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Introduction

At present, coordination compounds are widely applied in various fields of science and technology. One hundred and fifty years have passed since the time when Cato Maximilian Guldberg and Peter Waage formulated the Law of Mass Action. They suggested that the driving force (chemical affinity) for both forward and backward reactions is equal when the mixture is at equilibrium (today, the expression for the equilibrium constant is derived by setting the chemical potential of forward and backward reactions to be equal). The elaboration of successful theory became one of the cornerstones of coordination chemistry. This branch of science started to develop rapidly only in the middle of the past century after Jannik Bjerrum announced his thesis [1] in 1941, which was later translated into many languages. The key to Bjerrum's method was the use of the then recently developed glass electrode and pH meter to determine the concentration of hydrogen ions in solution. Bjerrum recognized that the formation of a metal complex with a ligand was a kind of acid–base equilibrium: there is competition for the ligand, L, between the metal ion, M^{n+} , and the hydrogen ion, H^+ .

Main conceptions of this work, which have not lost their value and importance up to date, provided a strong stimulus for further investigations. The number of publications devoted to the problems of coordination compounds started to grow at a fast rate. The first calculations were done by hand using the so-called graphical methods. The next key development was the use of computer programs. This permitted the examination of more complicated systems. One can judge the intensity of the development of this sphere having compared a small number of works published before 1941, containing abundance of data on the characteristics of various systems collected in several volumes of “Stability Constants” [2–7]. Later, these data were critically assessed when publishing a reference book [8] containing the most reliable values of constants. Currently, a lot of critical reviews were published (most of them in the *Pure and Applied Chemistry*), and thousands of stability constants can be found in different databases.

Coordination compounds found their application in various areas including plating, which did not lose its importance until now. Much interest in the recent investigations was shown in the problems of an applied nature, underlining the effect of plating parameters such as current density, deposition time, temperature, and pH in relation to the phase composition, structure, and quality of deposit.

To gain a better insight into the nature of electrochemical processes involving metal complexes, the kinetic regularities of the processes should be revealed and considered invoking adequate theoretical models. These problems take a considerable place in this book.

We start with the consideration of equilibrium processes taking place in the solutions containing metal complexes. As the relevant theoretical aspects are widely elucidated in the literature, we present only the most general knowledge that is closely related to the problems to be considered.

1.1

Equilibrium Properties of Complex Systems

1.1.1

General Definitions

A molecular entity formed by the reversible association of two or more chemical species (molecules, atoms, or ions) is referred to as *complex*. Very different kinds of bonds can be involved in this formation, but in the following, the charge transfer complexes will be considered for the most part. These compounds contain the central ion (most commonly a metal ion) that is bound with several groups of electron donors called *ligands*. They can be both neutral particles and ions.

The number of bonds that the central ion forms with electron-donor species is designated as its *coordination number* (π -bonds are not considered in determining the coordination number). In turn, depending on the number of bonds that a single ligand particle forms, they are classified as *uni-* or *monodentate*, *bidentate*, and so on, ligands. Ligands, bound with the central particle by coordination bonds, constitute an inner coordination sphere.

The so-called *chelates* belong to the category of inner-sphere complexes. The chelating ligands have several unshared electron pairs giving rise to two or more coordination bonds. The term *chelate* is derived from the Greek word for the claw of a crawfish, as the ligand grasps the metal ion like a crawfish grasps its catch with its claws. Such complexes are much more stable than the compounds made of monodentate ligands because of the liberation of a larger number of solvent molecules. This leads to an increase in the number of species present in the system and, therefore, an increase in entropy. An increase in entropy makes the formation of the chelated complex more favorable.

Depending on the number of central particles in a single molecule of a complex compound, complexes are categorized into *mononuclear* and *polynuclear* ones. In the latter, metal ions can be bound directly or through a ligand particle ("ligand bridge").

A certain part of ligands can have no direct contact with the central particle with which they are linked by weaker (electrostatic or van der Waals) interactions or a hydrogen bond. The position of such ligands in space around the central ion is not strictly defined. They constitute a second coordination sphere, and compounds of

this type are called *outer-sphere complexes*. Main attention in this book is concentrated on the processes involving mononuclear inner-sphere complexes.

1.1.2

Equilibrium in the Solutions of Complex Compounds

Solvated ions, which form when dissolving substances in some solvent W, in essence are coordination compounds with a saturated inner coordination sphere. If the solvent is water, the so-called aqua complexes form. In this case, the number of immediately bound monodentate ligands (H_2O molecules) is equal to the coordination number, N , of the metal ion.

Upon addition of ligands X and Y to the solution containing solvate complexes MW^{n+} , the former can displace part of W molecules in the inner coordination sphere forming extra complexes. Usually, this process takes place until equilibrium is established:



¹⁾The constant of this equilibrium is called *the overall or cumulative stability constant* of the $MX_pY_qW_r^{n+}$ complex. The quantitative expression for cumulative stability constant, β_{pq} , can be greatly simplified by removing those terms that are constant. The number of water molecules attached to each metal ion is constant. In dilute solutions, the concentration of water is effectively constant. Then, the equation written without indicating molecules of the solvent becomes:

$$\beta_{pq} = \frac{\{MX_pY_q^{n+}\}}{\{M^{n+}\}\{X\}^p\{Y\}^q}. \quad (1.2)$$

Here, $\{X\}$ should be read as “the activity of X” and likewise for the other terms in curly brackets. The reciprocal quantity is called *instability constant*. As activity is the product of concentration and activity coefficient (γ), this definition could also be written as

$$\beta_{pq} = \frac{[MX_pY_q^{n+}]}{[M^{n+}][X]^p[Y]^q} \times \frac{\gamma_{pq}}{\gamma_M\gamma_X^p\gamma_Y^q} \quad (1.3)$$

where $[X]$ represents the concentration of species given in square brackets.

To avoid the complications involved in using activities, stability constants are determined, where possible, in a medium consisting of a solution of a background electrolyte at high ionic strength, that is, under conditions in which γ can be assumed to be always constant. Any chemical interactions between the species in equilibrium and the background electrolyte are unwanted, but such interactions

1) For the sake of simplicity, here and hereinafter, we shall treat ligands as having no charge. This simplification is of no importance when equilibrium properties of complex systems or when regularities of diffusive mass transfer are considered. However, the charge of ligands and complexes is necessary to be taken into account, considering the structure of the double electric layer, migration mass transfer, the mechanism of the electrode reaction, and so on.

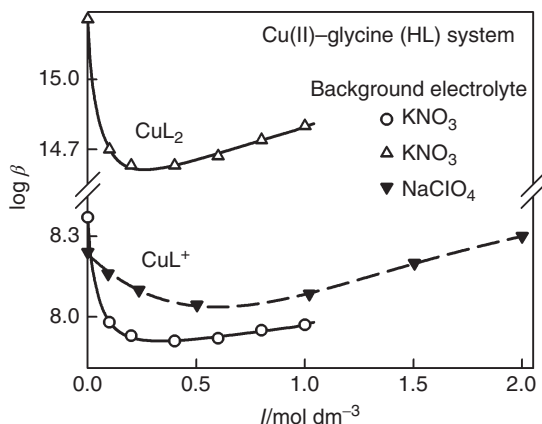


Figure 1.1 Stability constants of Cu(II)–glycine complexes obtained at different ionic strength with nitrate [9] and perchlorate [10] as background electrolytes.

might occur in particular cases. Stability constants are reported for a given ionic strength I (or extrapolated to $I = 0$). They refer to the specific ionic medium used in their determination and different values are obtained under different conditions. Furthermore, stability constant values depend on the specific electrolyte used, even at the same ionic strength. The effect of these factors can be seen from the example given in Figure 1.1.

Often, stability constants are determined for experimental conditions that deviate from the standard conditions used by convention in thermodynamics and refer to concentrations, but not to activities. Such *conditional (apparent) stability constants* are used whenever the activity coefficients and concentrations of the species are not known or not accessible, or when these simplifications are sufficient to treat certain equilibrium. As outlined next, β values expressed in concentration terms, that is,

$$\beta_{pq} = \frac{[MX_p Y_q^{n+}]}{[M^{n+}][X]^p[Y]^q}, \quad (1.4)$$

are preferable in material balance equations. Sometimes, the so-called *mixed stability constants* are found in the expressions in which both concentrations and activities are used. The latter characteristic is most often applied to H^+ ions whose activity is very easily obtained from the pH values.

The more the equilibrium Eq. (1.1) is shifted to the right, the more stable are the complexes. This concept of *stability* of complexes should not be confused with *lability* of complexes, which depends on the rate of direct and reverse reactions: the larger the rate constants of these reactions are, the sooner the state of equilibrium is reached and the more labile the complex formed is. As β values depend on the ratio of the rate constants only, complexes with the same β may be both labile and inert.

It should be noted that cumulative stability constants characterize complete dissociation of the complex compound. It is clear that the equilibria, representing the

splitting out of a single ligand particle, are depicted by a relevant *partial (stepwise) stability constant*. A cumulative constant can always be expressed as the product of stepwise constants. Conversely, any stepwise constant can be expressed as a quotient of two or more overall constants. There is no agreed notation for stepwise constants, though a symbol such as K_j is also found in the literature. It is best always to define each stability constant by reference to an equilibrium expression.

The β values depend on standard changes of enthalpy ΔH^0 and entropy ΔS^0 according to the following equation:

$$\ln \beta = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}. \quad (1.5)$$

If the temperature interval ΔT does not exceed ~ 30 K, dependence of thermodynamic functions on temperature may be ignored and the following isobar equation may be obtained:

$$\frac{d \ln \beta}{dT} = \frac{\Delta H^0}{RT^2}, \quad (1.6)$$

according to which the average ΔH^0 can be calculated. For that purpose, linear $\log \beta$ dependence on $1/T$ is depicted, the slope of which, according to Eq. (1.5), is equal to $-\Delta H^0/2.303R$.

In qualitatively describing equilibrium properties of complex system, certain functions are often used.

Function of formation (average coordination number) \bar{n} : Let us imagine that with gradual dissociation of complexes ML_N^{n+} , a certain number of species ML_j^{n+} involving less number of ligands forms until equilibrium is established. Then, the material balance equations relating total (analytic) concentrations of metal and ligand (c_M and c_L , respectively) to concentrations of specific particles acquire the following expressions:

$$[M^{n+}] + [ML^{n+}] + [ML_2^{n+}] + \dots + [ML_N^{n+}] = c_M, \quad (1.7)$$

$$[L] + [ML^{n+}] + 2[ML_2^{n+}] + \dots + N[ML_N^{n+}] = c_L, \quad (1.8)$$

According to the definition, the function \bar{n} represents the average number of ligand particles involving M^{n+} ions:

$$\bar{n} \equiv (c_L - [L])/c_M. \quad (1.9)$$

Having expressed concentration $[ML_j^{n+}]$ of each complex through the corresponding β_j , we obtain from Eqs. (1.7) to (1.9) the following:

$$\bar{n} = \frac{\sum_{j=0}^N j \beta_j [L]^j}{\sum_{j=0}^N \beta_j [L]^j}, \quad (1.10)$$

where $\beta_0 = 1$, N is the maximum number of ligand particles in the complex. If L is a monodentate ligand, which completely displaced molecules of the solvent in the inner coordination sphere of the solvate complex, N equals the coordination number of the complexing agent M^{n+} .

The degree of formation α_j is defined as a partial molar fraction of the complex ML_j^{n+} :

$$\alpha_j \equiv \frac{[ML_j^{n+}]}{c_M} = \frac{\beta_j [L]^j}{\sum_{j=0}^N \beta_j [L]^j}. \quad (1.11)$$

The complexation degree Φ shows to what extent the solvate complex concentration decreases in the complex system:

$$\Phi \equiv c_M / [M^{n+}] = \sum_{j=0}^N \beta_j [L]^j. \quad (1.12)$$

All the three functions depend solely on the concentration of free ligand $[L]$. The function α_j is used to characterize the distribution of complex species, whereas the remaining two are applied in different methods for determining the constants β_j . The following equation represents interrelation between these functions:

$$\alpha_j = \beta_j [L]^j / \Phi, \quad (1.13)$$

$$\bar{n} = \partial \ln \Phi / \partial \ln [L], \quad (1.14)$$

$$\bar{n} = j - \partial \ln \alpha_j / \partial \ln [L]. \quad (1.15)$$

At a certain $[L]$ value, \bar{n} becomes an integer, which is equal to j . Then, according to Eq. (1.15), $\partial \ln \alpha_j / \partial \ln [L] = 0$ and molar fraction of ML_j^{n+} acquires the maximum value.

1.1.3

Distribution of Complexes and Ligands in the Solution

Seeking to successfully investigate the electrochemical processes taking place in the metal|solution interphase, it is necessary to know the composition of the phases; therefore, first and foremost, it is necessary to establish the distribution of complexes and ligands in the solution volume. It follows from the above-presented equations that values of the stability constant β and the concentration of free ligand $[L]$ determine the molar fractions α_j of the components of the complex system unambiguously. Hence, α_j dependencies on $[L]$ are the simplest characteristics, which provide information about the composition of complex solutions. It is in this form that the largest part of data in literature is presented. Even a special atlas of diagrams was drawn to characterize the composition of some complex systems [11].

Despite the fact that it is quite simple to form α_j dependencies on $[L]$, such manner of provision of information has one major drawback: the concentration of free ligand in an actual solution is not known in advance, and therefore, it is to be evaluated. If the solution contains a sufficiently large excess of ligand, the inner coordination sphere of complexes becomes saturated and ML_N^{n+} prevails in the solution. Then, an approximate equation $[L] \approx c_L - Nc_M$ applies to the concentration of free ligand. However, some prevailing complexes are often impossible to distinguish. Moreover, free ligand L can react not only with M^{n+} but also with other ions, for example, with H^+ :



Then, it is also necessary to evaluate $[L]$ dependence on the solution pH by making use of the equilibrium constants of this type, β_m^H :

$$\beta_m^H = \frac{[LH_m^{m+}]}{[L][H^+]^m}. \quad (1.17)$$

Thus, in a general case to calculate the composition of the complex system, the material balance equations are necessary. If we assume that complexes of ML_j^{n+} type form in the monoligand system, and protonated ligand LH_m^{m+} is unable to form coordination bonds with M^{n+} ions, it follows from Eqs. (1.4), (1.7), (1.8), and (1.17) that

$$\sum_{j=0}^N \beta_j [M^{n+}] [L]^j = c_M, \quad (1.18)$$

$$\sum_{j=0}^N j \beta_j [M^{n+}] [L]^j + \sum_{m=0}^M \beta_m^H [L] [H^+]^m = c_L, \quad (1.19)$$

where all β values are expressed in concentration terms. As H^+ ion concentration can be calculated by means of the known pH value of the solution and the activity coefficient of these ions, two unknown quantities $[M^{n+}]$ and $[L]$ remain in Eqs. (1.16) and (1.19). Having determined these two quantities, the equilibrium concentrations of complexes and ligands are calculated by means of relevant expressions of the known stability constants β . When the system under investigation is made up of several ligands, or more complicated (mixed) complexes may be formed in it, it is necessary to change or supplement material balance equations accordingly. They are not difficult to solve using digital methods or personal computers.

We present several examples of distribution of complexes in the solution. In calculating their concentrations, β values taken from the reference book [4] were used. Figure 1.2 represents the composition of cyanide $Ag(I)$ solutions depending on free (part a) and total (part b) ligand concentrations. In the first case the amount of complexes is unambiguously determined by free cyanide concentration $[CN^-]$; therefore, the data of this part are valid for different solutions irrespective of what total $Ag(I)$ and cyanide concentrations and pH values of solutions are. Despite this advantage, such representation of the composition of the complex system has

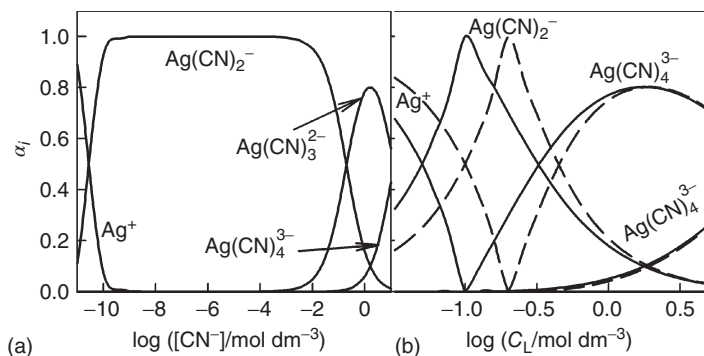


Figure 1.2 Distribution of Ag(I) cyanide complexes versus concentration of free (a) and total (b) cyanide. The total Ag(I) concentration in the part b is equal to 0.05 M (solid lines) and 0.1 M (dotted lines).

one serious drawback: free ligand concentration is not known in advance, and therefore, it is necessary to determine it somehow.

To control the composition of plating baths, several decades ago, attempts were made to titrate free cyanide by using AgNO_3 solution using KI as an indicator. This approach was often applied in analyzing Cu(I)–cyanide solutions, which were analogous by their complex composition and which were made from insufficiently pure reactants. According to [12], during titration, the following chemical reactions take place:



that is, after all CN^- ions are bound into the soluble Ag(I) complex, AgI precipitate forms, which shows that the equivalent point has been reached. It was Bek *et al.* [13] who drew attention to the fact that identification of concentrations (c_{titr}) of “free” cyanide determined in this way with true $[\text{CN}^-]$ was incorrect. Our analysis showed that, during titration, due to the shift of equilibrium Eq. (1.20), part of cyanide, displaced from complexes Cu(CN)_3^{2-} and Cu(CN)_4^{3-} , reacts and complexes Cu(CN)_2^- remain in the solution at the equivalent point. When the ratio $r < 3$, the value c_{titr} exceeds the true concentration of free cyanide by 2–3 orders of magnitude.

Those diagrams have a more real practical value in which such well-controlled values as total concentration of metal and ligand are used. It is seen from Figure 1.2 that when increasing ligand concentration, the complexation degree of the system increases. Complex ions Ag(CN)_2^- prevail in the region of lower ligand concentrations; however, in the region of higher concentrations, the number of cyanide ions in the inner coordination sphere of complexes grows up to 4. Abscises of the maxima of concentration profiles in the graphs a and b differ significantly. Moreover, distribution of complexes, as can be seen, depends to a certain extent on the total

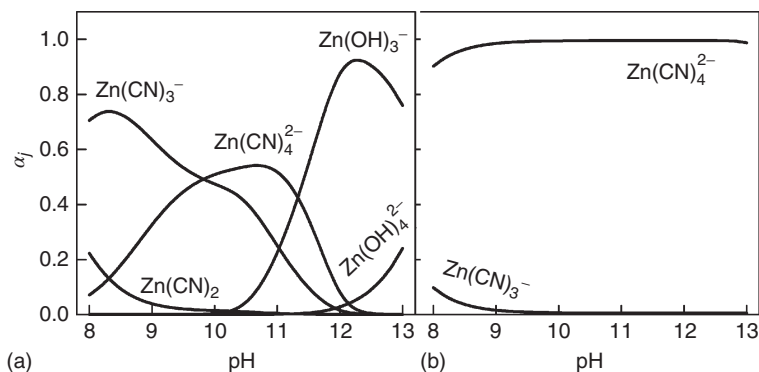


Figure 1.3 Distribution of Zn(II) cyanide and hydroxide complexes versus pH. Total Zn(II) and cyanide concentrations are equal, respectively, to 0.4 and 1.8 mM (a) and to 0.01 and 0.1 M (b).

concentration of metal. The data presented in part b apply to alkaline solutions in which the formation of HCN forms of protonated ligand may be ignored. Besides, the possibility of formation of insoluble AgCN, which can be checked by means of the product of solubility of this compound, is not taken into account here.

In case of more complicated systems, it is risky to forecast their composition even roughly. For example, from literature [3, 4] it is known that Zn^{2+} can form coordination compounds both with CN^- and with OH^- ions. Having used stability constants of such complexes and the material balance equations, it is possible to calculate the composition of the system whose example is presented in Figure 1.3. The amount of zinc cyanide and hydroxide complexes depends on Zn(II) concentration. If it is low (such solutions are usually used in polarographic investigations) within a certain pH interval, both complexes can exist (Figure 1.3a). If Zn(II) concentration is higher (such solutions are used in a voltammetric analysis and plating industry), cyanide complexes prevail in the system and formation of hydroxide complexes is very poor (Figure 1.3b).

It should be noted that data about formation of mixed complexes in this system could also be found. For example, in interpreting the data of potentiometric titration, the opinion was expressed [14] that with the aforementioned compounds such complex ions as $\text{Zn(CN)}_3(\text{OH})^{2-}$ or $\text{Zn(CN)}_3(\text{OH})_2^{3-}$ can be formed. However, the existence of the latter complexes has not been supported by other independent methods thus far; therefore, there is no final answer to this question. Mixed complexes can form in other systems as well, for example, in alkaline Cu(II) solutions containing various ethanolamines.

Figure 1.4 shows distribution of Ag(I)–thiocyanate complexes in solutions in which both mono- and polynuclear complexes can be found. Here, molar fractions α_j of the species containing two or three Ag^+ ions are not in line with the definition (1.10) and are enlarged two or three times, respectively. In this way, it is more convenient to represent the degree of di- or trimerization of Ag^+ ions. Furthermore, as in case of mononuclear complexes, the sum of all α_j remains equal to unity.

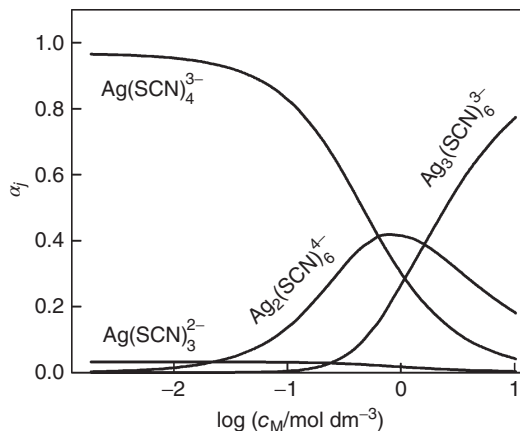


Figure 1.4 Distribution of Ag(I)–thiocyanide complexes versus total Ag(I) concentration. $c_L = 3 \text{ M}$, $T = 293 \text{ K}$.

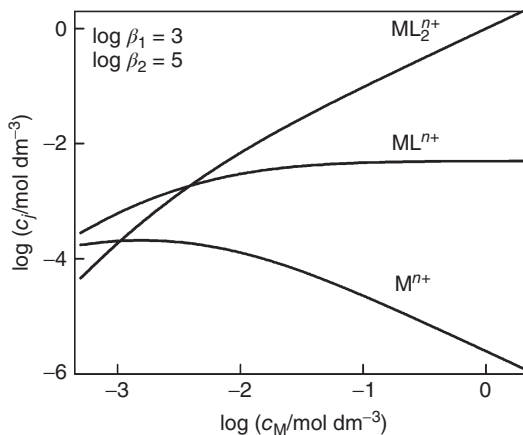


Figure 1.5 Distribution of complexes in the model system with dilution of the solution. The ratio r is constant and equal to 4.

We would like to draw the readers' attention to one peculiarity of complex systems related to changes in their composition when diluting solutions. In this case, c_L and c_M change accordingly; however, the ratio $r = c_L/c_M$ remains unchanged. It can be expected that in diluting solutions of the coordination compounds, concentrations of various species decrease proportionally. However, from the example presented (Figure 1.5), it can be seen that this supposition is absolutely incorrect. In this relation, it should be noted that in diluting solutions, the concentration of free metal ions (aqua complexes) $[M^{n+}]$, as a rule, increases.

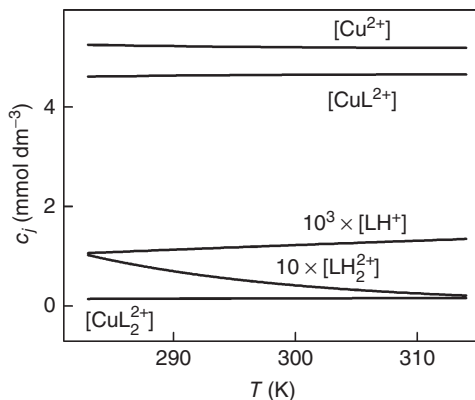


Figure 1.6 Temperature effect on the distribution of Cu(II)–ethylenediamine complexes. Total metal and ligand concentrations are equal to 0.01 and 0.005 M, respectively, at a pH of 5.3.

This is determined by relevant changes in chemical equilibria. This phenomenon is impossible in the solutions of simple salts.

The effect of temperature on the distribution of complexes is not definitive either. It is especially difficult to forecast when the solution contains forms of protonated ligand, which are unable to form coordination compounds with metal ions. The Cu(II)–ethylenediamine system in which such particles as Cu^{2+} , CuL^{2+} , CuL_2^{2+} , L , LH^+ , and LH_2^{2+} form (here, ethylenediamine is symbolized as L) may serve as an example of such an object. Entropy of formation of both Cu(II) complexes is negative; therefore, with the increase in temperature, their stability decreases. However, protonated forms of ethylenediamine, which, with an increase in temperature, decompose and increase the concentration of the active form of ligand L , have the same property. These competing interactions give the results shown in Figure 1.6: the concentration of the particles containing Cu(II) practically does not depend on temperature. A rather low concentration of L (it is not represented in the figure) and that of LH_2^{2+} change more significantly. This effect can be treated as the peculiarity of this ligand-deficient system.

In summing up, the conclusion may be drawn that the variety of the composition of complex systems is really wide. Distribution of the components depends on various factors, such as total concentration of metal and ligand, pH and temperature of solutions, and so on. Sometimes, it is possible to establish the concentrations of some components by means of experimental methods too using spectrophotometry or indicator (ion-selective) electrodes. Though, as mentioned earlier, some methods of the analysis may greatly distort the reality. Therefore, it is worth calculating the composition of the system in each specific case using reliable values of stability constants.

References

1. Bjerrum, J. (1941) *Metal-Ammine Formation in Aqueous Solution*, Haase, Copenhagen.
2. Bjerrum, J., Schwarzenbach, G., and Sillen, L.G. (1967) *Stability Constants. Part I. Organic Ligands*, Chemical Society, London.
3. Bjerrum, J., Schwarzenbach, G., and Sillen, L.G. (1958) *Stability Constants. Part II. Inorganic Ligands*, Chemical Society, London.
4. Sillen, L.G. and Martel, A.E. (1964) *Stability Constants of Metal-Ion Complexes*. Special Publication No. 17, Chemical Society, London.
5. Sillen, L.G. and Martel, A.E. (1971) *Stability Constants of Metal-Ion Complexes*. Special Publication No. 25, Chemical Society, London.
6. Högföldt, E. (1982) *Stability Constants of Metal-Ion Complexes. Part A. Inorganic Ligands*, Pergamon Press, New York.
7. Perrin, D.D. (1979) *Stability Constants of Metal-Ion Complexes. Part B. Organic Ligands*, Pergamon Press, New York.
8. Smith, R.M. and Martel, A.E. (1974–1977) *Critical Stability Constants*, vol. 1–4, Plenum Press, New York.
9. Daniele, P.G., Rigano, C., and Sammartano, S. (1982) Ionic strength dependence of formation constants. Part II: potentiometric study of the copper (II)-malonate-glycinate system In the range $0.01 \leq I \leq 1.0$. *Transition Met. Chem.*, **7** (2), 109–112.
10. Gergely, A., Nagypal, I., and Farkas, E. (1974) NMR study of the proton exchange process in aqueous solutions of copper(II)-amino acid parent complexes. *Magy. Kem. Foly.*, **80**, 545–549.
11. Kragten, J. (1978) *Atlas of Metal-Ligand Equilibria in Aqueous Solution*, John Wiley & Sons, Inc., New York.
12. Langford, K. and Parker, J.E. (1971) *Analysis of Electroplating and Related Solutions*, R. Draper LTD, Teddington.
13. Zhukov, B.D., Borodikhina, L.I., Shchekochikhin, V.M., Poddubny, N.P., and Bek, R.Y. (1973) Study of electrodeposition of copper from cyanide electrolytes. The composition of the cyanide copper plating electrolyte. *Izv. SO AN SSSR. Ser. Khim.*, **9** (4), 57–59.
14. Marsicano, F., Monberg, C., Martincigh, B.S., Murray, K., May, P.M., and Williams, D.R. (1988) The existence and stability of mixed-ligand complexes in aqueous solutions containing zinc and cyanide ions at elevated pH values. *J. Coord. Chem.*, **16** (4), 321–339.