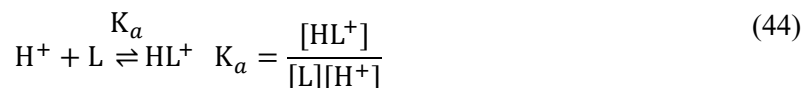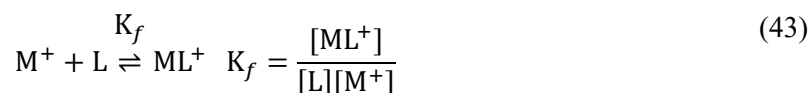## ❖ Determination of Binary Formation Constants by pH-metry and Spectrophotometry

The stability constants for metal complexes can be calculated using various techniques but the two of most popular experimental methods are pH-metry and spectrophotometric analysis owing to their simple setup and good accuracy.

➢ *pH-metric Method*

The alteration of hydronium ion concentration during the complex formation can be used to calculate the stability constant. Actually, H^+ ions are in direct competition with metal ions for the association with ligand species present in the solution.

Consider the ligand displacement reaction in which a metal ion along with some weak acid is added to ligand solution.

$$M^+ + L \overset{K_f}{\rightleftharpoons} ML^+ \quad K_f = \frac{[ML^+]}{[L][M^+]} \tag{43}$$

$$H^+ + L \overset{K_a}{\rightleftharpoons} HL^+ \quad K_a = \frac{[HL^+]}{[L][H^+]} \tag{44}$$

Where K_f and K_a are formation constants for the metal complex and acid association constant, respectively. Now let C_M, C_L and C_H as the molar concentration for metal ion, ligand and acid, we have

$$C_H = [H^+] + [HL^+] \tag{45}$$

$$C_L = [L] + [ML^+] + [HL^+] \tag{46}$$

$$C_M = [M^+] + [ML^+] \tag{47}$$

The above three equations can be solved as follows, From equation (47):

$$[M^+] = C_M - [ML^+] \tag{48}$$

The total ligand concentration can be calculated by using equation (44) and putting the value of $[HL^+]$ from equation (45) as:

$$[L] = \frac{C_H - [H^+]}{K_a[H^+]} \tag{49}$$

Now subtracting equation (45) from equation (46) and putting the value of [L] from equation (49), we get:

$$[ML^+] = C_L - C_H + [H^+] - \frac{C_H - [H^+]}{K_a[H^+]} \tag{50}$$

Thus, using the values of [M], [L] and $[ML^+]$ from equation (48), (49) and (50) in equation (43); we would be to calculate the formation constant by knowing C_M, C_L, C_H, K_a and the concentration of $[H^+]$ ion which is generally given the by the pH-meter. It has also been observed that the accuracy of the formation constant is high if the value to K_f is within the range of 10^5 times than that of K_a.

> *Spectrophotometric Method*

1. Conventional Spectrophotometric Method: The change in the absorbance during the complex formation can be used to find out the stability constant very easily. According to Beer-Lambert law:

$$A = \varepsilon.c.l \tag{51}$$

where A is the absorbance, l is the optical path length, ε is a molar extinction coefficient and c is a concentration of the solution. Thus, by measuring the absorbance at a particular wavelength for a metal complex solution of known path length and known concentration; the value of the molar extinction coefficient can be calculated. Consider the general metal-ligand equilibria:

$$M + L \overset{K_f}{\rightleftharpoons} ML \quad K_f = \frac{[ML]}{[M][L]} \tag{52}$$

Now let C_M and C_L as the molar concentration for metal ion and ligand, respectively. We have

$$C_M = [M] + [ML] \tag{53}$$

$$C_L = [L] + [ML] \tag{54}$$

Now if we measure the absorbance of ML complex at a known path length and molar absorption coefficient; its concentration can be given by using equation (51) as:

$$[ML] = c = \frac{A}{\varepsilon l} \tag{55}$$

Putting the value of equation (55) in equation (53) and (54), we get:

$$[M] = M_L - [ML] = M_L - \frac{A}{\varepsilon l} \tag{56}$$

$$[L] = C_L - [ML] = C_L - \frac{A}{\varepsilon l} \tag{57}$$

Here and now, we can calculate the value of formation constant (K_f) by put the values of [ML], [M] and [L] from equation (55), (56) and (57) in equation (52).

For example, the above method can successfully be used to calculate the stability constant for the following reaction:

$$Fe^{3+} + NCS^- \overset{K_f}{\rightleftharpoons} [Fe(NCS)]^{2+}; \quad K_f = \frac{[[Fe(NCS)]^{2+}]}{[Fe^{3+}][NCS^-]} \tag{58}$$
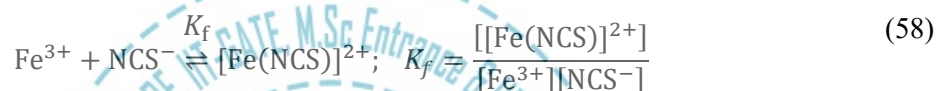
Ferric ion and thiocynate ions are colorless in aqueous solution but their metal-ligand equilibria generate instance blood-red color and its λ_{max} is at 450 nm. In order to find the value of ε, we will have to measure the absorbance of $[Fe(H_2O)_5(NCS)]^{2+}$ complex prepared by dissolving Fe^{3+} ions in excess of NCS^- ligand so that all the ferric ions convert into the complex. Once the value of ε for $[Fe(H_2O)_5(NCS)]^{2+}$ is known, its equilibrium concentrations can easily be obtained by recording the absorption spectra. Then, using these equilibrium concentrations in equation (58) will give you the value of formation constant.

Figure 22. (a) Fe^{3+} ion in water (b) $[Fe(SCN)]^{2+}$ ion in water.

2. Method of continuous variation or Job's method: This method is the variation of the spectroscopic method and is very useful in determining the composition of the metal complexes. This method is used when only one complex is formed under the given experimental conditions and the volume of the solution remains constant. Consider the metal-ligand equilibria:

$$M + nL \overset{K_f}{\rightleftharpoons} ML_n \quad K_f = \frac{[ML_n]}{[M][L]^n} \tag{59}$$
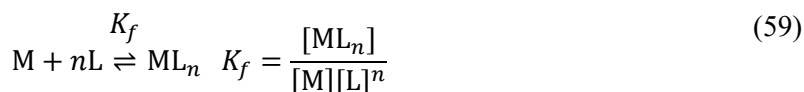
Prepare ten metal-ligand solutions with varying concentrations as given below.

Metal ion (*ml*)	0	1	2	3	4	5	6	7	8	9
Ligand (*ml*)	10	9	8	7	6	5	3	2	1	0

Now, let C_M and C_L as the molar concentration for metal ion and ligand, respectively. we have:

$$C_M + C_L = C \tag{60}$$

$$x = \frac{C_L}{C} \tag{61}$$

$$1 - x = \frac{C_M}{C} \tag{62}$$

Where C is a constant; while x and $(1-x)$ are the mole fractions for ligand and metal ion, respectively. Now by assuming that the complex absorbs much stronger than that of metal ion or ligand in the visible region, spectrophotometry can be used to determine the relative quantities of all three-species present at equilibrium. Thus, the maximum amount of complex and consequently maximum absorbance will be observed when the metal ion and the ligands are present in the stoichiometric ratio yielding the value of *n* for ML_n.
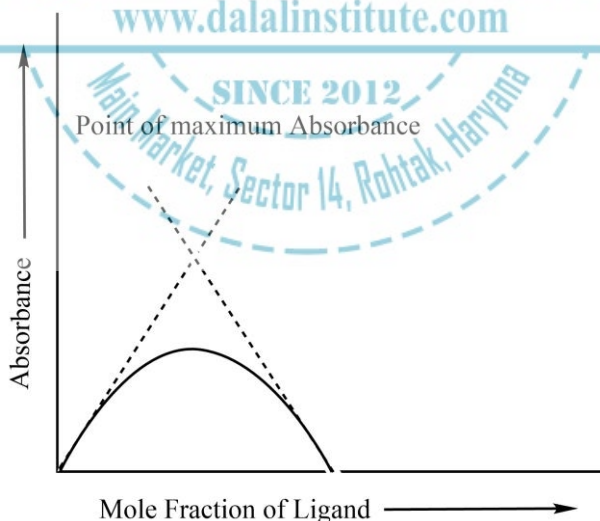
Figure 23. Continuous method of variation (Job's Plot).

$$\text{For complex } ML_n \qquad n = \frac{C_L}{C_M} \tag{63}$$

Dividing equation (61) by (62) we get:

$$n = \frac{C_L}{C_M} = \frac{C_L}{C} \times \frac{C}{C_M} = \frac{x}{1-x} \tag{64}$$

Thus, the composition of the complex is obtained by knowing the value of n. The absorbance calculated at the crossover point is the theoretical maximum amount of the complex formed that would occur if the equilibrium constant is very large. Here and now, as the absorbance is proportional to concentration, the extrapolated absorbance gives the maximum concentration of the complex while observed absorbance at the same mole fraction gives the concentration of the complex actually formed. Hence, we have:

$$\frac{[ML_n]_{\text{actual}}}{[ML_n]_{\text{maximum}}} = \frac{A_{\text{observed}}}{A_{\text{maximum}}} \tag{65}$$

Now the concentrations of all three species at equilibrium can be found and the equilibrium constant can be calculated using the relationship for K_f given in equation (59).

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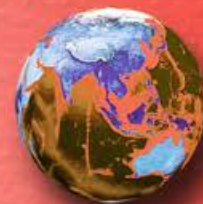
A TEXTBOOK OF INORGANIC CHEMISTRY

Volume I

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