
CHAPTER - I

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CHAPTER - I

FORMATION CONSTANTS AND THEIR DETERMINATION

The chemists are mainly interested in the interactions between different types of molecules. In a homogeneous solution medium, these interactions are often complicated. Hence the structures of species involved, the extent of formation of each species and their further tendencies to undergo chemical changes must be carefully studied. The thermodynamic parameters of ionic equilibria are important. The equilibrium constants of a number of systems are studied by using different methods. Solution of a metal ion and that of ligand are mixed, allowed to attain equilibrium and then concentrations of each of the species in the solution are measured by using suitable physico-chemical techniques.

Let us consider a system containing A and B as reactants which gives C as a product.



If we know the concentrations of the reactants and the product/s, equilibrium constant can be determined

$$K_c = \frac{[C]}{[A][B]} \quad \dots \quad 1.1$$

Where K_c is an equilibrium constant. Species in brackets represent their concentrations in moles per litre. In a simple

system measurements can be carried out by knowing initial and final concentrations of species A and B only. The amount of C can be determined from the difference in the initial and final concentrations of A and B. But when the system is complex which undergoes several sequential reactions and equilibria then the handling of the data becomes more and more difficult and manual calculations become impossible. So in some cases, looking at the aim of measurements, some less important species are ignored, some approximations are made and experimental conditions are selected so as to get useful data without deviating too much from reality. But due to severe approximations, some times the deductions become meaningless. And, hence, when the system is very complicated, but has theoretical, applied or analytical importance, the computation techniques using computer programmes are used.

The measurements of equilibrium concentrations of the species are rather difficult since the measurements should not disturb the equilibrium. The second difficulty in determination of equilibrium constant is that it depends on the activities rather than on concentrations. One can overcome this difficulty by keeping the concentrations of all species low, as the activities and concentrations are numerically almost equal in very dilute solutions. In second approach stability constant can be determined by using 'non-complexing' salt environment by adding salt such as NaClO_4 . It gives ions Na^+ and ClO_4^- . The deviations from unit activity are mainly due to Na^+ and ClO_4^- ions.

Stability constants in a series of solutions containing different amounts of salts is determined. By extrapolation to zero salt concentration stability constant is determined, where activity coefficients are unity.

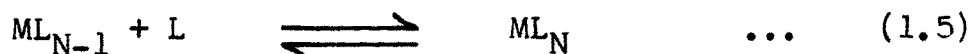
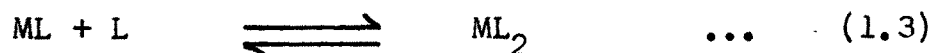
Complex formation between a metal ion and ligand involves competition between metal ions and protons. Most ligand species act as Lewis bases and form complexes with metal ions. They also act as Bronsted bases and hence combine with hydrogen ions. The competition between metal ions and protons for ligand allow us to measure the concentrations of L at equilibrium. But this situation has the disadvantage of increasing the number of different species which are present in solution.

FORMATION CONSTANT

When a metal ion M reacts with ligand L, in a homogeneous medium at a given temperature, reaction may lead to a series of reactions involving several stepwise dynamic equilibria, finally leading to formation of stable complex or chelate.

Normally metal ion is shown by M^{n+} , monoprotic ligand as HL and ligand ion as L^- , polyprotic ligand as $H_m L$ and ligand ion as L^{m-} . But for convenience the charges are omitted.

If N is the maximum number of ligand ions which can coordinate to metal ion, then series of equilibria involved during formation of chelate can be shown as -



For each of the above steps in the stepwise process the equilibrium constant can be defined as

$$K_i^T = \frac{a \cdot ML_i}{a \cdot ML_{i-1} \cdot aL} \quad \dots \quad (1.6)$$

Where, $K_i^T = i^{\text{th}}$ thermodynamic metal ligand stability constant i.e. formation constant for equilibrium as shown in (1.4), and

$a =$ activity of each species involved.

It is assumed that at low ionic strength the activity and concentration are the same. So at low concentration equation (1.6) becomes,

$$K_i^C = \frac{[ML_i]}{[ML_{i-1}][L]} \quad \dots \quad (1.7)$$

where square bracket represents concentration of different species in moles per litre.

$K_i^C = i^{\text{th}}$ stoichiometric metal ligand stability constant.

Let $K_1, K_2, K_3 \dots K_{i-1}$ and K_i are successive stepwise

stability constants, and β_i is overall metal ligand stability constant, then

$$\begin{aligned}\beta_i &= K_1 \times K_2 \times K_3 \times \dots \times K_{i-1} \times K_i \\ &= \prod_{i=1}^i K_i \quad \dots \quad (1.8)\end{aligned}$$

Let us consider overall metal ligand reaction,



Hence in dilute solution

$$\beta_i = \frac{[ML_i]}{[M][L]^i} \quad \dots \quad (1.10)$$

Equating equation No. (1.8) and (1.10) we get

$$\beta_i = \frac{[ML_i]}{[M][L]^i} = \prod_{i=1}^i K_i \quad \dots \quad (1.11)$$

The relation between the thermodynamic stability constant and the stoichiometric stability constant is

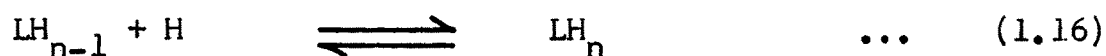
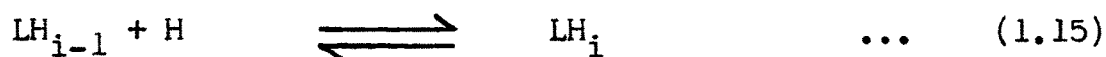
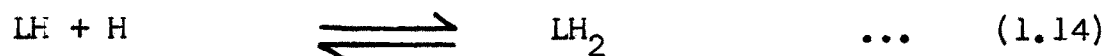
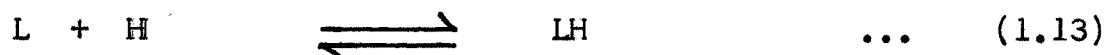
$$K_i^T = K_i^C \times \frac{f_M \cdot f_{L_i}}{f_{ML_i}} \quad \dots \quad (1.12)$$

where f represents activity coefficients of the respective species.

FORMATION CONSTANT OF THE LIGAND i.e. PROTON-LIGAND

STABILITY CONSTANT

The metal ligand stability constant is determined by working out metal ligand system. In the similar way proton-ligand stability constants i.e. formation constants of the ligands can be determined. Ligand ion may interact with proton. The stepwise protonation of ligand can be shown as



(For simplicity the charges on all the species are neglected.)

The corresponding equation for the thermodynamic formation constant can be represented by general equation

$$K_i^{T,H} = \frac{a.LH_i}{a.LH_{i-1} \cdot a.H} \quad \dots \quad (1.17)$$

where $K_i^{T,H}$ represents i^{th} thermodynamic proton ligand stability constant.

a = activities of corresponding species.

But in reality we know concentrations of the species. Again in dilute solution concentration and activity are same. And hence stoichiometric proton-ligand stability constant becomes

$$K_{iH}^C = \frac{[LH_i]}{[LH_{i-1}][H]} \dots (1.18)$$

[] represents concentration mole per litre.

When the ligand is completely protonated then corresponding proton-ligand stability constant is represented by β_{iH} which is obtained by equation

$$\beta_{iH} = \frac{[LH_i]}{[L][H]^i} = K_i \dots (1.19)$$

It is assumed that only those species which are present in above equilibria are present in solution. The species like polynuclear complexes, unionised metal salts, complexes containing hydroxyl groups and complexes containing protons in addition to ligands are not present.

\bar{n} and $\bar{n}A$

The most important term in solution equilibria introduced by J. Bjerrum¹ in his doctoral thesis, \bar{n} , is defined as the average number of ligand molecules bound per metal ion; mathematically,

$$\bar{n} = \frac{\text{Total concentration of ligand bound to metal}}{\text{Total concentration of metal.}}$$

$$\bar{n} = \frac{\sum_{i=0}^N i [ML_i]}{\sum_{i=0}^N [ML_i]} \dots (1.20)$$

But we know that

$$ML_i = K_i [ML_{i-1}] [L]$$

Putting this value in above equation and eliminating [M] we get,

$$\bar{n} = \frac{K_1[L] + 2K_1K_2[L]^2 + \dots + NK_1K_2 \dots K_N[L]^N}{1 + K_1[L] + K_1K_2[L]^2 + \dots + K_1K_2 \dots K_N[L]^N} \quad \dots (1.21)$$

But we know that

$$\beta_i = \beta_1 \times \beta_2 \times \beta_3 \times \dots \times \beta_{i-1} \times \beta_i$$

Putting this value in above equation, we get

$$\bar{n} = \frac{\beta_1[L] + 2\beta_2[L]^2 + \dots + N\beta_N[L]^N}{1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_N[L]^N} \quad \dots (1.22)$$

i.e.

$$\bar{n} = \frac{\sum_{i=0}^N i \beta_i [L]^i}{\sum_{i=0}^N \beta_i [L]^i} \quad \dots (1.23)$$

J. Bjerrum called above equation as formation function.

This equation is used to found \bar{n} .

In the similar way formation function equation for $\bar{n}A$ can be obtained. $\bar{n}A$ is defined as the average number of protons bound per not-complex-bound ligand molecules.

$$\bar{n}A = \frac{K_1^H[H] + 2K_1^H K_2^H [H]^2 + \dots + jK_1^H K_2^H \dots K_j^H [H]^j}{1 + K_1^H [H] + K_1^H K_2^H [H]^2 + \dots + K_1^H K_2^H \dots K_j^H [H]^j} \quad \dots (1.24)$$

But $\beta_n = K_1 K_2 \dots K_n$.

Putting this value in above equation we get,

$$\bar{n}_A = \frac{\beta_1^H [H] + 2\beta_2^H [H]^2 + \dots + j\beta_j^H [H]^j}{1 + \beta_1^H [H] + \beta_2^H [H]^2 + \dots + \beta_j^H [H]^j} \quad \dots \quad (1.25)$$

i.e.

$$\bar{n}_A = \frac{\sum_{i=0}^j i\beta_i^H [H]^i}{\sum_{i=0}^j \beta_i^H [H]^i} \quad \dots \quad (1.26)$$

and $\beta_0^H = 1$.

The total amount of metal ion concentration and total amount of ligand concentration in solution are as shown below.

$$T_m^0 = \sum_{i=0}^N [ML_i] \quad \dots \quad (1.27)$$

and

$$T_L^0 = \sum_{i=0}^j [LH_i] + \sum_{i=0}^N i [ML_i] \quad \dots \quad (1.28)$$

But we know that,

$$ML_i = K_i [ML_{i-1}][L]$$

Using this value in equation (1.27) we get,

$$T_m^0 = M \sum_{i=0}^N \beta_i [L]^i \quad \dots \quad (1.29)$$

Similarly,

$$LH_i = [L] \beta_i^H [H]^i$$

Putting this value in equation (1.28) we get,

$$T_L^0 = L \sum_{i=0}^j \beta_i^H [H]^i + M \sum_{i=0}^N i \beta_i [L]^i \quad \dots \quad (1.30)$$

The concentration of ligand not bound to metal is,

$$T_L^0 = \bar{n} T_M^0 \quad \dots \quad (1.31)$$

Substituting the values of T_L^0 and T_M^0 in above equation we get;

$$T_L^0 - \bar{n} T_M^0 = L \sum_{i=0}^j \beta_i^H [H]^i + M \sum_{i=0}^N i \beta_i [L]^i - \bar{n} M \sum_{i=0}^N \beta_i [L]^i \quad \dots \quad (1.32)$$

$$\therefore T_L^0 - \bar{n} T_M^0 = L \sum_{i=0}^j \beta_i^H [H]^i \quad \dots \quad (1.33)$$

$$\therefore L = \frac{T_L^0 - \bar{n} T_M^0}{\sum_{i=0}^j \beta_i^H [H]^i} \quad \dots \quad (1.34)$$

Taking log of both sides we get,

$$\log L = \log (T_L^0 - \bar{n} T_M^0) - \log \sum_{i=0}^j \beta_i^H [H]^i \quad \dots \quad (1.35)$$

$$\therefore PL = \log \sum_{i=0}^j \beta_i^H [H]^i / (T_L^0 - \bar{n} T_M^0) \quad \dots \quad (1.36)$$

DETERMINATION OF STABILITY CONSTANTS

The work on the stability constant is reviewed by Martel and Calvin², Martel³, Irving and Rosotti⁴, Rosotti and Rosotti⁵, Lewis and Wilkins⁶, Sillen and Martel⁷.

For determination of stability constant following experimental methods are used.

Spectrophotometry, Potentiometry Vibration Spectroscopy, N.M.R. spectroscopy, e.s.r. spectroscopy, Polarography, Colorimetry, spectropolarimetry, solvent extraction, solubility measurements, viscometry, Reaction kinetics, X-ray studies, Coagulation studies and Mossbauer studies etc. In above methods following three common steps are normally present.

- (1) Formation curve is obtained from experimental measurements.
- (2) Formation curve is used to determine stoichiometric stability constant.
- (3) By extrapolation to zero ionic strength the thermodynamic stability constant is obtained from the stoichiometric stability constant at given temperature and at various ionic concentrations.

pH metric method for determination of the formation constant

The pH metric method involves the measurement of H^+ ion concentration by using a pH meter. The measurement by pH meter does not disturb the equilibrium, and hence it is a popular and widely used method. This method is proper for those chelates which are soluble either in water or mixed organic solvents. Water-dioxane, water-methanol, and water-ethanol mixed organic solvents can be used, but the pH measurement in such media must be corrected by using appropriate corrections.⁸ The conversion table is given as Appendix A.

In the present study pH-metric method is used for measurements. These measurements are used for determination of formation curve, from which stability constant is determined. These formation curve are obtained by Calvin-Bjerrum pH titration technique as adopted by Irving and Rossotti⁴.

The Method of Irving and Rossotti⁴

In this method the stability constants were determined by using pH meter. The readings of pH meter in 50 % ethanol-water v/v were corrected for solvent effect by applying previously reported correction.⁸

In this method series of titrations are carried out with standard alkali solution. Extreme care should be taken for purification of solvent and preparation of standard solutions. Standard stock solution of strong alkali must be carbonate free.^{8a} Following three types of titration were carried out -

- (1) Standard HClO_4 solution vs standard NaOH.
- (2) [Standard HClO_4 solution + known amount of standard ligand solution] vs NaOH solution.
- (3) [Standard HClO_4 solution + known amount of standard ligand solution + known amount of metal ion solution] vs standard NaOH solution.

In all these titrations solvent composition and final volume was kept constant. During titration the temperature was controlled within $\pm 0.1^\circ\text{C}$ by using thermostat. The mixed solution is

stirred by magnetic stirrer before each reading. The mixed solution used for titration acts as an electrolyte. The cell used for the measurement contains two half cells. Calomel electrode acts as a reference electrode and the glass membrane electrode as a response electrode.

These measurements were used to draw formation curves. The first titration curve is characteristic of strong acid strong base titration; which is of a sigmoid type. In the second curve there is slight drooping in the upper portion of the sigmoid curve. Drooping in the curve is due to ligand which is weakly acidic in nature. In this titration ligand molecule get deprotonated with addition of base. This curve is used to determine \bar{n}_A and the proton ligand stability constant/s. If ligand contains two or more ionizable protons, their corresponding pK_1 and pK_2 values can be determined provided that the protons are released before the pH value goes to reasonably high limit i.e. upto pH 13.

The third curve is a more drooping sigmoid curve, as metal abstracts the proton from the ligand. Thus pH of the titrated solution for the corresponding volume of NaOH will be lower than ligand and acid titrations. Drooping of the third titration curve indicates the formation of complex or chelate. By using these curves metal-ligand stability constant is determined.

In the mixed solvent, the relation between pH meter reading and stoichiometric hydrogen ion concentration is given by Van Uitert and Hass⁹ as

$$- \log [H^+] = \text{pH} + \log f_H + \log U_H^0 - \dots \quad (1.37)$$

where,

f_H = activity coefficient of H^+ in organic solvent-water mixture at constant temperature.

U_H^0 = Correction factor at zero ionic strength.

By taking antilog of quantities on both sides (eq.1.37) and rearranging we get,

$$\frac{1}{\text{antilog pH}} = f_H [H] U_H^0 \quad \dots \quad (1.38)$$

$$\therefore [H] = \frac{1}{f_H U_H^0} \cdot \frac{1}{\text{antilog pH}} \quad \dots \quad (1.39)$$

By using the value of $[H]$ in (1.24) and (1.25), we get

$$\begin{aligned} \bar{n}_A = & \frac{\frac{K_1^H}{(f_H U_H^0)} \left[\frac{1}{\text{antilog pH}} \right] + \frac{2K_1^H K_2^H}{(f_H U_H^0)^2} \left[\frac{1}{\text{antilog pH}} \right]^2 + \dots}{1 + \frac{K_1^H}{(f_H U_H^0)} \left[\frac{1}{\text{antilog pH}} \right] + \frac{K_1^H K_2^H}{(f_H U_H^0)^2} \left[\frac{1}{\text{antilog pH}} \right] + \dots} \\ & + \frac{j K_1^H K_2^H \dots K_j^H}{(f_H U_H^0)^j} \left[\frac{1}{\text{antilog pH}} \right]^j \quad \dots \quad (1.40) \end{aligned}$$

But

$$\beta_n = K_1 \times K_2 \times \dots \times K_n$$

$$\begin{aligned}
& \frac{\beta_1^H}{(f_H U_H^O)} \left[\frac{1}{\text{antilog pH}} \right] + \frac{2 \beta_2^H}{(f_H U_H^O)^2} \left[\frac{1}{\text{antilog pH}} \right]^2 + \dots \\
& + \frac{j \beta_j^H}{(f_H U_H^O)^j} \left[\frac{1}{\text{antilog pH}} \right]^j \\
\therefore \bar{n}A = & \frac{\frac{\beta_1^H}{(f_H U_H^O)} \left[\frac{1}{\text{antilog pH}} \right] + \frac{\beta_2^H}{(f_H U_H^O)^2} \left[\frac{1}{\text{antilog pH}} \right]^2 + \dots}{1 + \frac{\beta_1^H}{(f_H U_H^O)} \left[\frac{1}{\text{antilog pH}} \right] + \frac{\beta_2^H}{(f_H U_H^O)^2} \left[\frac{1}{\text{antilog pH}} \right]^2 + \dots} \\
& + \frac{\beta_j^H}{(f_H U_H^O)^j} \left[\frac{1}{\text{antilog pH}} \right]^j \dots \quad (1.41)
\end{aligned}$$

Irving and Rossotti define proton-ligand formation constant or ionisation constant as :

$$pK_1^H = \frac{K_1^H}{f_H U_H^O} \dots \quad (1.42)$$

$$\therefore K_1^H = f_H U_H^O \cdot pK_1^H \dots \quad (1.43)$$

$$\text{and } p \beta_i^H = \frac{\beta_i^H}{[f_H U_H^O]^i} \dots \quad (1.44)$$

$$\therefore \beta_i^H = [f_H \cdot U_H^O]^i \cdot p \beta_i^H \dots \quad (1.45)$$

Determination of $\bar{n}A$, \bar{n} and pL

$\bar{n}A$, \bar{n} and pL can be calculated by using equations (1.24), (1.21) and (1.36) respectively. But these equations required concentration of H ions i.e. $[H]$. Again titration curves are

obtained by titrating mineral acid and ligand, in presence or absence of metal ions. Then in more acidic solutions $[Na]$ and $[OH]$ are negligible and $E \gg TL$, hence, $[H] \approx E$. The calculated value of $T_H - [H]$ are sensitive to $[H]$. Thus small error may give ridiculous results. This difficulty can be overcome by using following method.

The points on the acid curve are obtained by equation

$$[H'] = E' + [OH'] - [Na'] \quad \dots \quad (1.46)$$

Similarly points for mixture of mineral acid and ligand curve are obtained as

$$[H''] = E'' + [OH''] - [Na''] + Y TL'' - \bar{n}A^2 \quad \dots \quad (1.47)$$

where,

$Y TL''$ = Number of dissociable protons for complex formation in gram ions per litre.

Let pH meter readings be the same for both solutions,

then

$$[OH'] = [OH''] \quad \dots \quad (1.48)$$

$$\text{and } [H'] = [H''] \quad \dots \quad (1.49)$$

Then we get

$$\bar{n}''A \frac{(E'' - E') - ([Na''] - [Na']) + Y T_L''}{T_L''} \quad \dots \quad (1.50)$$

Let us consider,

V^0 = Initial volumes

E^0 = Mineral acid concentrations

T^0L = Total ligand concentration are same in each titration. And V' and V'' are the volumes of alkali solution of concentration N' are required to reach points $[Na']$ and $[Na'']$, hence

$$E' = \frac{V^0 E^0}{(V^0 + V')} \quad \dots \quad (1.51)$$

$$E'' = \frac{V^0 E^0}{(V^0 + V'')} \quad \dots \quad (1.52)$$

$$[Na'] = \frac{V' N'}{(V^0 + V')} \quad \dots \quad (1.53)$$

$$[Na''] = \frac{V'' N'}{(V^0 + V'')} \quad \dots \quad (1.54)$$

Using these values in equation (1.50) we get

$$\bar{n}A = \frac{YT_L^0 + \frac{(V' - V'')(N' + E^0)}{V^0 + V'}}{T^0L} \quad \dots \quad (1.55)$$

This equation is used to determine $\bar{n}A$ for proton-ligand stability constant/s in the present work.

The curves obtained for mixture of mineral acid, ligand and metal ions are used to determine metal-ligand stability constant/s. The $[H]$ concentration on metal ion curve for any point is obtained by equation,

$$[H^{m'}] = E^{m'} + YT_L^{m'} - [OH^{m'}] - [Na^{m'}] - \bar{n}A^{m'} T_L^{m'} \bar{n}^{m'} T_M^{m'} \quad \dots \quad (1.56)$$

When ionic strength is kept constant, the pH meter readings are same. Hence

$$[H^{\prime\prime}] = [H^{\prime\prime\prime}] \quad \dots \quad (1.57)$$

$$[OH^{\prime\prime}] = [OH^{\prime\prime\prime}] \quad \dots \quad (1.58)$$

and $[\bar{n}A^{\prime\prime}] = [\bar{n}A^{\prime\prime\prime}] \quad \dots \quad (1.59)$

then,

$$\bar{n}^{\prime\prime\prime} \frac{(E^{\prime\prime} - E^{\prime\prime\prime}) + (T_L^{\prime\prime} - T_L^{\prime\prime\prime})(Y - \bar{n}_A^{\prime\prime}) - (Na^{\prime\prime} - Na^{\prime\prime\prime})}{\bar{n}_A T_M} \quad \dots \quad (1.60)$$

If both the solutions have initial volume V^0 and concentrations of acid and ligand are E^0 and T_L^0 respectively, and $V^{\prime\prime}$ and $V^{\prime\prime\prime}$ are volumes of alkali of concentration N' required to add so as to reach points $Na^{\prime\prime}$ and $Na^{\prime\prime\prime}$, then above equation becomes

$$\bar{n}^{\prime\prime\prime} \frac{(V^{\prime\prime\prime} - V^{\prime\prime})(N' + E^0) + T_L^0 (Y - \bar{n}_A^{\prime\prime})}{(V^0 + V^{\prime\prime}) \bar{n}_A T_M^0} \quad \dots \quad (1.61)$$

The equation (1.30) can be rewritten by using equation (1.26)

$$T_L^{\prime\prime\prime} = [L^{\prime\prime\prime}] \sum_{i=0}^j \beta_i^H [H^{\prime\prime\prime}]^i + \bar{n}^{\prime\prime\prime} T_M^{\prime\prime\prime} \quad \dots \quad (1.62)$$

where,

$$\beta_i^H = 1.$$

$$\therefore \frac{1}{(L^{\prime\prime\prime})} = \sum_{i=0}^j \beta_i^H [H^{\prime\prime\prime}]^i + \bar{n}^{\prime\prime\prime} T_M^{\prime\prime\prime} - T_L^{\prime\prime\prime} \quad \dots \quad (1.63)$$

Taking logarithm on both side we get,

$$pL = \log \frac{\sum_{i=0}^j \beta_i^H [H^{n_i}]^i}{T_L^{n_i} - \bar{n}^{n_i} T_M^{n_i}} \quad \dots (1.64)$$

The equation (1.64) can be rewritten, using equations (1.38), (1.40), (1.43) and (1.45) as

$$pL = \log \frac{\sum_{i=0}^j p\beta_i^H \left[\frac{1}{\text{antilog pH}} \right]^i}{T_L^0 - \bar{n}^{n_i} T_M^0} \times \frac{V^0 + V''}{V^0} \quad \dots (1.65)$$

$$\therefore pL = \log \frac{1 + pK_1^H \left[\frac{1}{\text{antilog pH}} \right]}{T_L^0 - \bar{n}^{n_i} T_M^0} \times \frac{V^0 + V''}{V^0} \quad \dots (1.66)$$

where $y = 1$

and

$$pL = \log \frac{1 + pK_1^H \left[\frac{1}{\text{antilog pH}} \right] + pK_1^H \cdot pK_2^H \left[\frac{1}{\text{antilog pH}} \right]}{T_L^0 - T_M^0 \cdot \bar{n}^{n_i}} \times \frac{V^0 + V''}{V^0} \quad \dots (1.67)$$

where $y = 2$

By using above equations values of \bar{n} and pL are calculated, from which stability constant/s of complex compound can be determined.

Determination of stability constants from the formation curves

Formation constant is considered through various angles. There are different methods which can be used for determination

of stability constant/s. Some of the important methods are accounted here in brief.

Method - 1 : Graphical Method

This method is used in determination of stability constant in present work. Let us consider equation,

$$\bar{n} = \frac{K_1[L]}{1 + K_1[L]}$$

$$\therefore \bar{n} + \bar{n} K_1[L] = K_1[L] .$$

$$\begin{aligned} \therefore \bar{n} &= K_1[L] - \bar{n} K_1[L] \\ &= K_1[L] (1 - \bar{n}) \end{aligned}$$

$$\therefore \frac{1}{[L]} = K_1 \frac{(1 - \bar{n})}{\bar{n}}$$

Taking logarithm on both sides we get,

$$pL = \log K_1 + \log \frac{(1 - \bar{n})}{\bar{n}} \quad \dots \quad (1.68)$$

The plot of $\log \frac{(1-\bar{n})}{\bar{n}}$ vs pL is a straight line

$$\text{When } \log \frac{1 - \bar{n}}{\bar{n}} = 0$$

$$pL = \log K_1$$

Similarly, $\log K_2$ can be obtained by equation,

$$pL = \log K_2 + \log \frac{(2 - \bar{n})}{(\bar{n} - 1)} \quad \dots \quad (1.69)$$

$$\text{When } 2 - \bar{n} = \bar{n} - 1$$

$$pL = \log K_2$$

Method - 2 : Bjerrum's Method

In this method stability constant is obtained by solving simultaneous equations. Let us consider equation

$$\sum_{n=0}^N (\bar{n} - n) \beta_n [L]^n = 0 \quad \dots \quad (1.70)$$

Sullivan and Hindman¹⁰ solved this equation by determinant method.

$$\begin{vmatrix} (\bar{n} - 1) [L_1] + \dots (\bar{n}_N - N) [L_1]^N \\ (\bar{n} - 1) [L_N] + \dots (\bar{n}_N - N) [L_N]^N \end{vmatrix} \neq 0$$

By solving above determinant, N linear simultaneous equations are obtained from which N stability constants for $ML_1, ML_2 \dots ML_N$ complexes can be determined.

Let us consider equation when $N = 2$.

$$\bar{n} + (\bar{n} - 1) K_1 [L] + (\bar{n} - 2) K_1 K_2 [L]^2 = 0 \quad \dots \quad (1.71)$$

and

$$\bar{n} + (\bar{n} - 1) \beta_1 [L] + (\bar{n} - 2) \beta_2 [L]^2 = 0 \quad \dots \quad (1.72)$$

The values of \bar{n} and $[L]$ can be experimentally determined while values of β_1 and β_2 are not known. Two equations are then used to find β_1 and β_2 .

The values of K_1 and K_2 are obtained by using equation (1.71).

$$K_1 = \frac{1}{[L]} \cdot \frac{\bar{n}}{(1-\bar{n}) + (2-\bar{n}) K_2 [L]} \quad \dots \quad (1.73)$$

and

$$K_2 = \frac{1}{[L]} \cdot \frac{\bar{n} + \frac{(\bar{n}-1)K_1[L]}{(2-\bar{n})K_1[L]}}{\dots} \quad (1.74)$$

Same procedure is used to determine N values of values of stability constants.

Method - 3 : Interpolation of Half Integral Values

This is second method which is used in this present work. The values of K_1 and K_2 as obtained in method 2, give the following type of equations.

$$\log K_1 = pL \ 1/2 + \log [2/(1+\sqrt{1+12 K_2/K_1})] \quad \dots \quad (1.75)$$

and

$$\log K_2 = pL \ 3/2 + \log [2/1+\sqrt{1+12 K_2/K_1}] \quad \dots \quad (1.76)$$

where $pL \ 1/2$ and $pL \ 3/2$ are free ligand exponent when $\bar{n} = 0.5$ and 1.5 .

When $K_{n-1} \gg K_n$, the



In this case contribution of other species such as ML_{n-2} and ML_{n+1} are neglected.

When K_2/K_1 is very small then,

$$\sqrt{1 + 12 K_2/K_1} \approx 1.$$

$$\therefore \log K_1 = pL \ 1/2 \quad (\because \log 1 = 0) \quad \dots \quad (1.77)$$

Similarly

$$\log K_2 = pL_{3/2} \quad \dots \quad (1.78)$$

In general we get,

$$\log K_i = pL_i - 1/2 \quad \dots \quad (1.79)$$

Thus $\log K_1, \log K_2 \dots \log K_i$ which are corresponding to $ML, ML_2, \dots ML_n$ are obtained at $\bar{n} = 0.5, 1.5, 2.5, \dots (n - 0.5)$ respectively. But it should be remembered that the value of K_2/K_1 causes significant error if they do not differ to sufficient extent. If $\log K_1$ and $\log K_2$ values differ by at least 4 pH units, then we achieve accuracy upto 0.001 for pK_1^H and pK_2^H .

Method - 4 : Schwarzenbach's Graphical Method

Schwarzenbach¹¹ et al first proposed this method for the determination of ionisation constants of dibasic acids by using a potentiometer. Then it was extended by Schwerzenbach and Ackerman¹² for determination of stability constants of complexes.

In this method \bar{n} and $[L]$ are first determined, by plotting the values of $A = (\bar{n} - 1) [L] / \bar{n}$ as abscissae and $B = (\bar{n} - 1) / (2 - \bar{n}) [L]$ as ordinates. All lines passing through pairs of point (A,B) should intersect when extrapolated at the point $1/K_1, K_2$.

Method - 5 : Rossotti and Rossotti's Graphical Method

The plot of $\frac{\bar{n}}{(1 - \bar{n})[L]} = A$ against $\frac{(2 - \bar{n})[L]}{(1 - \bar{n})} = B$

is used to evaluate β_1 and β_2 . The plot is a straight line but it deviate from straight line for higher value of $[L]$. The slope of the graph is β_2 and the intercept on Y axis is β_1 .

When more than two complexes coexist graphical method¹³ is used to determine successive stability constants from the values of the degree of formation of the system. Plot

$$\sum_{n=0}^{n=t-1} [(\bar{n}-n) / (t-\bar{n})] \beta_n [L]^{n-t} \text{ against } (t+1-\bar{n})[L] / (t-\bar{n})$$

Where \bar{n} = average number of ligands per central atom, t is the number of ligands in the complex for which stability constant is β_t and $[L]$ is the concentration of free ligand species. The intercept is β_t , and the limiting slope as $[L] \rightarrow 0$ is $\beta_t + 1$.

Method - 6 : Least-Squares Method

Let us consider equation (1.71)

$$\bar{n} + (\bar{n} - 1) K_1 [L] + (\bar{n} - 2) K_1 K_2 [L]^2 = 0$$

Devide equation by $\bar{n} + (\bar{n} - 1)$

$$\frac{\bar{n}}{(\bar{n}-1)[L]} + K_1 + \frac{(\bar{n}-2)K_1K_2[L]}{\bar{n}-1} = 0$$

$$\frac{\bar{n}}{(\bar{n}-1)[L]} = \frac{(2-\bar{n})[L]}{\bar{n}-1} \cdot K_1K_2 - K_1 \quad \dots \quad (1.80)$$

This is an equation of a straight line, hence the plot of

$$\frac{\bar{n}}{(\bar{n}-1)[L]} \quad \text{vs} \quad \frac{(2-\bar{n})[L]}{(\bar{n}-1)} \quad \text{is a straight line.}$$

The slope of the graph is K_1K_2 and intercept is $-K_1$. Thus values of K_1 and K_2 can be calculated if \bar{n} and pL are determined by experimental method.

Method - 7 : Bjerrum's Mid-Point Method

At the mid-point of the formation curve $\bar{n} = 1$, then

$$K_1K_2 [L_1]^2 = 1 \quad \dots \quad (1.81)$$

Taking logarithm on both sides we get -

$$\log K_1K_2 + 2 \log L_1 = 0$$

$$\therefore \log K_1K_2 = -2 \log L_1 \quad \dots \quad (1.82)$$

The abscissa of the mid-point gives the value of β_2 .

Method - 8 : Computer Method

All methods given above are based on graphs or on calculations. These methods can be used when simple systems are studied. But when more complex systems are considered then handling of data becomes more difficult, and due to lack of proper judgement, there is deviation from true values. Such type of complex systems can be studied by a computer. It is a new powerful technique to handle complicated data.

Sillen¹⁴ used the computer technique for determination of stability constant of complex compounds. Now a days it is often used by a number of workers.^{15,16} The results obtained by this method are more accurate and hence, more useful.

Thermodynamic Aspects

It is appropriate at this stage to take a brief account of the aspects of thermodynamic parameters preferably the influence on the stability of species involved in chemical reactions. This enables one to have a comprehensive overview of the reaction and the species involved.

The values of overall changes in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) accompanying complexation are determined using the temperature co-efficient and Gibbs-Helmholtz equation.¹⁷

The free energy change ΔG° is related to the corresponding equilibrium constant K by the equation

$$\Delta G^\circ = - 2.303 RT \log K \quad \dots \quad 1.83$$

Calculation of the enthalpy change can be carried out by substituting a pair of values K_1 and K_2 at two temperatures T_1 and T_2 into the equation

$$\Delta H = 2.303 R T_1 T_2 (\log K_2 - K_1) / T_2 - T_1 \quad \dots \quad 1.84$$

But the graphical method is preferred over this method. However,

it is better to use more than two values of K to obtain a graphical solution to the equation

$$\log K = (\Delta S - \Delta H/T) / 2.303 R \quad \dots \quad (1.85)$$

where ΔS is the entropy change.

If ΔH varies appreciably with temperature, it is possible to obtain the values of the parameters a, b and c by fitting at least three values of K to the equation

$$\log K = a + bT + cT^2 \quad \dots \quad (1.86)$$

The values of ΔH can be obtained from the relations

$$\delta(\log K) / \delta T = b + 2 cT = \Delta H / 2.303 RT^2 \quad \dots \quad (1.87)$$

which may be rewritten as

$$\frac{\delta(\log K)}{\delta(1/T)} = \frac{\Delta H}{4.576} \quad \dots \quad (1.88)$$

The values of $\log K$ obtained at different temperatures are plotted as a function of $1/T$. The gradient of the tangent drawn at the point corresponding to 40° are determined and are equated to $-\Delta H/4.576$. The value of ΔH can thus be obtained.

The entropy change can be calculated from equation (1.85), or from the equation

$$\Delta S = (\Delta H - \Delta G) / T \quad \dots \quad (1.89)$$

THERMODYNAMIC FUNCTIONS AND THEIR SIGNIFICANCE

In applying a particular technique of experimentation or computation we usually keep our eye on the goal and try to

develop a simple relation by sacrificing certain aspects. Sometimes in order to maintain simplicity of the model we resort to severe approximations. It may so happen that these compromises might be detrimental to the cause. It is very important here to note that final value may be of use only if we know how we got the value. At times, it may so happen, that the chosen set of values may not be applicable in a specific circumstances and the result may be ridiculous or disastrous.

The complex formation is accompanied by changes in entropy and enthalpy. Complex formation is favoured when entropy changes are positive and heat changes are negative. Complex formation depends upon entropy and enthalpy and hence for fuller understanding of the reaction they must be considered separately. It is not possible to depend completely on the thermodynamic data reported in the literature. Because the data obtained by various methods may not be the same. But still certain trends are apparent. For many reactions, both the heat and entropy changes are favourable for complex formation. But for some reactions entropy change or enthalpy change may oppose the formation of the complex. It is noted that negative entropy changes oppose the formation of complex to large extent.¹⁸ Thus heat and entropy changes may mutually supporting or opposing complex formation.

Ligational Entropy Changes

The change in entropy during complex formation is expected to be negative due to the conversion of translational to

vibrational and rotational entropy. In case of polyatomic ligands there will be additional loss due to rotational entropy. Phipps¹⁹ showed that N_3^- and SCN^- are linear ions which might possess rotational entropy which would be lost on association. For gas phase association, Evans and Nancollas estimated that rotational entropy loss for N_3^- is $11 \text{ cal. degree}^{-1} \text{ mole}^{-1}$. Similar calculation for SCN^- showed its gas phase rotational entropy loss to be $16 \text{ cal. degree}^{-1} \text{ mole}^{-1}$. This value is sufficiently large to change the total entropy of complex formation.

Role of solvent is also important in ligational entropy changes. While studying the association of ferric ions with chloride, bromide and hydroxyl ions Rabinowitch and Stockmayer²⁰ have shown for the first time that the entropy change accompanied by a complex formation is usually positive which is then supported by many others.²¹⁻²³ Entropy change for an outer sphere complex is less favourable than for the corresponding inner sphere complex.

Change in entropy when an unidentate charged ligand forms a complex is due to decrease in the number of ions, neutralization of electrical charge, attenuation of the remaining charge and by displacement of water from the hydration spheres. The entropy change for an uncharged unidentate ligand is less than that for a charged ligand, because ligation by an uncharged ligand is not accompanied by reduction in the number of ions and by neutralization of charge. Ligand is also less hydrated

than a charged ligand. On the molar scale they are usually negative.²³ Similarly entropy change for charged multidentate ligand is more than that for a neutral ligand. For multidentate ligand entropy change is due to change in the configuration and displacement of the reactants from the hydration spheres. The entropy change associated with the chelation is greater than that associated with the formation of a similar non-chelate complex. Spike and Parry²⁴ determined the entropy change for chelate and non-chelate complexes of Cd^{++} with ethylenediamine and ammonia, over the temperature range of 10 to 40°C. They found that entropy of $\text{Cd}(\text{en})_2^{++}$ is greater than the entropy change of $\text{Cd}(\text{NH}_3)_2^{++}$.

Standard Entropies

Let us consider mononuclear reaction



The entropy change for above complex forming reaction depends upon the standard entropies in solution of the complex and of its constituent metal ion and ligands which can be shown as

$$\Delta S_n^{\circ} = S^{\circ}(\text{ML}_n) - S^{\circ}(\text{M}) - nS^{\circ}(\text{L}) \quad \dots \quad (1.91)$$

The standard entropies for monoatomic cations and anions are well established.²⁵ George and his coworkers²⁶ claimed that the values of $S^{\circ}(\text{ML}_n)$ can be determined by the charge, and the number and nature of ligands by using three parameter equation.

The linear correlation was claimed between ΔS_1 and $[S^\circ(M) + S^\circ(L)]$ for complexes formed by a number of metal ions with different inorganic ligands by Williams.²⁷ Charles obtained ΔS_1 values by calorimetric data for EDTA complexes of 13 bivalent metal ions and a linear plot of ΔS against $S^\circ(M)$ with unit slope and deviations of ± 2.5 e.u. was claimed.

Martel²⁸ noted that the values of ΔS° (standard entropy) for a number of aminopolycarboxylato complexes increase with the number of donor atoms and also with the decrease in the radius of the metal ion.

Hydrational Entropies

A standard entropy in solution is the sum of the standard entropy in the gas phase and the hydrational entropy.

$$\Delta S_n = \Delta S_g + \Delta S_h (ML_n) - \Delta S_h(M) - n\Delta S_h(L) \quad \dots \quad (1.92)$$

where ΔS_g is the ligational entropy in the gas phase and ΔS_h terms are hydrational entropies.

The values of ΔS_h are obtained by subtracting the standard entropy in the gas phase from the standard entropies in solution.

Ligational Enthalpy Changes

Enthalpy changes during complex formation are important because complex formation is either supported or opposed by

enthalpy change. Complex formation is favoured when heat changes are negative. Step-wise ligational enthalpies are usually between 0 to ± 5 K cal/mole, for complex formation with ionic ligands in aqueous solution. But they may be as large as - 10 K cal/mole for certain reactions e.g. silver(I) or mercury(II) with cyanide or iodide ions. The values of enthalpy changes are usually between 0 and - 5 K cal/mole for neutral unidentate ligands, but may be large as - 20 K cal/mole with neutral multidentate ligands.

When covalent bond, which is having appreciable double bond character is formed during complex formation, then it is accompanied by large enthalpy change. Arthur E. Martell²⁸ determined thermodynamic parameters for complexation of nitrilotriacetic acid with bivalent metal ions. And showed that all the acid dissociation constants reported show a non-linear variation as a function of temperature. Therefore, enthalpy change varies with temperature. Same type of variation in ligational enthalpies of metal ions is shown by others.^{29,30} The ligational enthalpies in aqueous solution are the small heat changes which are accompanied by the replacement of water by other ligands. Grinberg and Yastimirskii³¹ showed that ΔH_n i.e. change in standard enthalpy differs from change in enthalpy in solution. He determined ΔH_n by replacement of water by another ligand in the gas phase. And predict the sequences Na < Mg < Al, Mg > Ca > Sr and Ca < Mn < Co < Ni < Cu > Zn for values of ΔH_n accompanying metal ammine formation.

The heats of formation for a metal complex in the gas phase can be calculated by using equation

$$\Delta H_n = \Delta H_g + \Delta H_h (ML_n) - \Delta H_h(M) - n\Delta H_h(L) \quad \dots \quad (1.93)$$

where ΔH_g is the ligational enthalpy in the gas phase and ΔH_h are hydrational enthalpies.

The sum of ($\Delta H_n + \Delta H_h(M)$) will give measure of ΔH_g for the reaction of one ligand with a series of metal ions.



Here it is assumed that the $\Delta H_h (ML_n)$ terms are approximately constant within the series.

Overall heats of hydration of metal ions $\Delta H_h(M)$ are well known^{32,33} and range from - 100 to - 1500 K cal/mole. Uusitalo³⁴ found linear correlation between Haissinsky electronegativity of metal ions and ΔH^0 for the reactions of number of bivalent metal ions with 7-phenylazo- and 7-(4-nitrophenylazo)-substituted 8-hydroxyquinoline 5-sulphonic acids. But Charles³⁵ could not find simple correlation with electronegativity of metal ion and ΔH_1 for ethylenediamine-tetra-acetato M(II) complex formation.

In the presence of an octahedral field due to six ligands, the degenerate d orbitals of transitional metal ions split into two sets, d_E triplet of lower energy and d_Y doublet of higher energy. The energy separation between two levels is ~ 30 K cal/mole for the bivalent aqua ions and ~ 60 K cal/mole for the

trivalent aqua ions of the first transitional series which are rather higher for second and third transitional series. Ions with d^0 , d^5 and d^{10} configurations are spherically symmetrical. There is decrease in size with increasing nuclear charge and hence ΔG very smoothly with atomic numbers d^1 , d^2 , d^3 , d^6 , d^7 and d^8 will occupy $d\epsilon$ levels in high spin complex and require about 5 per cent excess stabilization energy. The d^4 , d^5 , d^9 and d^{10} electrons are forced to occupy the $d\gamma$ levels and the extra stabilization is cancelled out. When six ligands are coordinated to chromium(II) and copper(II) having d^4 and d^9 configuration usually they have tetragonally distorted octahedral configuration.³⁶ If four ligands in xy plane are closer to metal ion than two ligands in z plane, then additional Jahn-Teller stabilization energy is required, which depends upon the nature of the ligand.

The following sequence for the negative ligational enthalpies for bi- and tri-valent transitional metal ions is predicted

$$d^0 < d^1 < d^2 < d^3 \lesssim d^4 > d^5 < d^6 < d^7 < d^8 \lesssim d^9 > d^{10}$$

The sequence $d^3 > d^4$ and $d^8 > d^9$ is expected when there are five or six coordinated donor atoms and/or when the Jahn-Teller stabilization is low. The sequence $d^3 < d^4$ and $d^8 < d^9$ is expected when the Jahn-Teller stabilization is relatively high.³⁷ Deviations from above sequences may occur with ligands which form strong bonds or when ground state electronic configurations get changed during complex formation.

The values of ΔH_n for complexes of different metal ions may be expected to follow above sequences. Some values of ΔH_1 for complexes of the first transition series are given in following table. Besides large experimental errors they follow the general trend predicted.

Ligational Enthalpies at 25°C in K cal/mole.

	$-\Delta H_1$					
	Mn	Fe	Co	Ni	Cu	Zn
EDTA ³⁸	5.45	-	4.4	8.35	8.67	5.61
trien ³⁹	4.0	9.0	9.0	13.00	22.0	9.8
acac ⁴⁰	2.5	-	1.2	6.7	4.7	1.9
2,2-dimethyl-1, 3-propanediamine ⁴¹	-	-	7.0	8.0	12.0	5.0

Free energy changes

Free energy changes accompanying complex formation is expressed in terms of standard free energies G° by the equation

$$\Delta G_n = G^\circ(\text{ML}_n) - G^\circ(\text{M}) - nG^\circ(\text{L}) \quad \dots \quad (1.95)$$

The general correlation of ligational free energies of complexes is difficult, but the free energy changes may vary in the same way as the entropy or enthalpy changes.

Foreman and Smith⁴² found a linear correlation between the logarithms of stability constants of the EDTA complexes and the

standard entropies of the lanthanide ions. In attempting to correlate the measured stability constants for the plutonium chelates of EDTA, they showed that stability constant is not itself a fundamental quantity but is related to the entropy and enthalpy of the system by equation,

$$- RT \ln K_a = G^{\circ} = H - T\Delta S \quad \dots \quad (1.96)$$

For chelates of high stability the entropy term becomes predominant, as demonstrated by Carini and Martel.⁴³ Of the factors contributing to the increase in entropy on chelate formation the most important is the increase in the number of particles in the system arising from the release of water molecule from the hydrated cation to the bulk solution. The graph of $\log K$ for the EDTA chelates against entropy is reasonably linear.

The ligational entropy changes for the formation of transitional metal ion complexes of manganese(II) to Copper(II) are either essentially constant or related to the enthalpy changes^{44,45} so that the free energy sequence is the enthalpy sequence.

The free energy sequence for halogen complexes is $F > Cl > Br > I$ when the entropy term preponderates. But it is reversed when the enthalpy term is more important.⁴⁶

Correlations with properties of the metal ion

Ionic charge and radius : It is commonly observed that within each family of the elements, the stability of complexes formed

with small ionic ligands, highly charged unidentate ligands or with multidentate ligands increase as the size of the metal ion decreases.

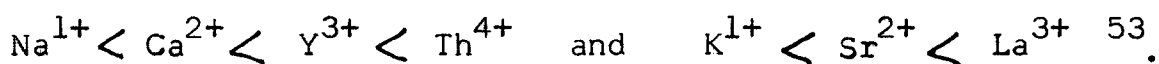
The stability sequence for complexes with dibenzoylmethane in 75 per cent dioxane for alkali metals is ⁴⁷



Williams⁴⁸ showed that stabilities of alkaline earth metals for oxalate, malonate, succinate and malate ligands, are in the sequence $\text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$.

Again they showed that the solubilities of the thiosulphates, sulphates, iodates, bromates, chromates and nitrates, all strong-acid salts, fall in the sequence $\text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$. Now the entropy of solution of different cations would favour exactly the opposite order of solubilities and therefore it must be assumed that the heats of solution for the salts of these cations with a given strong-acid are in the order of decreasing radius of cation. The same order is discussed by others.^{49,50} The sequence $\text{La} < \dots < \text{Gd} < \dots < \text{Lu(III)}$ has been established with carboxylate^{51,52} aminopolycarboxylate and diketone ligands.

For the metal ions of the almost same size, stabilities increase with the charge of metal ion. e.g.



Yastsimirskii⁵³ and Williams⁵⁴ have showed that the ligational heat changes are expected to produce observed sequence. Again

it is significant that the common orders occur with ligands which have negative standard entropies and are expected to produce large entropy changes. While common order is reversed with those ligands which have positive standard entropies and produce small changes in entropy.

Correlations with properties of the ligand

Nature of the Donor Atom

The atoms which either singly or in combination with other atoms can donate pair of electrons to form complex compound are listed in following table :

Atoms which are Bound Directly to Metal Ions in Complexes

	:		:		:	H
C	:	N	:	O	:	F
	:	P	:	S	:	Cl
	:	As	:	Se	:	Br
	:	Sb	:	Te	:	I

For polynuclear complexes, bridging occurs through the same atoms or through direct M-M intractions.

In most complexes, one of the atoms listed in above table donates a lone pair of electrons to s or p orbital of metal ion (acceptor) to form coordinate covalent bond. In some cases, the

donor atom of the ligand may act as an acceptor. The availability of the pair of electrons for donation to metal ion is affected by the rest of ligand, e.g. it is less available in a N-heterocyclic compound than in ammonia. The donor atoms of the first row can accept pair of electrons to form $d\pi - p\pi$ bonds, while heavier atoms have π vacant d orbitals to form $d\pi - d\pi$ bonds. The majority of metal ions form their most stable complexes with the donor atoms in the first row. But metal ions with full or nearly full d orbitals immediately under the valence shell, e.g. platinum(II), silver(I), mercury(II) and their neighbours form their most stable complexes in combination with the heavier atoms.

Formation of complexes of the first group is accompanied by comparatively large, positive entropy changes and small heat changes. For the alkaline earth cations the relative order of stabilities is oxygen $>$ sulphur. For transitional metal ions it is reversed as oxygen $<$ sulphur $<$ selenium.

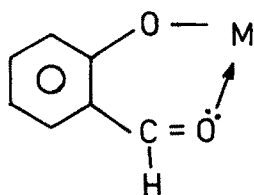
Irving and Williams⁵⁴ noted that the stability sequence for the manganese(II) bis complexes is salicylaldehyde (O + O donors) $>$ glycine (O + N) $>$ ethylenediamine (N + N) and that sequence is reversed for latter members of transitional series. Izatt, Fernelius and Block noted that the enthalpy changes for the formation of copper(II) complexes decrease in the order of donor atoms (N + N) $>$ (N + O) \sim (S + O) $>$ (O + O).

TRENDS AND DEVELOPMENTS

The data is not fully available and available data requires consolidation to check interpretative speculations, and therefore, consistently useful and coherent sets of values. Only free energy data is also sufficient for exploratory studies, e.g. complexes of transitional metal ions with ligands having heavier donor atoms and with selective stereochemistry, of mixed and polynuclear complexes, of inert systems, effect of solvent upon M-L bonds, etc. and free energy changes. Very less is known about equilibria between inner and outer sphere, chelated and non-chelated or between high and low spin isomers. The differentiation of isomeric pairs is rather difficult because the stability constants determined by different methods may not be the same. The distinction between inner and outer sphere complexes of transitional metal ions is carried out by visible and ultraviolet absorption spectra⁵⁵⁻⁵⁷. But for further study new spectroscopic or relaxation method should be developed. Still there is need for new independent methods for studying equilibria, technique and calculation of thermodynamic functions is essential. To obtain more accurate data for heat and entropy for systems new calorimeters are required. In addition to it sources of errors should be minimized to avoid guilty results.

Salicylaldehyde acts as a bidentate ligand. It contains one -OH group which can use one proton for bonding. It also contains one -CHO group. The carbonyl oxygen can donate the

pair of electrons to form coordinate covalent bond. Thus salicylaldehyde forms chelate with metal ions.



Calvin and Wilson⁵⁸ studied the cupric chelates of salicylaldehyde, its derivatives and other enolic ligands. This work is a report of more or less quantitative survey to determine the influence of certain structural factors upon the stability of the chelate compounds of divalent copper in water-dioxane medium.

Heither-Wirgin and Shamir⁵⁹ determined the stability constants of Salicylaldehyde complexes and showed the relation between H^+ liberated and the concentration of the complex results in an equation that is a straight line function. This equation permits the determination of the stability constants from different points of the titration curve by graphical method.

Jones et al⁶⁰ studied the relation between proton dissociation constants and the stability constant. They determine the proton dissociation constants of some derivatives of salicylaldehyde and 8-quinolinol, and compared with the stability constants of complexes formed by the ligand derived from these

acids and the Ni^{++} , Fe^{++} , Fe^{3+} , Zn^{++} and Mn^{++} ions. They showed that the general equation of Bjerum, $\log K = apK + b$ has no general validity, particularly if ligands of somewhat different character are compared.

Mellor and Maley⁶¹ reported the stability of complexes of divalent metal ions and established the order of stability. They found that the order of stability was substantially the same for bidentate chelating agents, salicylaldehyde, glycine and 8-hydroxy quinoline. They also pointed out that the stability seemed to decrease with increasing basicity of the metal. Thus weakly basic Cu and Pd form strong chelates and more basic metal like Mg forms the weakest chelates.

Rostmus Jr.⁶², Magnusson and Craig reported the association constants for 1:1 complexes for Cu(II), Zn(II), La(III) and Y(III) with ions of salicylaldehydes by spectrophotometric data.

Kamat, Laxmeshwar and Datar⁶³ studied the proton-ligand stability constants of substituted salicylaldehydes. They found the order : $5\text{-NO}_2 < 3\text{-NO}_2 < 5\text{-SO}_3\text{H} < 4\text{-NO}_2$, for substituted salicylaldehyde at 30°C , and at ionic strength μ 0.1 M NaClO_4 in a mixed solvent 75 % dioxane 25 % water vol/vol. The metal ligand stability order $\text{Cu} > \text{Zn} > \text{Mn} > \text{Mg}$ was observed for these ligands without exception.

Gomez Lara⁶⁴ studied the formation of salicylaldehyde complexes in 50:50 water dioxane mixture at $15\text{-}50^\circ\text{C}$. The

successive thermodynamic stability constants K_1 and K_2 were detected for Cu(II), Ni(II), Zn(II), Mg(II) and Ca(II), Ba(II). K_1 and K_2 values increased with increasing temperature.

Ratolikar and Jahagirdar⁶⁵ studied the complexation reactions of Cu^{++} , Ni^{++} , Co^{++} , Zn^{++} and Mn^{++} ions with salicylaldehyde and 3-chloro, 4-hydroxy-5 methyl-, 5 iodo-, 6-chloro, 3 chloro - 5 nitro -, 3 methyl and 3-nitro - 5 methyl - salicylaldehydes, by Calvin Bjerrum potentiometric titration stability constants of 1:1 and 1:2 complexes of Cu^{+2} , Ni^{+2} , Co^{+2} and 1:1 complexes of Zn^{+2} and Mn^{+2} are determined at 30°C in 75 vol % aq. dioxane. Ratolikar⁶⁶ extended the same work for UO_2^{+2} , VO_2^{+2} , Ce^{+3} and Nd^{+3} ions and salicylaldehyde and its 3-chloro, 4-hydroxy, 5-methyl, 5-iodo, 6-chloro, 3 methyl- 5-nitro, 5-methyl-3-nitro, derivatives.

Dessouki, Issa and Ghoneim⁶⁷ studied the Co(II), Ni(II), Cu(II) complexes of phenylazosalicylaldehyde derivatives by using spectrophotometric and potentiometric methods. The structure of the ligands in the solid MLCl ($m=\text{Co, Ni, Cu}$) was studied by IR spectroscopy. Chelate formation takes place through phenolic O and aldehyde O through proton displacement from the ligand.

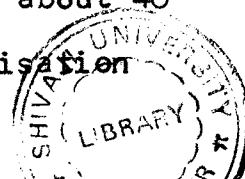
Stability constants of the complexes of substituted salicylic acid with Co(II) and Ni(II) were studied by Sathpak⁶⁸. The dissociation constants of the ligands, and formation constants of the metal complexes were calculated. No 1:2 complexes were formed. The structure of the metal complexes are discussed.

The thermodynamic parameters ΔG , ΔH and ΔS were determined for the complexation reactions of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with some substituted salicylic acids.⁶⁹ Crystal field stabilization energy values of 1:1 chelates were also calculated. The increase in $10 Dq$ values for all these ligands is comparable with those of certain O donating ligands like oxalic acid, malonic acid and salicylaldehyde.

Jahagirdar⁷⁰ studied the complexation reactions of Cu^{++} , Ni^{++} , Zn^{++} , Co^{++} and Mn^{++} ions with salicylic acid and 3-bromo, 3,5-dibromo, 3-5 dichloro, 4-hydroxy, 5-hydroxy, 3-nitro, 5-nitro, 3-5 nitro, 5-chloro, 4-bromo and 4-iodosalicylic acids, by Calvin-Bjerrum titration technique in aqueous medium at $30^{\circ}C$ and 0.1 M ionic strength. The effects of substituents on the dissociation of $-COOH$ (pK_1) and $-OH$ (pK_2) groups in different acids have been discussed. The relation $\log K = apK + b$ is examined for the metal complexes which are found to obey the Irving-Williams order.

Formation constants and thermodynamic parameters of Zinc(II) complexes with 5-chloro-5-amino and 5-sulphosalicylic acids were studied conductometrically and pH-metrically by Mandlik⁷¹. Formation constants of the complexes were determined by employing Bjerrum's method and various thermodynamic parameters were obtained. The bonding in the complexes are discussed on the basis of IR study.

Recently, Ryabokobylko⁷² and coworkers prepared about 40 derivatives of salicylaldehyde and studied their ionisation



constants at 25°C in aqueous solution. Salicylaldehyde and its derivatives are also used as catalysts in the kinetic studies⁷³.

Substituted salicylaldehydes behave similarly but the basic structures of different derivatives offer an interesting series of ligands giving 4 and 6 coordinating metal complexes.

Vic-Hydroxy aldehydes give interesting analytical reagents like oximes⁷⁴, thiosemicarbazones, semicarbazones⁷⁵ and versatile ligands like Schiff's bases and anils. For proper understanding of complex compounds, their ionic equilibria in solution is also important.

Thiosemicarbazones

Aldehydes and Ketones give crystallizable thiosemicarbazone derivatives, therefore, this property is used for the identification of aldehydes and ketones in the laboratories^{75a}. The first analytical application of thiosemicarbazone derivative appeared as late as 1945⁷⁶. But after that enough has been done on thiosemicarbazone derivatives.

Thiosemicarbazones are pharmacologically important. Kai, Arne and coworkers⁷⁷ showed that thiohydrazides and thiohydrazones are antibacterial and fungistatic substance. Thiohydrazides were prepared from the esters of dithio acid or free dithio acid with N_2H_4 ; and thiohydrazones were prepared by condensation of thiohydrazides with aldehydes.

Kurt Liebermeister⁷⁸ showed that sulfathiocarbamide, methylthiouracil and p-acetylamino benzal thiosemicarbazone are useful on pathogenic strains of pleuropneumonia-like organisms. They are also effective against sacchromyces, streptococci, staphylococci and c.diphtheriae.

Domagk⁷⁹ showed that thiosemicarbazone and their complexes have antitubercular activity. Thiosemicarbazones are found to be useful in the treatment of influenza, small-pox and certain kinds of tumors. The activity of the compound depends on the ability to form chelate with the trace metals present in the body of the host.

As thiosemicarbazones and allied derivatives are used as antibacterial substance; there is unidirectional growth in the field of physiological activity.

Scott⁸⁰ used 4-Allylthiosemicarbazide derivatives in analytical chemistry. He showed that p-hydroxybenzaldehyde gives test for bismuth ion. Again he showed that the 4 allyl-thiosemicarbazone of 3,4-dihydroxybenzaldehyde may be used for the detection of nitrites in the presence of nitrates and many other ions. Thiosemicarbazides and diphenylthiosemicarbazones have been recommended as organic precipitating agents for certain metallic ions.⁷⁵

Stakoviansky used β -resorcylic thiosemicarbazone in gravimetric determination⁸¹ of Cd^{++} . The ions, NH_4^+ , Mg^{++} , Ca^{++} , Sr^{++} , As^{+++} , As^{5+} and SO_4^{--} , SCN^- and OAC^- not interfere with the determination.

Synergistic⁸² extraction of nickel with salicylaldehyde thiosemicarbazone is carried out by Vlacil and coworkers.

The spectra of thiosemicarbazone their derivatives and their complex compounds with metal ions is studied by various workers^{83,84,85,86,87}. Wiles studied the C=S stretching vibration in the infrared spectra of thiosemicarbazone and aldehyde thiosemicarbazones containing aromatic group. The uv spectra of thiosemicarbazide and it's condensation product with Me₂CO, glucose, MeCOPh, PhCHO, p-O₂NC₆H₄CHO and o-HOC₆H₄CHO were studied by Vladzimirskaya⁸³. They showed absorption max at 239 nm.

Ablov and his coworkers prepared transition metal ion thiosemicarbazones of salicylaldehyde and studied their γ-resonance spectra.^{86,88}

The thiosemicarbazones and their derivatives are used as chelating agents and used to prepare complex compounds with metalions. The spectra and antibacterial action are studied by number of workers. But there is no significant investigation about the properties of complexes in solution. Very few workers have studied the ionic equilibria of thiosemicarbazone in solution i.e.

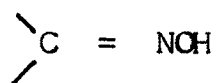
1) Gulya and coworkers prepared⁸⁹ thiosemicarbazides complex of Ni⁺⁺, Co⁺⁺, Vo⁺² and Cr⁺³ and studied their magnetic properties; and also determined the stability constants by

N.M.R. method. The cation complexing capacity of these ligands in aqueous solution i.e.



Sawhney and coworkers⁹⁰ studied the stability and thermodynamics of metal. P-nitrobenzaldehyde thiosemicarbazone systems with bivalent metal ions Cu^{++} , Ni^{++} , Co^{+2} , Mn^{+2} and Zn^{+2} . The formation constants of complex were evaluated as well as the thermodynamic parameters at 28 and 38°C are determined.

Oxime - The term oxime is shortened version of the oxy-imine



The oxime group exhibits slightly basic character due to the nitrogen atom in it, when as the hydroxyl group imparts mildly acidic character. Hence, the oxime group is amphiprotic.

Literature survey shows that oximes are having uses in analytical chemistry. They are also used in spectro photometric and gravimetric analysis. Salicyladoxime, Benzoin oxime, dimethyl glyoxime and ferron oxime are some of versatile analytical reagents.

Taylor⁹¹ described the α -acyloins and the corresponding oximes as highly specific groups. These substance form strong chelates with only a very limited number of metals : Fe, Co, Ni, Cu. The remarkable specificity of dimethyl glyoxime and other 1,2-dioximes has been described by Diehl⁹².

The structure of the oxime group was not confirmed till 1960.

There were two structures of the oxime - one with OH(I) and other with nitron structure



Hamiltons⁹³ work on Neutron diffraction of dimethyl glyoxime prove the presence of O=H bonds with the bond distance of $1.02 + 0.04A^{\circ}$. Thus structure(I) was proved and accepted.

Mukherjee used resorcyal aldoxime as an organic reagent⁹⁴. Resorcyal aldoxime is used for the gravimetric determination of Cu and Ni in the presence of other metallic ions by controlling the pH. Cu is detected in presence of bivalent Cd, Zn, Pb and Cr between 1.8 to 2.4. pH and Ni are detected in the presence of bivalent Cd, Co, Zn, Mn and Pb.

The most of the work of oxime is related to analytical application, while study on ionic equilibria is neglected. Very few have tried to study ionic equilibria in solution.

Manku and coworkers⁹⁵ studied the β -Resorcyaldehydeoxime in dioxane aqueous solution. The stability constants of the the lanthanide complexes, La^{+3} to Lu^{+3} except for Pm^{+3} were determined. The complexes with oximes have comparatively lower

stability constants than the corresponding ketone compounds. The stability constants of the complexes gradually increases with atomic number from La to Eu and from Gd to Yb.

Studies on Copper(II), Nickel(II), Cobalt(II), Manganese(II) and Zn(II) complexes with 2 hydroxyl naphthaloxime was carried by Ramesh⁹⁶. Thermal and solution stabilities of 2 hydroxy-1-naphthaloxime (H.L.) chelates of type ML_2 (M = Cu, Ni, Co, Mn, Zn) were measured, in 50 % vol/vol dioxane H_2O using Bjerrum-Calvin pH titration technique as modified by Irving and Rossotti.

The order of thermal stabilities is $Co > Ni > Mn > Cu > Zn$ and that for solution stabilities is $Cu > Ni > Co > Zn > Mn$ which is in agreement with the Irving Williams series.

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