Stepwise and Overall formation Constant

By 1941 J. Bjerrum Suggested that the formation of a Complex in Solution proceeds with stepwise addition of the Ligands to the metal ion.

Let us Consider the formation of a Complex ML_n. (Stepwise formation of Mon Complex)

Where M is the metal ion and
'L' is a monodental Ligand,
& 'n' is the maximum Co-ordination number.

Now Suppose that the formation of the Complex ML_n takes place by the following n consecutive steps and equilibrium Constants.

$$M + L \underset{}{\overset{K_1}{\rightleftharpoons}} ML \qquad \therefore K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \overset{K_2}{\rightleftharpoons} ML_2 \qquad \therefore K_2 = \frac{[ML_2]}{[ML][L]}$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$ML_{n-1} + L \overset{K_n}{\rightleftharpoons} ML_n \qquad \therefore K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

Where n is the maximum Co-ordination number of a metal ion for the Ligand L.

The equilibrium Constant $K_1\ K_2 \cdots K_n$ are Called Stepwise formation Constant or Step wise Stability Constant.

Overall formation of complex ML$_n$

Now the formation of the complex ML_n may be expressed by the following steps and equilibrium constants are as

$$M + L \overset{\beta_1}{\rightleftharpoons} ML, \quad \therefore \beta_1 = \frac{[ML]}{[M][L]}$$

$$M + 2L \overset{\beta_2}{\rightleftharpoons} ML_2 \quad \therefore \beta_2 = \frac{[ML_2]}{[M][L]^2}$$

$$M + 3L \overset{\beta_3}{\rightleftharpoons} ML_3, \quad \therefore \beta_3 = \frac{[ML_3]}{[M][L]^3}$$

$$M + 4L \overset{\beta_4}{\rightleftharpoons} ML_4 \quad \therefore \beta_4 = \frac{[ML_4]}{[M][L]^4}$$

" "

" "

" "

$$M + nL \overset{\beta_n}{\rightleftharpoons} ML_n \quad \therefore \beta_n = \frac{[ML_n]}{[M][L]^n}$$

The Equilibrium Constants, $\beta_1, \beta_2, \beta_3, \beta_4 \ldots\ldots \beta_n$ are called Overall or Cumulative formation Constant.

or, Overall or Cumulative Stability Constant.

The value of stability constant regularly decrease from K_1 to K_4. It is illustrated by the following data.

$$Cd^{2+} + NH_3 \underset{}{\overset{K_1}{\rightleftharpoons}} [Cd(NH_3)]^{2+}, \quad K_1 = 10^{2.25}$$

$$[Cd(NH_3)]^{2+} + NH_3 \overset{K_2}{\rightleftharpoons} [Cd(NH_3)_2]^{2+}, \quad K_2 = 10^{2.10}$$

$$[Cd(NH_3)_2]^{2+} + NH_3 \overset{K_3}{\rightleftharpoons} [Cd(NH_3)_3]^{2+}, \quad K_3 = 10^{1.44}$$

$$[Cd(NH_3)_3]^{2+} + NH_3 \overset{K_4}{\rightleftharpoons} [Cd(NH_3)_4]^{2+}, \quad K_4 = 10^{0.93}$$

But value $\beta_4 = 10^{7.12}$

(b) When the Ligands are Charged Molecules: —

$$Cd^{2+} + CN^- \underset{}{\overset{K_1}{\rightleftharpoons}} [Cd(CN)]^+, \quad K_1 = 10^{5.48}$$

$$[Cd(CN)]^+ + CN^- \overset{K_2}{\rightleftharpoons} [Cd(CN)_2], \quad K_2 = 10^{5.12}$$

$$[Cd(CN)_2] + CN^- \overset{K_3}{\rightleftharpoons} [Cd(CN)_3]^-, \quad K_3 = 10^{4.63}$$

$$[Cd(CN)_3]^- + CN^- \overset{K_4}{\rightleftharpoons} [Cd(CN)_4]^{2-}, \quad K_4 = 10^{3.65}$$

but, $\beta_4 = 10^{18.8}$

The steady decrease in the value of $K_1, K_2 \cdots K_n$ with increasing number of Ligands is due to the fact that as more and more ligands moves into the co-ordination zone, then less and less aqua-molecules are available to fresh ligands for replacement. As the number of ligands increases the metal ion becomes less greedy for the complex containing charged ligands, the important factor which is responsible for the steady decrease are statistical, steric hindrance and Coulombic factors.

The step wise stability constant is also expressed as $\log_{10} K_1$, $\log_{10} K_2$ --- $\log_{10} K_n$ and $\log_{10} \beta_n$ respectively.