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**Manish Kumar Jha**

Assistant Professor,

Department of Chemistry,

R.K. College, Madhubani,

LNMU, Darbhanga, Bihar,

India

## Study of stability constant and related thermodynamics

**Manish Kumar Jha**

### Abstract

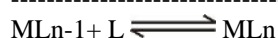
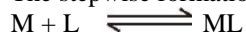
The term stability is used without qualification, it means that the complex exists and under suitable conditions it may be stored for long time. The term cannot be generalised for reaction of complex compounds. The main objective in this paper is to study the thermodynamic stability constant, the value of stability constants are determined at various ionic strength in the atmosphere of large excess of then the values of stability constants are plotted against ionic strength. Thus the thermodynamic stability constant is obtained by extrapolating stability constant curve to zero ionic strength.

**Keywords:** Thermodynamics, ionic strength, stability constants

### Introduction

Thermodynamic stability is a measure of the extent to which the complex will form from or will be transformed into another species under certain conditions, when the system has reached equilibrium. This type of stability is measured in terms of metal ligand bond energies, stability constants etc.

The stepwise formation of  $ML_n$  complex ion involve the successive equilibria,



The overall formation is  $M + nL \rightleftharpoons ML_n$  where M and L stand for metal ion and ligand respectively (Charges on M, L or on complex species formed are omitted for convenience). Each reaction is governed by equilibrium

$$K_1 = [ML] / [M] [L]$$

$$K_2 = [ML_2] / [ML] [L]$$

$$K_3 = [ML_3] / [ML_2] [L]$$

$$K_n = [ML_n] / [ML_{n-1}] [L]$$

Constants  $K_1, K_2, K_3, \dots, K_n$  are called stepwise stability constants. The overall stability constant is equal to the product of successive (i.e. stepwise) stability constants.

The stability constant is related with a system in equilibrium, it can be used in the calculation of thermodynamic functions of the system like  $\Delta G, \Delta H$  and  $\Delta S$ .

The stability constant is related with thermodynamic function as

$$\Delta G^\circ = -2.303 R T \log K \quad \dots\dots\dots (1)$$

We know that  $\Delta G = \Delta G^\circ$ . Thus  $\Delta G$  at a given temperature becomes known from equation (1). When  $\Delta G$  is negative, the reaction tends to go in the forward direction. Generally, the measurement of K are done at different temperature at the interval of  $10^\circ C$  and values of  $\Delta H$  are calculated with the help of the following equation.

$$\Delta H = 2.303 R T_1 T_2 (\log K_2 - \log K_1) / (T_2 - T_1) \quad \dots\dots\dots (2)$$

### Correspondence

**Manish Kumar Jha**

Assistant Professor,

Department of Chemistry,

R.K. College, Madhubani,

LNMU, Darbhanga, Bihar,

India

Then mean value of  $\Delta H$  is calculated. Knowing the values of  $\Delta G$  and  $\Delta H$  (mean) we can find out the value of  $\Delta S$  with the help of following relation.

$$\Delta G = \Delta H - T\Delta S \quad \text{..... (3)}$$

From equation (2) and (3)

$$2.303R \log K_1 = \Delta S_i = \frac{\Delta H_i}{T}$$

The values of thermodynamic functions like  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  have been determined by many workers [1-3]. But the determination of  $\Delta H$  by calorimetric method is very useful [4].  $\Delta H$  is the amount of heat either consumed or liberated per mole of product and is related to the strength of the ligand to metal bonds compared to that of the metal to a solvent bonds. Greater, the amount of heat evolved the most stable are the reaction products. The entropy change relates to the amount of order in the products compared to that in the reactants.

### Methodology

A fairly large number of methods for computing stability constant from Experimental data have been used by number of authors [5, 6, 7] some of the more generally applicable computational methods are as follows:-

(a) Methods of solving simultaneous equation derived from Bjerrum's formation [8].  $(\bar{n} - n) (L)^n \beta_n = 0$  where  $\beta_n = K_1 \cdot K_2 \dots K_n$  and  $\beta_0 = 1$  by definition. Experimental methods for the determination of stability constants, developed by Leden, Bjerrum and Frenaeus, have recently been discussed by Sullivan Hindman who pointed out that sets of equation of the type (4) can be solved for unique, nontrivial values of  $K_1 \cdot K_2$  and  $K_n$ , if the determinant.

$$\begin{vmatrix} (\bar{n}-1)[L_1] + & - & - & +(\bar{n}_N - N)(L_1)^N \\ (\bar{n}-1)[L_N] + & - & - & +(\bar{n}_N - N)(L_N)^N \end{vmatrix} \neq 0 \quad \text{..... (4)}$$

The expressed the condition that  $N$  in homogeneous equations of the type are needed for the evaluation of  $N$  stability constants in systems where the highest complex has the formula  $ML_N$

(b) **Successive approximation method:** From equation the following transformations were obtained.

$$K_1 = \frac{1}{[L]} \frac{\bar{n}}{[1 - \bar{n}] + [2 - \bar{n}]K_2[L]} \quad \text{..... (5)}$$

and

$$K_1 = \frac{1}{[L]} \frac{\bar{n} + (\bar{n} - 1)K_1[L]}{[2 - \bar{n}]K_1[L]} \quad \text{..... (6)}$$

Bjerrum applied these equations to define the approximate constants obtained by other methods.

(c) **Interpolation at half  $\bar{n}$  values.** For  $N = 2$  the following

relations may be derived from equation (5) and (6)

$$\log K_1 = p^L \frac{1}{2} + \log \left[ 2 / (1 + \sqrt{1 + 12K_2 / K_1}) \right] n = \frac{1}{2} \quad \text{..... (7)}$$

$$\log K_2 = p^L \frac{3}{2} + \log \left[ 2 / (1 + \sqrt{1 + 12K_2 / K_1}) \right] n = \frac{3}{2} \quad \text{..... (8)}$$

where  $p^L$  represents the free ligand exponent when  $\bar{n} = a$ , provided that  $K_{n-1} \gg K_n$ . Approximately equal amounts of  $ML_{n-1}$  and  $ML_{n+1}$  will be present in the solution when  $\bar{n} = n - \frac{1}{2}$  and the contributions of  $ML_{n-2}$  and  $ML_{n+1}$  may be neglected. Following Bjerrum we may write:

$$\log K_n = p^L n - \frac{1}{2} \quad \text{..... (9)}$$

Thus

$$\log K_1 = p^L \frac{1}{2} \quad \text{..... (10)}$$

$$\log K_2 = p^L \frac{3}{2} \quad \text{..... (11)}$$

unless  $K_1/K_2 \geq 10^{2.5}$ . This very commonly used approximation can introduce considerable error and in the case where  $\bar{N} = 2$  it has the disadvantage of using only two points on the formation curve. Kabadi *et al.* [9] have concluded the maximum permissible values of  $\log (K_1/K_2)$  for certain desired accuracies of half integral  $\log K_1$  values.

(d) **Interpolation at various  $n$  values** [10]: The  $\log K_1$  and  $\log K_2$  are given by the equation.

$$\log K_1 = p^L (1-d) + \log \left[ \left( \frac{1-d}{d} \right) \right] \quad \text{when } K_1 \gg K_2 \quad \text{..... (12)}$$

$$\log K_2 = p^L (1-d) + \log \left( \frac{1-d}{d} \right) \quad \text{..... (13)}$$

The use of these equations over the whole range of the formation curves ( $0 < d < 1$ ) is only justified if  $K_1/K_2 > 10^4$ . If  $K_1/K_2 < 10^4$ , the calculated values of stability constants show a drift which is more pronounced for the lower value of  $d$ .

(e) **Mid point slope method.** At the mid point of the formation curve where  $\bar{n} = 1$  (system  $n = 2$ )  $K_1 \cdot K_2 (L)^2 = 1$  or  $\log (K_1 K_2) = 2p^L - 1$  ..... (14)

The abscissa of the mid point will therefore give the value for the overall stability constant  $\beta_n$  whose precision is limited only by that of the experimental measurements. The common practices of evaluating individual values of  $K_1$  &  $K_2$  from the product  $K_1 \cdot K_2$  so obtained, together with equation  $\log K_n = p^L n - 1/2$  demands a full appreciation of the implicit approximations and does not make full use of the experimental data. Bjerrum defines spreading factor  $x = \sqrt{K_1/4K_2}$  and relates to the mid point slope 'D' of the

formation curve at the point  $\bar{n} = 1$  as

$$'D' = -2.303 / (1+x) \quad \dots\dots (15)$$

From the measured mid point slope 'D' the ratio  $K_1/K_2$  may be calculated and individual values of  $K_1$  and  $K_2$  obtained by using  $K_1/K_2$  values and relation  $\log (K_1K_2) = 2 P^L$ .

$$\text{For } N = 2, D \text{ is given by } D = \frac{-4.606}{2 + \sqrt{K_1K_2}}$$

and thus to introduce the concept of a spreading factor was not necessary. This method was only applicable where  $K_1/K_2$  lies between  $10^3$  and  $10^{-2}$  (as  $K_1/K_2 \rightarrow \infty, D \rightarrow 0$ ) and  $K_1/K_2 \rightarrow 0, D \rightarrow -2.303$  and it uses only a very small portion of the formation curve in the region of the mid point. Significant errors may be introduced both in plotting the "best" formation curve to pass through the experimental points and in measuring its mid point slope.

The choice of method for calculating stability constant depends on the complexity of the system which can often be judged from the shape of the formation curve.

Irving and Rossotti suggested recalculation of  $\bar{n}$  from experimental values of  $P^L$  and the calculated values of  $K_n$  using relation.

$$\bar{n}(\text{cal}) = \frac{K_1[L] + 2K_1K_2[L]^2}{T + K_1[L] + K_1K_2[L]^2} \quad \dots\dots (16)$$

Standard deviation is given by

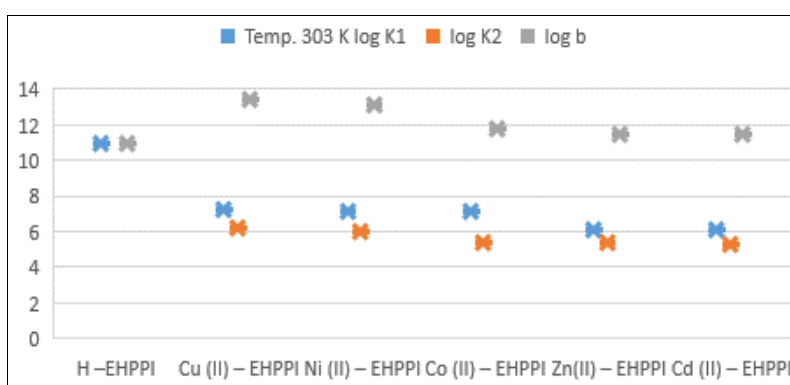
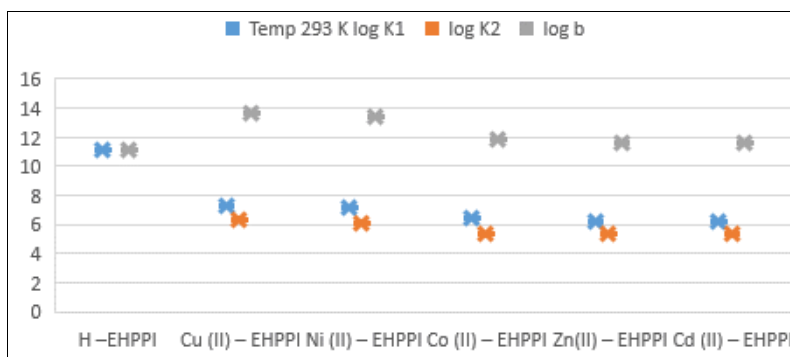
$$\sigma = [(\Delta \bar{n})^2 / \text{no. of observation}]^{1/2}$$

Where  $\Delta \bar{n} = \bar{n}_{\text{exp}} - \bar{n}_{\text{cal}}$ .

It is determined to check the validity of the constants. The most representative values of  $\log K_1$  and  $\log K_2$ , are given in table 1.

**Table 1:** Overall stability constants of complex compounds of various metals at 293 and 303 K temperature respectively. Ligand – EHPPI  $\mu^0 = 0.10$  (M)  $\text{KNO}_3$  Water – dioxane medium (V/V) = 50:50

System	Temp 293 K			Temp. 303 K		
	log $K_1$	log $K_2$	log $\beta$	log $K_1$	log $K_2$	log $\beta$
H – EHPPI	11.10		11.10	11.00		11.00
Cu (II) – EHPPI	7.31	6.31	13.62	7.21	6.21	13.42
Ni (II) – EHPPI	7.22	6.14	13.36	7.12	6.03	13.15
Co (II) – EHPPI	6.49	5.42	11.91	7.12	5.34	11.75
Zn(II) – EHPPI	6.24	5.42	11.66	6.14	5.34	11.48
Cd (II) – EHPPI	6.21	5.39	11.60	6.12	5.31	11.43



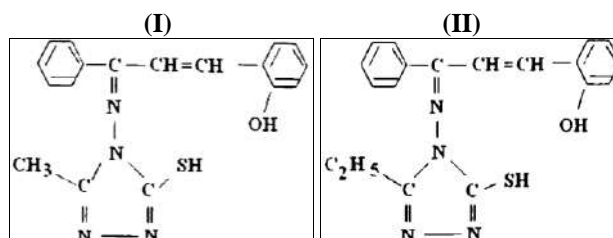
### Thermodynamic parameters

The values of the change in standard free energy ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H$ ) and entropy ( $\Delta S$ ) have been calculated at two temperature and at ionic strength 0.10 (M)  $\text{KNO}_3$  with the help of standard expressions.<sup>[11-13]</sup>

### Proton ligand stability constant

The ligands have one hydroxyl group, one thiohydroxy group and one imino group.

### Structure of ligands



The stability of the chelates is greatly affected by the electron density around the imino nitrogen ( $-C=N-$ ). Higher the electron density around the nitrogen atom greater is the metal ligand bond. The stability constant of chelates with N-(3'-methyl-5'-mercapto-1',2',4'-triazolyl)-3-(2''-hydroxy phenyl)-1-phenyl prop-2-en-1-imine is greater than the corresponding values of the stability constants in the case of N-(3'-methyl-5'-mercapto-1',2',4'-triazolyl)-3-(2''-hydroxy phenyl)-1-phenyl prop-2-en-1-imine.

Metal ligand formation curve for all the metal ions in the case of both ligands show that function n is attained its maximum not beyond 2. It indicates the formation 1:2 chelates of type  $ML_2$

The values of the first stepwise stability constant ( $\log K_1$ ) of Cu(II) is relatively higher than that of other metal ions in the case of both the ligands. Thus it was observed that Cu(II) chelates are relatively more stable than the other metal chelates.

Similar observations have been made by other workers. The higher stability of Cu(II) chelates might be due to the square planar configuration commonly observed for Cu(II) chelates.

The behaviour of the other metal ion chelates with both the ligand were similar to Cu(II) chelates.

The difference between the successive stepwise stability constant is large. This suggests that the formation of ML and  $ML_2$  chelates take place independently<sup>[14]</sup>.

#### Variation of stability constant with the nature of metal ions.

This may be understood by comparing the stability constants of the chelates formed by the series of metal ions with the given ligand irrespective of its nature. The order of the stability constant of the chelates of bivalent metal ions of the first transition series are usually in natural order sometimes called Irving William order as



A theoretical justification of the order of stability constants follows from the consideration of the reciprocal of the ionic radii and second ionization enthalpy of the metal concerned.

In the present investigation the order of stability constant is



The same order has been observed by several workers

Complexes show a regular increase of stability constant from  $La^{III}$  to  $Eu^{III}$  with a discontinuity at  $Gd^{III}$  which is commonly known as Gadolinium break. After  $Gd^{III}$  stability constant increases up to  $Dy^{III}$  and then decreases for  $Ho^{III}$ . This shows occasional maxima and minima after gadolinium break.

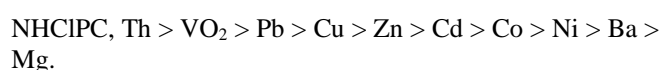
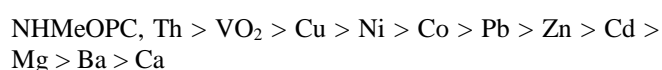
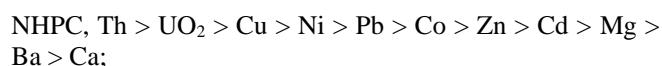
The  $\log K_1$  and  $\log K_2$  values decrease with the increase in temperature indicating that the high temperature does not favour the formation of stable complexes.

M. B. Halli *et al.*<sup>[15]</sup> determined the stability constant of 1:1 and 1:2 metal complexes formed between  $Th^{IV}$ ,  $UO_2^{II}$ ,  $Cu^{II}$ ,  $Pb^{II}$ ,  $Co^{II}$ ,  $Cd^{II}$ ,  $Ba^{II}$ ,  $Ca^{II}$  and  $Mg^{II}$  metal ions with Schiff bases NHPC, NHMPCS, NHMCOPC and NHCIPC by potentiometric titration technique. Calvin – Bierrum pH

metric titration were used to calculate the  $PK_{III}^H$ ,  $\log K_{ML}^M$ ; values in 60:40% (v/v) alcohol water medium at  $30 \pm 0.1$  °C. Temperature and at constant ionic strength of 0.1 M  $NaClO_4$ .

#### Conclusion

In this study they observed that  $\log K_1 > \log K_2$ . This may be due to interaction of second ligand molecules is weaker than the first one. In the present study, they observe the stability order for different ligands and metal ions as:



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