of the titrating solution. The end point is the point of intersection of two lines giving the charge of current before and after the equivalence point.

ADVANTAGES OF AMPEROMETRIC TITRATIONS

i) Titration can be carried out rapidly: a few current measurements before and after the end point is sufficient to detect the end point.

ii) Titrations can be carried out, when potentiometric or visual - indicator methods arc unsatisfactory

iii) Titration can be carried out at dilute-conditions (10^{-4} N)

iv) 'Foreign' salts may be present without interference.

TYPES OF TITRATION CURVES

The most common types of curves encountered in amperometric titrations are given below.

Fig. (8a) AMPEROMETRIC TITRATION CURVES

a. When the electroactive metal from solution is removed by the addition of electro-inactive reagent, the shape of curve is as shown in Fig. A.

Eg. removal of Pb^{2+} by addition of $C_20_4^{2-}$ or $S0_4^{2-}$ Here . diffusion current decreases to the residual current when all Pb^{2+} ion has reacted with $X(C_2 0_4^{2-}/ S0_4^{2-})$. Since x is inactive, further addition of x will not affect the diffusion current.

b. When the subsance in solution is electro-inactive, $(S0_4^{2-})$ the residual current will flow initially. When electroactive reagent (Pb^{2+}/ Ba^{2+}) is added it will increase the diffusion current after the end point and the shape of the curve is shown in B.

c. When both the solute and titrating agent are electroactive, they contribute toward the diffusion current and a sharp 'v' shaped curve is obtained.

eg: Pb^{2+} ion titrated with $Cr2\ 0_7^{2-}$

Ni^{2+} ion titrated with dimethylglyoxime

d. The solute is oxidised at the DME and gives the anodic diffusion current at the same potential as the titrating reagent gives a cathodic diffusion current. Here the current changes from anodic to cathodic or vise versa and the end point of he titration is indicated by zero current.

eg: titration of I^- with Hg^{2+}

titration of Cl^- with Ag^-

SUCCESSIVE DETERMINATION OF Cl^-, BR^- and I^-

The three halide ions Cl^-, BR^-, I^- in a mixture can be determined by amperometric titration with Ag^+ ion. A known volume of the mixture is placed in cell containing 0.1 to 0.3 N solution of ammonia. Under this condition only AgI is precipitated by the addition of Ag^+. When all the I^- ions are precipitated the current increases. The cell is then acidified with 0.8N $HN0_3$ and the titration continued. Under this condition only AgBr is precipitated. After the deduction of end point gelatin is added and Cl^- is estimated. The amperometric titration curve is shown in Fig.8(b)

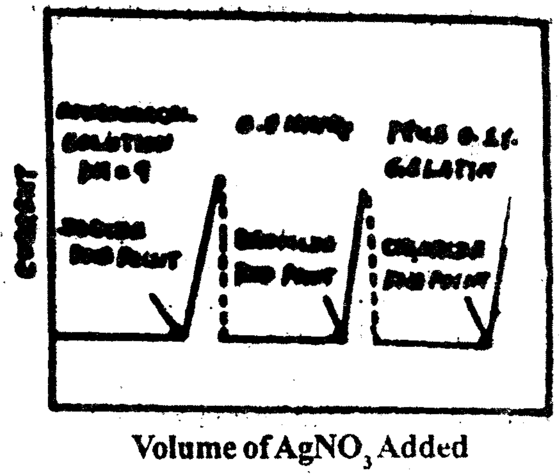


Figure 8b. Amperometric Titration curve for a mixture of Cl^-, BR^-, I^-

AMPEROMETRIC TITRATION WITH TWO INDICATOR ELECTRODES DEAD-STOP END POINT

AMPEROMETRIC TITRATION WITH TWO INDICATOR ELECTRODES DEAD-STOP END POINT

When two small but similar platinum electrodes are immersed in A uniformly stirred solution containing a reversible oxidation - reduction system, a small amount of electrolysis takes place and an appreciable amount of current flows through the cell. The amount of substance reduced at cathode is equal to the amount of substance oxidised at anode. Both electrodes are depolarised. When one of the components, either oxidised form or reduced form is completely consumed by the titrant, only one electrode remains depolarised. So at the end point the system becomes one electrode system connected to reference electrode and the current virtually drops to zero.

In the titration of iodine by thiosulphate initially both Iodine and Iodide ions are present in the system.

$$I_2+2e \rightleftharpoons 2r$$

Therefore current flows even at the low applied potential (15mV). As the titration proceeds iodine is consumed. At the end point no free iodine remains and therefore a rapid decrease in current was observed in the neighbourhood of end point, This gave rise to the name DEAD STQP END POINT.

CYCLIC VOLTAMMETRY

Cyclic voltammetry (CV) is perhaps the most versatile electroanalytical technique for the study of electroactive species. The system contains two electrrodes. At the working electrode oxidation/reduction of electroactive species occurs. The potential of this working electrode is controlled versus a reference electrode such as saturated calomel electrode (SCE) or a silver/silver chloride electrode (Ag/ AgCl). The measurement of current-voltage curves are done under diffusion controlled, mass transfer conditions at stationary electrode . The voltage applied to the "working" electrode is scanned linearly from an initial value E_i to a predetermined limit E_s and then the direction of scan is reversed back to E_i

CYCLIC VOLTAMMOGRAM

The controlling potential applied across these two electrodes can be considered as excitation signal. The excitation signal for CV is a linear potential scan with a triangular waveform as shown in Figure. 9.

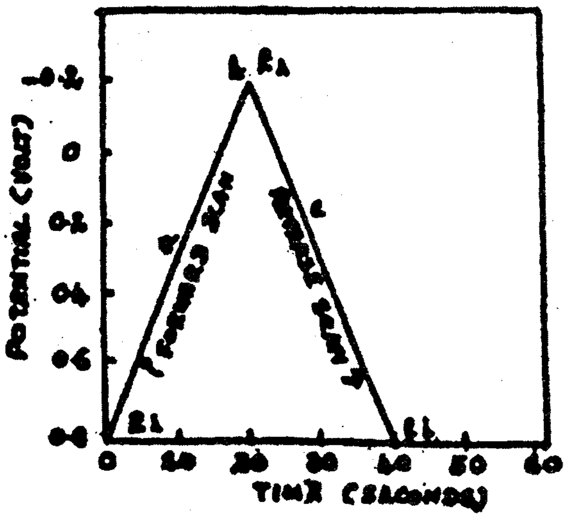


Fig.9. Linear Potential Scan

The excitation signal in Figure 9 causes the potential first to scan negatively from +0.80 to -0.20V versus SCE at which the scan direction is reversed; causing a positive scan back to the original potential of +0.80V .

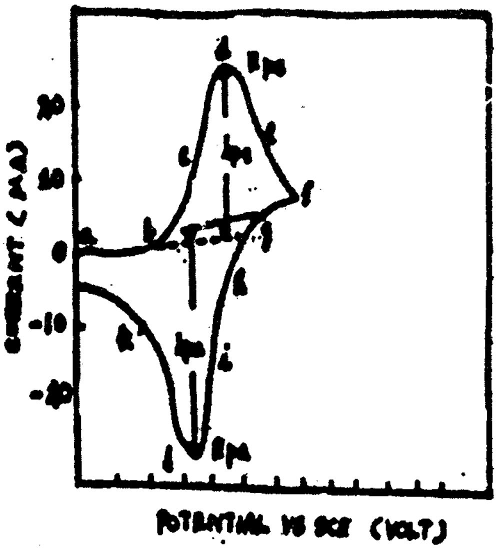


Fig.10. Cyclic Voltammogram

A cyclic voltammogram is obtained by measuring the current at the working electrode during the potential scan. The current can be considered the response signal to 'the potential excitation signal. The voltammogram is a display of current (in the vertical axis) versus potential (horizontal axis)

A typical cyclic voltammogram for platinum working electrode in a solution containing 6.0mM of $K_3Fe(CN)_6$ as the electro-active species in 1.0M $KN0_3$ as supporting electrolyte. The initial potential E_i of 0.80V is chosen to avoid any electrolysis of $Fe(CN)_6^{3-}$ When the electrode is switched on, the potential is then scanned negatively (forward scan). When the potential is sufficiently negative, the following reaction takes place at the electrode.

$$Fe^{III}(CN)_6^{3} + e \rightarrow Fe^{II}(CN)_6^{4-}$$

and cathodic current begins to flow at the point b. The cathodic current increases rapidly (b—d) until the concentration of $Fe^{III}(CN)_6^{3-}$ at the electrode surface is substantially diminished, causing the current to peak (d). The current then decays (d-g) as the solution surrounding the electrode is depleted of $Fe^{III}(CN)_6^{3-}$ due to its electrolytic conversion to $Fe^{II}(CN)_6^{4-}$ .The scan direction is switched to positive at -0.15 v (f) for the reverse scan. The potential is still sufficiently negative to reduce $Fe^{III}(CN)_6^{3-}$ so cathodic current continues even though the potential is now scanning in positive direction. When the electrode becomes a sufficiently strong oxidant, the following reaction takes place.

$$Fe^{II}(CN)_6^{4-} \rightarrow Fe^{III}(CN)_6^{3-} + e^-$$

This causes the anodic current (i - j - k). The anodic current rapidly increases until the surface concn. of $Fe^{II}(CN)_6^{4-}$ is diminished, causing the current to peak (j). The current then decays (j - k) as the solution surrounding the electrode is depleted of $Fe^{II}(CN)_6^{4-}$. The first cycle is completed when the potential reached $+0.80V$.

In the forward scan $Fe^{II}(CN)_6^{4-}$ is electrochemically generated from $Fe^{III}(CN)_6^{3-}$ as indicated by cathodic current. In the reverse scan $Fe^{II}(CN)_6^{4-}$ is oxidised back to $Fe^{III}(CN)_6^{3-}$ as indicated by anodic current. Thus cyclic voltammetry is capable of rapidly generating a new species during the forward scan and then monitoring its fate on the reverse scan.

The important parameters of a cyclic voltammogram are the magnitudes of the anodic peak current (i_{pa}), the cathodic peak current (i_{pc}), the anodic peak potential (E_{pa}) and the cathodic peak potential (E_{pc}).

A redox couple in which both species are stable and rapidly exchange electrons with the working electrode is termed an electrochemically reversible couple. The formal reduction potential (E°) for reversible couple is centered between E_{pa} and E_{pc}.

$$E^{\circ} = \frac{E_{pa} + E_{pc}}{2}$$

The number of electrons transferred in the electrode reaction (n) for a reversible couple can be determined from the separation between the peak potentials

$$\Delta E_p = E_{pa} - E_{pc} = \frac{0.058}{n}$$

Thus a one-electron process should ideally exhibit ΔE_p of 0.058V

The peak current for a reversible system is described by Randles-Seveik equation for the forward sweep of the first cycle.

$i_p = 2.69 \text{ X } 10^5 n^{3/2} A D^{1/2} V^{1/2} C$

i_p = peak current, amperes

n = number of electrons involved in electrode process

A = electrode area, cm^2

C = concentration, mol/cm^3

V = Scan rate volts/second

According to the eqn (11) 'i' increases with square root of scan rate and is directly proportional to concentration. For a reversible couple (i_{pa} / i_{pc}) =1.

APPLICATION

This technique yields information about reaction reversibilities and also offers a very rapid means of analysis for suitable systems. The method is particularly valuable for the investigation of stepwise reactions, and in many cases direct investigation of reactive intermediates is possible. By varying the scan rate, systems exhibiting a wide range of rate constants can be studied and transient species with half lives of the order or milli-seconds are readily detected.

CV is also used to determine E^{o} values by means of eqn - 9) and 'n' values by eqn (10). Reversibility can be determined by plotting $(E_{pa} - E_{pc})$ Vs $\sqrt{V}$ which should be a straight line if the process is reversible.

FUEL CELLS

A fuel cell is a galvanic cell in which the reactants are continuously fed to each electrode from outside the cell. Thermal energy is converted into electrical energy. H_2, lower alcohols, hydrazine, NH_3 etc, are generally used as fuels. These fuels are generally used as anodically reacting materials in combination with an oxygen electrode.

Fuel cells are classified according to the temperature or operation.

1. Low temperature fuel cells operate below 150°C
2. High temperature fuel cells that operate above 150°C

The principle problem in low temperture cell is electrocatalysis i.e., low to rise the exchange current density for the oxidation of cheap fuels. The problem in high temperature cells is the stability of materials that are confined to the electrodes, under corrosive action of electrodes.

$$n = \frac{\Delta G}{\Delta H} = \frac{E}{E - T(\delta E/\delta T)_p}$$

where

E = EMF of the fuel cell

ΔG = Free energy change of the reaction

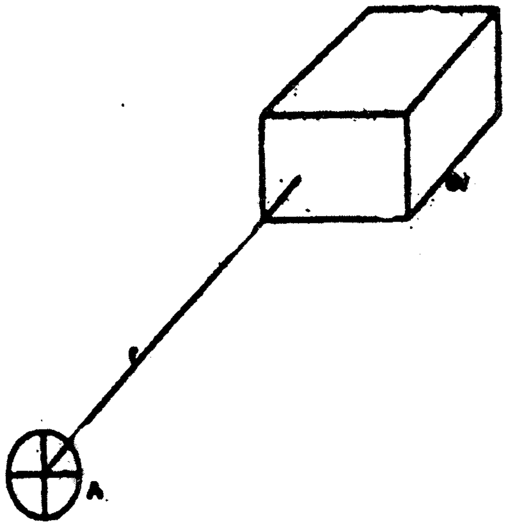
ΔH = Enthalpy change of the reaction

There are 3 types of fuel cells:

1. $H_2 - O_2$ fuel cell
2. Hydrocarbon - air fuel cell
3. $CH_3OH - O_2$ Fuel cell

This is the best known of electrochemical generator having power levels (5KW). A schematic representation of genini hydrogen oxygen fuel cell is as shown in figure (11).

A unique feature of this cell is the use of a thin cation exchange membrane as electrolyte. (Polystyrene sulphonic acid intimately mixed with a Ke⁻ F⁺ spine) each side of this rectangular membrane is covered by a Ti screen coated with a Pt screen. The thickness of the entire cell is about 1/2 mm. The reactions taking place in the cell are



. Figure. 11. The Ionic atmosphere

At anode $2H_2 \rightarrow 4H^+ + 4^{e-}$

At cathode $0_2 + 4H^+ + 4e^- \rightarrow 2H_20$

Since the conductivity of the membrane is strongly dependant as the water content, the water balanced is maintained by wicks draining or supplying water by capillary action.

The performance of a cell is shown in the fig.(11) An important overpotential loss is, in these cells due to the membrane resistance and also as usual to the oxygen electrode.

A storage stream built in these cells having an average power of about 900w and a max power of 2kw was used previously. A noteworthy feature of this storage system is the self contained provision for collecting water (a by polt of the cell m for drinking purpose in space (1 pt kwh^{-1}). At present, some H_2-0_2 fuel cells have attained a power level of 1 w cm^2

REFORMER SUPPLIED HYDROGEN AIR CELLS

Unsaturated hydrocarbons can be oxidized at relatively low temperatures for e.g.

$$C_3H_8 + 6H_20 \longrightarrow 3C0_2 + 20 + 20\,e^-$$

The supporting electroyle is con. H_3P0_4.

The pure hydrogen is expensive. Conversely hydrogen is an excellent fuel because of its large value are the resulting possibility of catalyzing its dissolution well (i.e with small over potential) on cheap materials such as nickel. To meet this situation a series of fuel cells utilize a system in which a cheap hydrocarbon fuel is the origin of the hydrogen, this being produced in the adjoining apparatus, separated from other gases and fed into the cell.

The system hydrocarbon process is

$$C_nH_{2n+2} + nH_2O \rightarrow (2n+1)H_2 + nCO$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

CO_2 May be removed by absorption in ethylamine or hydrogen separated by diffusion through Pd (or) Ag-Pd membranes

Hydrocarbon - Air cells

Many hydrocarbons including the main constitutents of the disel one, have been oxidized electrochemically at levels of more than 99% completion. Pt is the only suitable catalyst material at the present time.

The electrodes are constructed by depositing finely divided, Pt in a porous reflex substrate attached to a base of tantalum (which after oxidation, resists further corrosion in strong acid)

Power density of such cell is about 0.1 w cm^{-3}

$CH_3OH - O_2$ Fuel Cell:

It can work in the temperature range of 70 - 80°C NaOH (or) KOH can be used as electrolyte, with Pt as cathode as well as anode.

6N KOH is used when Pt is made anode and carbon as cathode

The cell reaction is $CH_3OH + \frac{3}{2}O_2 \rightarrow 2H_2O + CO_2 \quad E = 1.2V$

M.Sc. DEGREE EXAMINATION, APRIL 2004.

First Year - Non - Semester Chemistry

PAPER: III - PHYSICAL CHEMISTRY - I

(For those who joined in July 2003 and afterwards)

Time : Three hours Maximum : 100 marks

PART A - (10 x 2 = 20 marks)

Answer All questions.

1. What is an open system? How does it differ thermodynamically from a closed system?
2. What is the necessity of non- equilibrium thermodynamics? Illustrate with an example.
3. What is the significance of wave function? Comment on its importance in quantum mechanics.,
4. Explain the meaning of commuting and non-commuting operators with suitable examples.
5. What are secular determinants? Illustrate with an example.
6. State and explain Born-Oppenheimer approximation.
7. What is partition function? Why is the value of translational partition function of a molecule is very high?
8. Is the negative Kelvin temperature attainable? Comment on it.
9. Derive Tafel equation from Butler - Volmer equation and comment on the significance of Tafel plot.
10. What are the advantages of dropping mercury electrode? What do you mean by half - wave potential?

PART B - (5 x 6 = 30 marks)

Answer All questions.

11. a) Explain the phase diagram of a three component system involving two solid and water forming a congruently saturating type double compound.

    (OR)

    b) Derive the two thermodynamic equations of state .

12. a) Show that the wave functions sin x and sin 2x are eigen functions of the operator d^2/dx^2 with eigen values -1 and -4 respectively. Verify that the two wave functions are mutually orthogonal.

    (OR)

    b) Calculate the average value of the distance of an electron from the nucleus in the hydrogen atom in its state of lowest energy.

13. a) Apply variation method to helium atom and obtain the eigen functions and eigen values.

(OR)

b) What are the basic ideas of the perturbation theory? Explain with an example

14. a) The equilibrium inter nuclear distance of 1_2^{127} is 2.67x10^{-10}m. Calculate the moment of inertia and rotational partition function at 300 and 1000k.

(OR)

b) Show that the limiting nature of heat capacity of solids at constant volume and at high temperature, calculated by Debye's formula is 3R.

15. a) Explain the following:

i) Tafel curves ii) Electrical double layer iii) Zeta potential.

(OR)

b) Discuss briefly the principle and application of polarography.

PART B - (5 x 10 = 50 marks)

16. a) i) Define fugacity of gas. How is fugacity determined with the aid of an equation of state?

ii) Derive any two Maxwell's thermodynamic relations. (6+4)

(OR)

b) i) Explain the concept of entropy production and apply it to chemical reactions.

ii) Show from the principle of microscopic reversibility that cross coefficients in the appropriate phenomenological equations are equal.

17) a) i) Set up the Schrodinger wave equation for a particle in a three-dimensional box and obtain the expression for the energy.

ii) Explain commuting and non- commuting operators with examples. (6+4)

(OR)

b) i) Set up and solve the Schrodinger wave equation for a rigid rotor with a fixed axis.

ii) For a particle in a one dimensional box the quantum number n = 0 is trivial and not allowed. Justify this statement. (8+2)

18. a) i) Get the normalized MOs for H_2 species in the ground state.

ii) Taking ground state Li atom show how slater determinant is consistent with Pauli's antisymmetry principle. (5+5)

(OR)

b) i) Bring out the differences between MO and VB treatments of normal hydrogen molecule.

ii) Discuss the application of Hartree Fock self-consistent field method to helium atom. (4+6)

19. a) i) Derive Debye's equation for the specific heat of solids and give its validity at high and very low temperatures.

ii) Indicate how Debye theory of heat capacity of solids may be regarded as an improvement over Einstein's approach. (6+4)

(OR)

b) i) Obtain the expression for the internal energy of a system in terms of its partition function.

ii) Calculate the total entropy of Xe (g) at 298K and 1 atm pressure. At this temperature Xe is in its lowest electronic state.

iii) Show that in a system of three particles in which six units of energy is to be divided, the number of Bose-Einstein states is three and the number of Fermi-Dirac state is one. (4+3+3)

20. a) Derive Debye-Huckel limiting law and explain its importance. What is the concentration limit of the applicability of Debye - Huckel limiting law? How is it modified at higher concentration?

(OR)

b) Discuss briefly the principle, experimental details and important applications of the following electro analytical techniques:

i) Coulometry ii) Chronopotentiometry iii) Cyclic voltammetry (3+3+4)