By PH Method for Calculation of Formation Constant

Potentiometric Method or Bjerrum Method

Bjerrum determined the formation constant of metal complexes and chelate compounds in aqueous solutions. Bjerrum described the stepwise formation of series of metal complexes of the type ML, ML_2 ---- ML_n. Which is defined by the following equation.

$$M + L \underset{}{\overset{K_1}{\rightleftharpoons}} ML$$

$$\therefore K_1 = \frac{[ML]}{[M][L]} \quad \text{—— (i)}$$

$$ML + L \overset{K_2}{\rightleftharpoons} ML_2$$

$$\therefore K_2 = \frac{[ML_2]}{[ML][L]} \quad \text{—— (ii)}$$

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$$ML_{(n-1)} + L \rightleftharpoons ML_n$$

$$\therefore K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \quad \text{—— (iii)}$$

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

Now eqn (i) can be written as $[ML] = K_1[M][L]$ —— (iv)

and eq (ii) can be written as $[ML_2] = K_2[ML][L]$ —— (v)

On substituting the value of [ML] from (iv) to (v)

we have, $[ML_2] = K_1K_2[M][L][L]$

$$[ML_2] = K_1K_2[M][L^2] \quad \text{—— (vi)}$$

Similarly Equation (iii) can be written as

$$[ML_n] = K_1 \cdot K_2 \cdot K_3 \cdots K_n [M][L^n] \quad \text{—— (vii)}$$

Bjerrum introduced a function '$\bar{n}$' which is defined as the average number of ligand molecule bonded per mole of metal. It may be mathematically expressed as,

$$\bar{n} = \frac{1[ML] + 2[ML_2] + 3[ML_3] + \cdots + n[ML_n]}{[M] + [ML] + [ML_2] + [ML_3] + \cdots + [ML_n]} \quad \text{—— (A)}$$

On substituting the value of [ML], $[ML_2]$ ------ and $[ML_n]$ from above eqn.

$$\bar{n} = \frac{K_1[M][L] + 2K_1K_2[M]L^2 + \cdots + n(K_1 \cdot K_2 \cdot K_3 \cdots K_n)[M][L^n]}{[M] + K_1[M][L] + K_1K_2[M][L^2] + \cdots + (K_1 \cdot K_2 \cdots K_n)[M][L^n]}$$

Now cancelling M through out, we get

$$\bar{n} = \frac{K_1[L] + 2K_1K_2[L^2] + \cdots + n(K_1 \cdot K_2 \cdot K_3 \cdots K_n)[L^n]}{1 + K_1L + K_1K_2[L^2] + \cdots + (K_1 \cdot K_2 \cdot K_3 \cdots K_n)[L^n]} \quad \text{(B)}$$

This equation (B) is called Bjerrum formation function.

continues...

If the Concentration of Unbonded Ligand [X] Can be Calculated experimentally, then $\bar{n}$ Can be Calculated from the equation

$$\bar{n} = \frac{L_t - L}{M_t}$$

Where L_t and M_t denotes the total Concentration of Ligand and Metal.

Now Solution of equation (B) for the known values of $\bar{n}$ and Corresponding [L] values, provides the value of the formation Constants i.e., $K_1, K_2, \cdots, K_n$.

Now we illustrate Bjerrum method to Calculating formation Constant for Complex formed by interacting of $CuSO_4$ and 5 sulphosalicylic acid (H_3L)

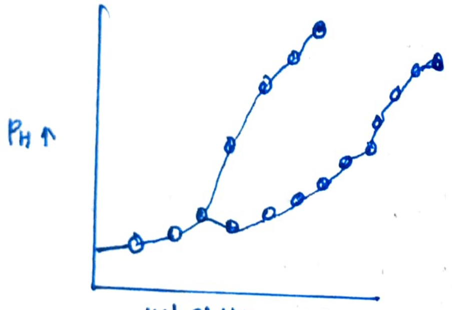
Procedure:—

100 ml of each Solution ($CuSO_4$ & 5 sulphosalicylic acid) is titrated against Standard NaOH Solution at 25°C and the PH is noted after addition of titrant base (NaOH).

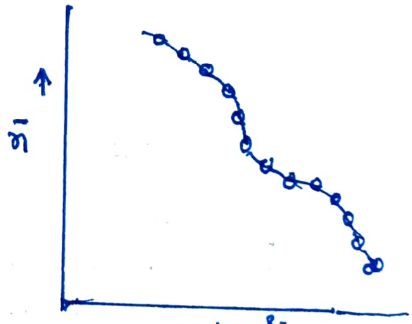
Now PH is plotted against NaOH and the point of inflexion of the Curve Corresponds to the mixed Solution.

Again the Horizontal distance between the Curve is noted. In this way we find the value of $\bar{n}$.

Now $\bar{n}$ is plotted against $-\log L^{3-}$ (which is determined from the relation at various PH) in the formation Curve.



Potentiometric titration of 5-sulphosalicylic acid (H_3L) in the presence of $CuSO_4$



Formation Curve

Now,

$$L^{3-} = \frac{[HL_3]_{Total} - [CuL^-] - 2\,[CuL_2^{4-}]}{\frac{[H^+]^2}{K_{II} \cdot K_{III}} + \frac{H^+}{K_{III}} + 1}$$

where K_{II} and K_{III} are the 2nd and 3rd dissociation Constants of HL_3 which are $K_{II} = 3.23 \times 10^{-3}$ & $K_{III} = 1.81 \times 10^{-12}$

The value of K_1 and K_2 found from the formation Curve, at $\bar{n} = 0.5$ and $\bar{n} = 1.5$, $K_1 = 2.2 \times 10^{9}$ & $K_2 = 6.3 \times 10^{6}$ respectively.

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