

MSc II SEM

Paper Inorganic Chemistry

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Unit -IV

Stability constant :

Stability of Metal complexes:

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.

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.

(2) 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.

Methods for the Determination of stability constant ,

1. pH-metric method

2. Spectrophotometric method.

Determination of stepwise stability constants by pH-metric method

As complexing processes are coered as occurring 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:





The constants $K_1, K_2, K_3, \dots, K_n$ are called the stepwise stability constants. The stepwise constants are related to the overall stability constant by the simple relation:

$$\beta_1 = K_1 \quad \beta_2 = K_1.K_2 \quad \beta_3 = K_1.K_2.K_3 \quad \beta_4 = K_1.K_2.K_3.K_4 \quad \dots$$

therefore $\beta_n = K_1.K_2.K_3. \dots. K_n$ (1)

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 ($HClO_4$) E°
2. $A + X_1$ mL ligand
3. $B + X_2$ 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 \bar{n}_A, \bar{n} and pL can be computed from the following equations:

$$\bar{n}_A = Y = \frac{(V_1 - V_2)(N^\circ - E^\circ)}{(V^\circ + V_1)T_{Cl^-}} \quad (14)$$

$$\bar{n} = \frac{(V_1 - V_2)(N^\circ + E^\circ)}{(V^\circ + V_1)(\bar{n}_A)(T_{CM^-})} \quad (15)$$

$$pL = \log_{10} \frac{1 + K_1^H [H] + K_1^H K_2^H [H]^2 + \dots}{T_{CL} - \bar{n}T_{CM}} \times \frac{V^* + V_3}{V^*}$$

$$pL = \log_{10} \frac{\sum_{n=0}^{\infty} \beta_n^H \cdot \frac{1}{(\text{anti log } B)^n}}{T_{CL} - \bar{n}T_{CM}} \times \frac{V^* + V_3}{V^*} \quad (16)$$

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

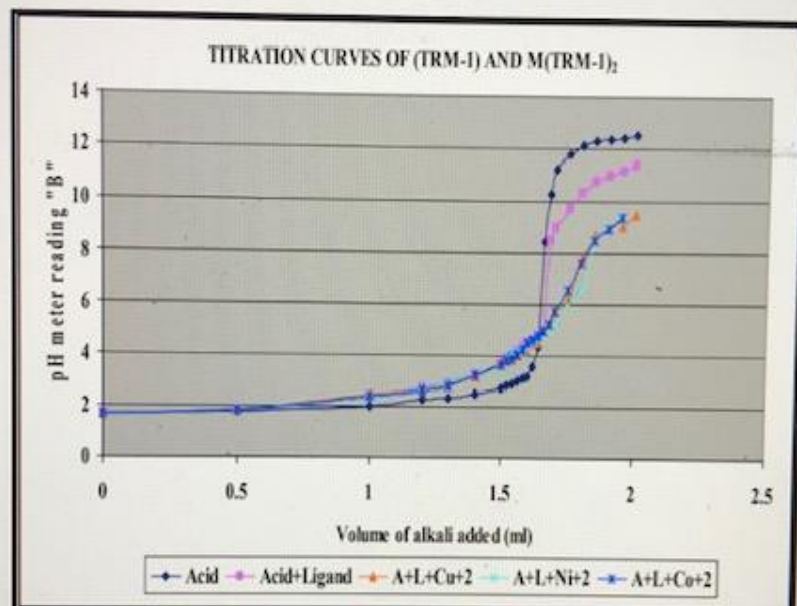
T_{CL} = total concentration of the ligand

T_{CM} = total concentration of metal ion

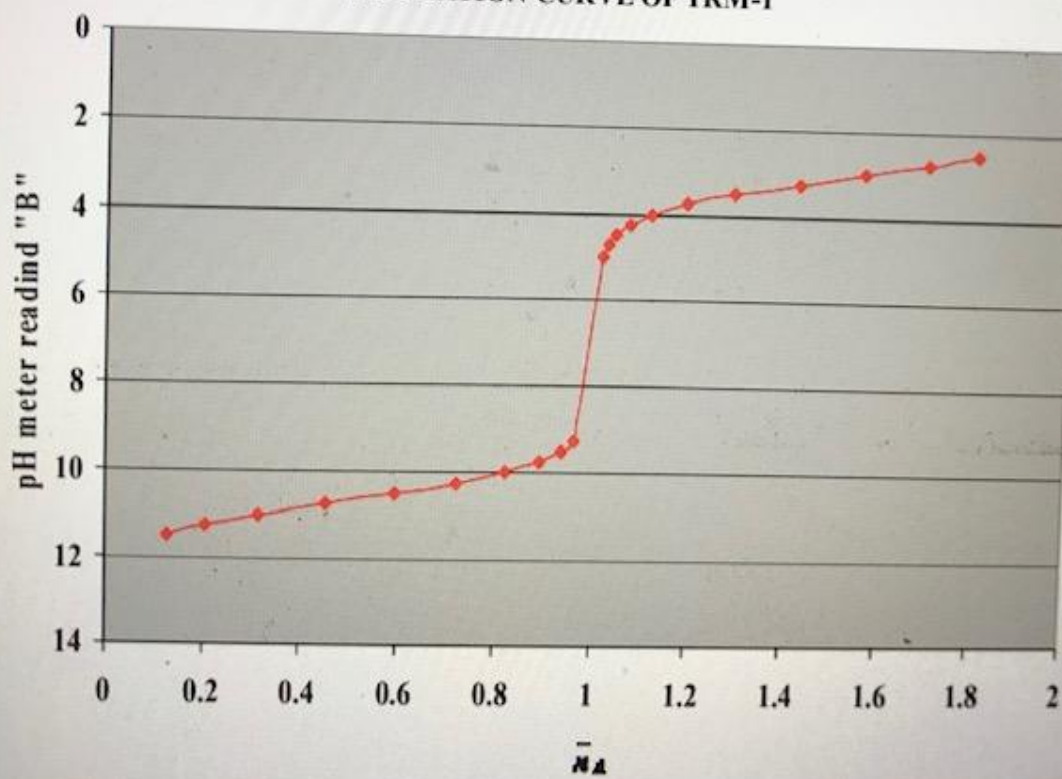
By the knowledge of \bar{n}_A , \bar{n} , pH and pL protonation and stepwise stability constants can be computed by different methods such as:

3.1.4 Determination of stoichiometric stability constant

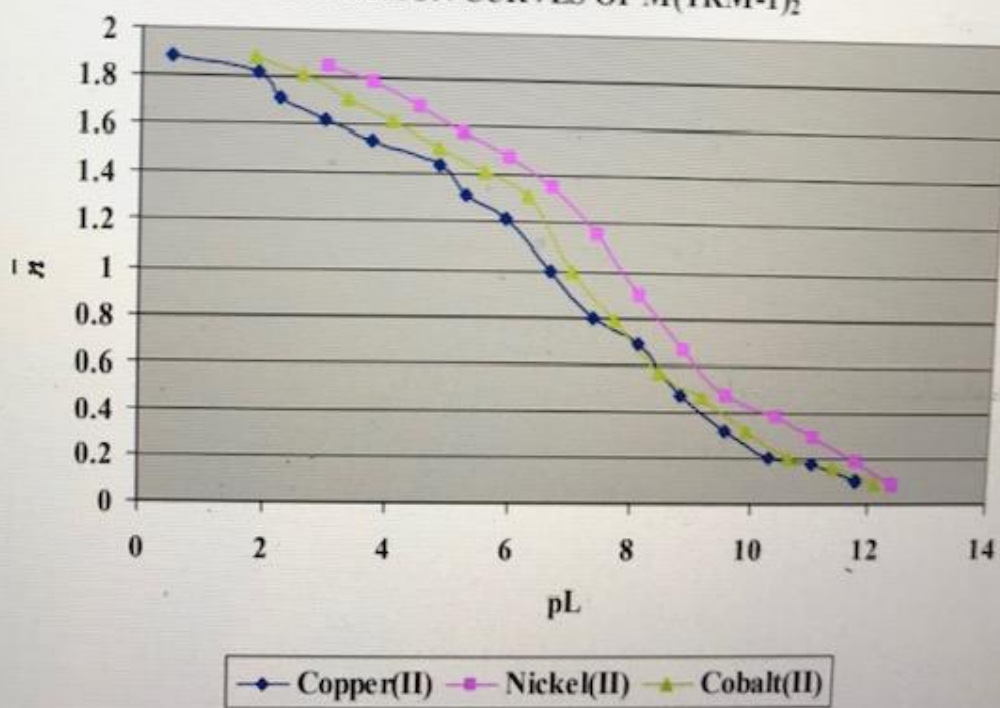
A fairly large number of methods for computing stability constants from experimental data have been used by number of authors^[2-4] Some of the more generally applicable Computational methods are as follows :



FORMATION CURVE OF TRM-1



FORMATION CURVES OF $M(\text{TRM-1})_2$



3.1.4 Thermodynamic constants

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

$$\Delta G = -2.303 RT \log K \quad (29)$$

$$\Delta H = 2.303R \frac{T_2 T_1}{T_2 - T_1} \log \frac{K_2}{K_1} \quad (30)$$

$$\Delta S = \frac{(\Delta H - \Delta G)}{T} \quad (31)$$

Where, K_2 and K_1 are the stability constants at the absolute temperatures T_2 and T_1 respectively.

3.1.5 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,

Where,

Y = number of dissociable protons

V_1, V_2 and V_3 = volume of alkali employed bring the solution 1, 2 and 3 to same pH value

T_{CL} = total concentration of the ligand

T_{CM} = total concentration of metal ion

By the knowledge of \bar{n}_A, \bar{n}, pH and pL protonation and stepwise stability constants can be computed by different methods such as: