**Stability constants of Metal Complexes**

# THEORETICAL

* + 1. **Stability of co-ordination compounds**

The stability of compounds means in a most general sense, the compounds exist under suitable conditions may be stored for a long period of time. However when the formation of complexes in solution is studied, two types of stabilities, thermodynamic stability and kinetic stability are considered.

In the language of thermodynamics, the equilibrium constants of a reaction are the measure of the heat released in the reaction and entropy change during reaction. The greater amount of heat evolved in the reaction, the most stable are the reaction products. Secondly, greater the increase in entropy during the reaction, greater is the stability of products. The kinetic stability of complexes refers to the sped with which transformation leading to the attainment of equilibrium will occur. Here we are mainly concerned with the thermodynamic stability of the complex compound.

# Determination of stability constant of complexes

In complexes the term stability is employed in two ways (1) thermodynamic stability and kinetic stability. Thermodynamic stability deals with the bond energy, stability constant and redox potential. Kinetic stability deals with the rate of the reaction, mechanism of reaction, formation of intermediate complexes, and activation for the process etc.

The thermodynamic stability of a species is a measure of the extent to which the species will form or be transformed into other species under certain conditions, when the system has reached equilibrium.

Let metal ion (Mn+) combines with ligand (L) to form complex MLn, then

M + nL  MLn

MLn 

K  MLn

Thus by knowing the value of [M], [L] and [MLn] the value of K, stability constant of the complex MLn, can be computed.

The knowledge of stability constant is needed for computing quantitatively the concentration of free metal ion, ligand and any of its complexes formed in the system, under different conditions of pH. These data are extensively employed in analytical chemistry, stereochemistry, and biochemistry and in the technology of non ferrous and rare metals, solvent extraction, ion exchange etc.

There are so many techniques for the computation of stability constants. Here only two methods are explained known as pH-metric method and spectrophotometric method.

# Determination of stepwise stability constants by pH-metric method

As complexing processes are considered as occurring by a series of stages thus

it is possible to express the formation (stability) constants referring specially to the addition of ligands in a stepwise manner as follows:

M + L  ML

K  ML

1 ML

 [ML] = K1[M][L] (a)

ML + L  ML

K  ML2 

 [ML ] = K [ML][L] (b)

2 2 MLL 2 2

ML2 + L  ML3

ML 

ML2 L

K 3   3

 [ML3] = K3[ML2][L] (c)

…………….. ………………

………………. ………………

………………. ………………

ML + L  ML

K  MLn 

 [ML ] = [ML

][L] (n)

n-1 n

n ML

n1

L

n n-1

The constants K1, K2, K3,………Kn are called the stepwise stability constants. The stepwise constants are related to the overall stability constant by the simple related:

1 = K1

2 = K1.K2

3 = K1.K2.K3

4 = K1.K2.K3.K4

Therefore n = K1.K2.K3. …… Kn (1)

A large number of techniques of great diversity are now being employed for the determination of stepwise stability constants. The most generally utilised and probably the most accurate and reliable method for the determination of stability constant is based on the potentiometric measurement of hydrogen ion concentration. This depends on the fact that pH of the solution is directly affected by complex formation, which is accompanied by the displacement of a proton from the acidic ligand. The magnitude of the observed pH change may be employed to determine the stability constant of the metal complexes by Bjerrum’s method, Calvin and Wilson’s method.

Out of these techniques Bjerrum’s method is better as used by Calvin and

Wilson. Bjerrum suggested certain formation functions such as functions are employed to calculate the stepwise stability constans.

n A , n , pL. These

The formation function ( n ) of a metal ligand (M, L) system can be defined as:

n  Total concentration of L bound to M Total concentration of M

n  [ML]  2[ML2 ]  3[ML3 ]  .......

[M]  [ML]  [ML2 ]  [ML3 ]  .....

(2)

Substitute the values of eq. (a), (b), (c) and (n) in (2)

n  K1[M][L]  2K2 [ML][L]  2K3[ML2 ][L]  .......

[M]  K1[M][L]  K2 [ML][L]  K3[ML2 ][L]  .......

(3)

Now substitute the value of eq. (a) and (b) in (3)

K [M][L]  2K K [M][L]2  3K K [ML][L]2  ........

n 1 1 2 2 3

(4)

[M]  K [M][L]  K K [M][L]2  K K [ML][L]2  ......

1 1 2 2 3

Now the value of eq. (a) substitute in (4)

K [M][L]  2K K [M][L]2  3K K K [M][L]3  ........

n 1 1 2 1 2 3

(5)

[M]  K [M][L]  K K [M][L]2  K K K [M][L]3  ......

1 1 2 1 2 3

Now taking [M] common form eq. (5)

K [L]  2K K [L]2  3K K K [L]3  ........

n  1 1 2 1 2 3

1  K [L]  K K [L]2  K K K [L]3  ......

(6)

1 1 2 1 2 3

Now according to eq. (1) n = K1.K2.K3….Kn,  b1 = K1, 2 = K1.K2, 3 = K1.K2.K3, and so on, substitute in the (6)

[L]  2[L]2  3[L]3  ........

n  1  [L]  [L]2  [L]3  ......

n

i [L]

i

i

n  i0

1   [L]i

n

i

(7)

i0

n

n  i(n 1) [L]

i (8)

i

i0

In this same way for ligand-proton (L, H) system formation function

defined as

n A is

n A 

Total concentrat ion of H bound to L Total concentrat ion of L not bound to M

n A 

[HL ]  2[H 2 L]  3[H 3 L]  ......

[L]  [HL ]  [H 2 L]  [H 3 L]  .....

KH [H][L]  2KH KH [H] 2 [L]  3KH KH KH [H]3 [L]  .....

n A 1 1 2 1 2 3

[L]  KH [H][L]  KH KH [H] 2 [L]  KH KH KH [H]3 [L]  .......

1 1 2 1 2 3

KH [H]  2KH KH [H] 2  3KH KH KH [H]3  .....

n A 1 1 2 1 2 3

1  KH [H]  KH KH [H] 2  KH KH KH [H]3  .......

1 1 2 1 2 3

H [H]  2H [H] 2  3H [H]3  .....

n A 1 2 3

1  H [H]  H [H] 2  H [H]3  .......

1 2 3

n

i [H]

H i

i

n A  i0

H [H] i

n

i

(9)

i0

Now formation function n is

n  TCL  Concentration of L not bound to M

TCM

Where TCL = Total concentration of ligand L and TCM = Total concentration of metal M

 n TCM = TCL - Concentration of L not bound to M

 Concentration of L not bound to M = TCL - n TCM (10) From the value of n A ,

Total concentration of L not bound to M = [L]1  H[ H]  H[ H]2  H[ H]3 

1 2 3

n

M  [L] [H]

H i (11)

i

Substitute the value of eq. (11) in (10)

i0

n

 [L] [H] = TCL - n TCM

H i

i

i0

 [L]  TCL  nTCM

H[H]i

n

i

i0

n

 [H]

H i

i

 [L]1  i0

TCL  nTCM

(12)

Taking log in eq. (12)

log[L]1  log

n

H i

 [H]

i

i0 , log[L]-1 = pL

10 T  nT

CL CM

n

 [H]

H i

i

 pL  log10 i0

TCL  nTCM

(13)

Calvin and Wilson have demonstrated that pH measurements made during titrations with alkali solution of ligand in the presence and absence of metal ion could

be employed to calculate the formation functions

n A , n

and pL and stability

constants can be computed. Irving and Rossotti**[1]**, titrated following solutions against standard sodium hydroxide solution N keeping total volume V constant.

1. X mL mineral acid (HClO4) E
2. A + X1 mL ligand
3. B + X2 mL metal ion

On plotting the pH value of the solution with the addition of sodium hydroxide solution three graphs are achieved.

The formation functions eqations:

n A , n

and pL can be computed from the following

n  Y  (V1  V2 )( N   E )

A (V  V )T

(14)

1 CL

n  ( V3  V2 )( N   E )

(15)

( V  V1 )(n A )(T  )

CM

1 *K H* [*H* ]  *K H K H* [*H* ]2 *V*   *V*

*pL*  log

1 1 2 3

10

*T*



*CL*

*n*

*H*

* *nTCM* *V*

1

*pL*  log10

 **

*n*0

*n*

*T*



(*anti* log *B*) *n*

* + *nT*

*V*   *V*

3

*V* 

(16)

*CL* *CM* 

Where,

Y = number of dissociable protons

V1, V2 and V3 = volume of alkali employed bring the solution 1, 2 and 3 to same pH value

TCL = total concentration of the ligand TCM = total concentration of metal ion

By the knowledge of n A , n , pH and pL protonation and stepwise stability

constants can be computed by different methods such as:

# Determination of stoichiometric stability constant

A fairly large number of methods for computing stability constants from experimental data have been used by number of authors**[2-4]** Some of the more generally applicable Computational methods are as follows :

# Least square method[5]

From eq. (7)

n

i [L]

i

i

n  i0

1   [L]i

n

i

i0

For i = 1; n 

K1[L] 1  K1[L]

or K1 

n

(1  n)[L]

(17)

or log K1

 log

n

1  n

* pL

(18)

K [L]  2K K [L]2

for i = 2, n  2 1 2

1  K1[L]  K1K2 [L]

or n

(n  1)[L]

 (2  n)[L]K1K2 K

(n 1) 1

(19)

or K2

 1 [L]

 n  (n 1)K1[L]

(2  n)K1[L]

or log K2

 pL  log n  (n 1)K1[L]

(2  n)K1[L]

(20)

The term ( n -1)K1[L] is negligible when n > 0.5

Hence, log K2

 2pL  log

n

(2  n)K1

(21)

The equations (18) and (20) are straight line equations. Thus by plotting different values of n and [L] straight line will be achieved. Thus the values of K1 and K2 can be computed.

# Half integral method[2] / Interplotation at half n values[6]

By putting the value n = 0.5 in equation (18) we obtain logK1 = pL

Similarly by putting the value n = 1.5 in the equation (20) we obtain logK2 = pL

It means if we plot a graph between n and pL then the corresponding values of pL at n equal to 0.5 and 1.5 gives log K1 and log K2 respectively.

In the same manner if

KH , log KH etc. can be computed.

nH is plotted against pH the values of log

1 2

# Linear plot method[2]

Eq. (6) for N = 2 system may be written in form

yp1 + xp2 = 1 (22)

Where x and y are function of n and [L] and the parameter p1 and p2 are related to the stability constants. The six possible transformation of eq. (6) are



1  *n*  [*L*]  **



1

*n*



 2  *n*  [*L*]2  **  1



2

*n*

(23)



*n* 1  1



 [*L*] **



 (*n* 2)  [*L*]  **



2

**1  1

(24)

(1  *n*) 2 1  *n*



*n* 1





**

(2  *n*)[*L*]2 2



(*n* 1)





(2  *n*)[*L*]

 **1

** 2  1

(25)

The other three transformations are obtained mearly be interchanging the values of x and y in the above equation. Eq. (22) can be rearranged as

*y*   *p*2 *x*  1

*p*1 *p*1

(26)

Thus if y is plotted against x, a straight line of slope

* *p*2 *p*1 and intercept

1 *p* should result. Such plots had been used by several authors**[7,8]**. They were quite convenient in cases where the measurements spread over a rather narrow range of free ligand concentration.

1

# Point wise calculation method[9]

Hearon and Gilbert have suggested the following methods for point wise calculation of K1 and K2.

Here 2 = K1K2 is obtained graphically from a number of independent experiments. K1 is then calculated at several points using eq. (6) in the form of

(2  n).K K [L]2  n

K1 1 2

(n 1).[L]

And pointwise calculation of K2 is made using the relation.

(27)

K1K 2

 K1[L]  n1  K1[L]

n  2 [L]

 

(28)

# 3.1.4 Thermodynamic constants

The stability constants of the metal complexes are related to thermodynamic properties such as free energy charge (G), enthalpy (H) and entropy change (S). These values can be computed by usual equations:

G = -2.303 RT log K (29)

H  2.303R

T2T1 T2  T1

log K 2

K1

(30)

S  (H  G)

T

(31)

Where, K2 and K1 are the stability constants at the absolute temperatures T2 and T1 respectively.

# Limitations to applicability of computation methods

The assumptions made in deriving the formation function viz. absence of metal ion hydrolysis, poly nuclear complex formation, anion complexing etc. sets limits to the applicability of computation methods described above, in addition to those arising from the particular conditions under which the methods hold. Accordingly, the methods for detecting the presence of these neglected factors and also correcting for them, if possible, have been suggested by some workers.

Irvin and rossotti**[6]** associate the absence of perfect symmetry about the mid point of the formation curve with the presence of poly nuclear species; formation of several types of complexes when ligands have several coordination sites and with incomplete formation of one of the complexes. The symmetry of the formation curve, therefore, can be of great value in revealing such factors.

Rossotti and Rossotti**[7]** have suggested that n would be independent of TCM in absence of polynuclear complex formation. Where only one polynuclear species is formed, determination of n at different values of TCM and then extra potation to low values of TCM has been recommended.

Mathematical methods of computing mononuclear stability constant, even when polynuclear species are present, have been suggested**[10,11]** but these seem to have been applied only to complexes arising in metal ion hydrolysis.

Metal ion hydrolysis, if it occurs in the pH range of complex formation, would result in higher than the true values of stability constants. Fraiser et al.**[12]** Studied hydrolysis of several bivalent metal ions in dioxane-water and have shown that, for these ions, computations made in the pH range 3 – 6 are least deviated by metal ion hydrolysis. Use of high ligand-metal ratio has been recommended to depress the pH range of complex formation if necessary.

We have studied the proton ligand stability constants and metal ligand stability constants at 30  0.2C temperatures for synthesized ligands and metal complexes by the Calvin Bjerrum titration technique adopted by Irvin and Rossotti.

1. Interpolation at half n values
2. Least square method
3. Linear plot method
4. Point wise calculation method