CHAPTER 2

Metal-Ligand Equilibria in Solution:

❖ Stepwise and Overall Formation Constants and Their Interactions

The formation of a complex between a metal ion and a bunch of ligands is in fact usually a substitution reaction. However, ignoring the aquo ions, the formation of the complex can be written as:

$$\mathrm{M} + n\mathrm{L} \overset{\beta}{\rightleftharpoons} \mathrm{ML}_n \tag{1}$$

Where M represents the metal center, L is the ligand type involved, *n* represents the number of ligands, and β is the equilibrium constant for the whole process. The expression for β (or β_n) for the above equilibria can simply be written as:

$$\beta_n = \frac{[\mathrm{ML}_n]}{[\mathrm{M}][\mathrm{L}]^n} \tag{2}$$

Now because the magnitude of β_n is proportional to the molar concentration of complex formed, the equilibrium constant β_n is also called formation constant of the metal complex.

The formation constant or stability constant may be defined as the equilibrium constant for the formation of a complex in solution.

The magnitude of β_n is actually a measure of the strength of the interaction between the ligands, which come in contact to form the complex, and the metal center. However, it has also been observed that the complex formation in the solution phase occurs via a step-to-step addition of the ligands to the metal center used. For instance, the chemical equation (1), which shows the formation of a complex ML_n, can also be written as a combination of many other equations representing a corresponding series of individual steps. In other words, the overall formation process of ML_n complex can be resolved into the following steps:

$$\mathrm{M} + \mathrm{L} \overset{K_1}{\rightleftharpoons} \mathrm{ML} \quad K_1 = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]} \tag{3}$$

$$\mathrm{ML} + \mathrm{L} \overset{K_2}{\rightleftharpoons} \mathrm{ML}_2 \quad K_2 = \frac{[\mathrm{ML}_2]}{[\mathrm{ML}][\mathrm{L}]} \tag{4}$$

$$\mathrm{ML}_2 + \mathrm{L} \overset{K_3}{\rightleftharpoons} \mathrm{ML}_3 \quad K_3 = \frac{[\mathrm{ML}_3]}{[\mathrm{ML}_2][\mathrm{L}]} \tag{5}$$

The equations (3–5) and corresponding equilibrium constants can further be extended for the attack of *n* number of ligands as given below.

$$ML_{n-1} + L \overset{K_n}{\rightleftharpoons} ML_n \quad K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \tag{6}$$

Where K_1, K_2, K_3…...K_n are the equilibrium constants for different steps, which in turn also imparted their conventional label of stepwise stability or the stepwise formation constants. The magnitude of these individual equilibrium constants indicates the extent of the formation of different species in a particular step.

Nevertheless, the stepwise stability constant of any particular step does not include the information about the previous ones. Therefore, to include the extent of formation of a complex up to a particular step, say 3rd, the overall formation constant β_3 should be used as it indicates the extent of formation of ML_3 as a whole. Moreover, it can also be shown that the overall formation constant up to the 3rd step (β_3) can be represented as the product of K_1, K_2, K_3.

$$\beta_3 = K_1 \times K_2 \times K_3 \tag{7}$$

$$\beta_3 = \frac{[ML]}{[M][L]} \times \frac{[ML_2]}{[ML][L]} \times \frac{[ML_3]}{[ML_2][L]} \tag{8}$$

$$\beta_3 = \frac{[ML_3]}{[M][L]^3} \tag{9}$$

$$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \times K_5 \times K_6 \times \ldots K_n \tag{10}$$

The overall stability constant is generally reported in logarithmic scale as log β as given below

$$\log \beta_n = \log K_1 + \log K_2 + \log K_3 + \log K_4 + \log K_5 + \log K_6 + \cdots \log K_n \tag{11}$$

Or

$$\log \beta_n = \sum_{i=1}^{i=n} \log K_i \tag{12}$$

The whole process of calculating the overall formation constant can be exemplified by taking the case of $[Cu(NH_3)_4]^{2+}$ complex.

$$Cu^{2+} + NH_3 \overset{K_1}{\rightleftharpoons} [Cu(NH_3)]^{2+} \quad K_1 = \frac{[[Cu(NH_3)]^{2+}]}{[Cu^{2+}][NH_3]} \tag{13}$$

$$[Cu(NH_3)]^{2+} + NH_3 \overset{K_2}{\rightleftharpoons} [Cu(NH_3)_2]^{2+} \quad K_2 = \frac{[[Cu(NH_3)_2]^{2+}]}{[[Cu(NH_3)]^{2+}][NH_3]} \tag{14}$$

$$[Cu(NH_3)_2]^{2+} + NH_3 \overset{K_3}{\rightleftharpoons} [Cu(NH_3)_3]^{2+} \quad K_3 = \frac{[[Cu(NH_3)_3]^{2+}]}{[[Cu(NH_3)_2]^{2+}][NH_3]} \tag{15}$$

$$[Cu(NH_3)_3]^{2+} + NH_3 \overset{K_4}{\rightleftharpoons} [Cu(NH_3)_4]^{2+} \quad K_4 = \frac{[[Cu(NH_3)_4]^{2+}]}{[[Cu(NH_3)_3]^{2+}][NH_3]} \tag{16}$$

The overall reaction with overall formation constant can be given by the equation (17) as:

$$Cu^{2+} + 4NH_3 \overset{\beta_4}{\rightleftharpoons} [Cu(NH_3)_4]^{2+} \quad \beta_4 = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} \tag{17}$$

Now putting the experimental values of log K_1 = 4.0, log K_2 = 3.2, log K_3 = 2.7 and log K_4 = 2.0 in equation (12); the value of log β_4 can be calculated as follows:

$$\log \beta_4 = 4.0 + 3.2 + 2.7 + 2.0 \tag{18}$$

$$\log \beta_4 = 11.9 \tag{19}$$

Finally, it should also be noted that the thermodynamic stability of metal complexes is calculated by the overall formation constant. If the value of log β is more than 8, the complex is considered as thermodynamically stable; suggesting pretty much high stability for $[Cu(NH_3)_4]^{2+}$ complex. Moreover, the term dissociation or instability constant of a metal complex may also be defined here as the reciprocal of the stability constant.

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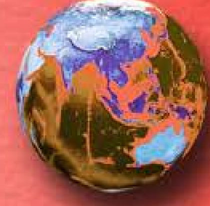

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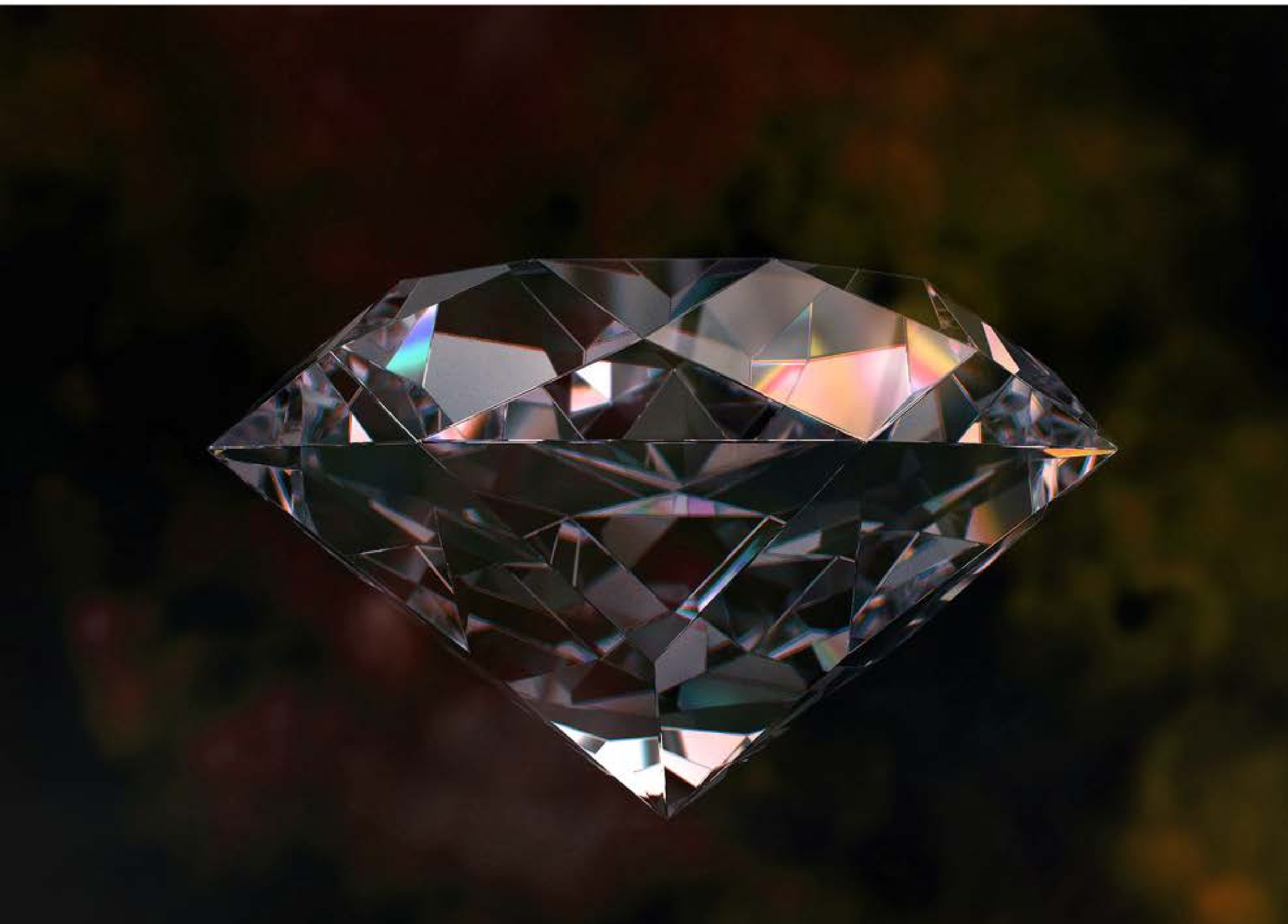

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ISBN: 978-81-938720-0-0
MRP: Rs 800.00

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