Chemistry of Complex Equilibria

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Preface to the first edition

During the last two decades an enormous amount of information concerning complex equilibria has been published. Many experimental methods have been devised to obtain quantitative data on complex formation, and calculation methods have been developed for the evaluation of stability constants from such data. In addition, thousands of important papers, and some excellent reviews and books have appeared. The most comprehensive of these books is *The Determination of Stability Constants* by *F. J. C. Rossotti* and *H. Rossotti,* a fundamental mathematical treatment of most aspects of complex equilibria in solution, with which I in no way intend to compete here. I feel, however, that perhaps none of these publications gives a sufficiently broad and realistic account of complex equilibria, the chemistry often remaining hidden behind the algebraic equations. One fact in particular has not been adequately pointed out, viz. that the formation of mononuclear complexes with one kind of ligand only, a problem considered in most of the papers, occurs only under fairly artificial conditions. In fact, the only complex equilibrium which does not involve species other than mononuclear complexes with a completely homogeneous co-ordination sphere is the formation of a co-ordinatively saturated complex in a single step. In the present treatment, therefore, a much stronger emphasis is laid on mixed ligand, protonated, polynuclear and outer sphere type complexes, which are treated in some detail. These species are still frequently regarded as somewhat exotic, but their existence must be taken into consideration in general.

This book is based on a Hungarian version originally published in 1965, but has been completely rewritten and the literature intended to be covered up to 1968.

I should like to express my gratitude to *Professor P. Huhn* for many discussions, to *Professor J. Bjerrum* for his critical comments on a considerable part of the manuscript, to *Professor J. Rydberg* for an unpublished figure, to *Dr. R. A. Chalmers* and *Dr. D. A. Durham* for improving the English text and to *Mrs. E. K. Kállay-Tóth* for her careful editorial work.

My thanks are due to many Publishing Houses and many authors for their permission to reproduce previously published figures. Acknowledgement of the source is given under the appropriate figures.

I am much obliged to all those authors who have kindly provided me with reprints and preprints of their papers.

Debrecen, March, 1969 *Mihály T. Beck*

Perface to the second edition

The first edition of this book is out of print for many years. Since progress in this field is still continuous, and in the meantime no other book was published to provide a balanced treatment of the theoretical and practical aspects of complex equilibria, we have decided to prepare a new edition.

Based on the results published in the past two decades it has become possible to give a unified treatment of all types of complex equilibria and, as a result of the computational revolution, it was necessary to change some parts of the former book fundamentally. Based on a long scientific cooperation and considering that our knowledge and interest in this vast field are complementary, we have decided to prepare this new version jointly.

The structure of the first edition has been essentially retained, but the polynuclear, mixed ligand, protonated and outer sphere complexes are not treated in separate chapters. Twenty years ago it was necessary to lay particular emphasis upon these species, since at that time they were regarded as curiosities and not as the most common ingredients of solutions. In the meantime, the ubiquitous nature of these species have been generally recognized, and as the same experimental and computational methods can be applied for any type of complexes, we deem that separate treatment is no longer justified.

We are much obliged to Professors Kálmán Burger and David R. Williams for their valuable comments, to Dr. David Durham for the translation, and to Mrs. E.K. Kállay-Tóth for her superb editorial work. Technical assistance by Mrs. Katalin Bíró and Mrs. Ágnes Juhász is gratefully acknowledged.

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Chapter 1

Introduction

The tremendous development in inorganic chemistry following the Second World War surprised even those working in this field. The main factor involved in this upswing was undoubtedly the wide-ranging research relating to coordination chemistry*.

The foundations of complex chemistry were laid primarily by Alfred Werner. His work was mainly preparative in nature, though his conductivity studies too made a significant contribution to the application of physical chemical methods in complex chemical research. His investigations of isomerism in complex compounds shed light on the structure of such substances.

Werner dealt almost exclusively with inert** complexes; in the course of his work, therefore, equilibrium problems did not arise at all, or at most gave rise only to minor difficulties. The event most strongly connected with the sudden impetus in the chemistry of complex equilibria was the publication in 1941 of the thesis of Jannik Bjerrum [3].

Bjerrum provided a general method of determination of the stability constants of metal-ammine complexes. Complex formation and dissociation equilibrium constants had been determined earlier too. As concerns the history of science, it would be extremely interesting to establish why we had to wait so long for

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* The treatment of coordination chemistry as part of inorganic chemistry is not an exact reflection of the actual situation. The vast majority of coordination compounds contain organic ligands, and a sharp boundary cannot be drawn between complex compounds and organometallic compounds either. Investigative methods based on the various physical chemical principles are particularly important in the study of complex equilibria. Similarly to quantum chemistry, therefore, coordination chemistry is a branch of science tending to integrate the whole of chemistry [1].

** The expression inert serves to characterize the kinetic behaviour of the complexes; it is not to be confused with the stability, which is a thermodynamic concept [2]. The everyday meaning of inert is that the kinetic properties of the complex in question can be studied by means of the classical methods.

a solution to this problem, even though the conditions were already given for a quantitative treatment of complex equilibria.

The problem of complex equilibria is naturally inseparable from that of the structure of electrolyte solutions. Preconditions for the treatment of complex equilibria included recognition of the principle of electrolytic dissociation and the law of mass action. Nevertheless, even before these were known, results were found which showed that the formation of some form of 'complex'* must be considered in solutions of certain metal salts. The discovery by Hittorf [5] is certainly the most important of these. The transport numbers he defined are concentration-dependent and may also be negative. In more modern terminology, this means that, under given conditions, a negatively charged complex is formed from the positive metal ion on the action of anions, by charge overcompensation, the complex migrating to the anode on electrolysis.

Ostwald [6] combined the Arrhenius theory of electrolytic dissociation with the law of mass action, and calculated the dissociation constants of various weak acids from the results of conductivity measurements. The existence of complex ions could be deduced from distribution experiments [7], solubility behaviour [8] and kinetic properties too.

Some of these early studies even provided data on the stability of complex ions. The formation of a complex ion MeL_n is expressed by the following equation

$$\mathrm{Me} + n\mathrm{L} \rightleftharpoons \mathrm{MeL}_n \, .$$

Applying the law of mass action to this

$$K_n = \frac{[\mathrm{MeL}_n]}{[\mathrm{Me}]\,[\mathrm{L}]^n} \, .$$

Of course, in a solution containing the central ion Me and the ligand L, not only one specific complex, but a whole series of complexes may exist, their compositions being given in general by $\mathrm{Me}_q\mathrm{L}_r$.

It is obvious that the usual chemical methods do not permit us to determine all of the large number of constituents in a given equilibrium solution, and thus the corresponding equilibrium constants cannot be calculated directly either. In light of this, in the early work Bodländer and his school [9] in particular strived to determine the composition of the complex predominating under the given conditions. For this, Bodländer [10] gave a method based on potentiometric measurements. The essence of this method is that the free metal ion concentration is calculated from the EMF of an appropriately constructed concentration cell. If the law of mass action is applied to the dissociation of

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* The history of the introduction of the expression "complex" is discussed by Szabadváry and Beck [4].

Me_qL_r

$$K=\frac{[\mathrm{Me}]^q[\mathrm{L}]^r}{[\mathrm{Me}_q\mathrm{L}_r]}\,.$$

For two solutions with different concentrations, therefore

$$\frac{[\mathrm{Me}]_1^q}{[\mathrm{Me}]_2^q}=\frac{[\mathrm{Me}_q\mathrm{L}_r]_1}{[\mathrm{Me}_q\mathrm{L}_r]_2}\cdot\frac{[\mathrm{L}]_2^r}{[\mathrm{L}]_1^r}\,.$$

Let the ligand be present in large excess in both cases, i.e. let us take a high ligand concentration and a very low central ion concentration. Then

$$[\mathrm{L}]_1=[\mathrm{L}]_2$$

Accordingly

$$\frac{[\mathrm{Me}]_1^q}{[\mathrm{Me}]_2^q}=\frac{[\mathrm{Me}_q\mathrm{L}_r]_1}{[\mathrm{Me}_q\mathrm{L}_r]_2}\,.$$

The EMF of the concentration cell is

$$E=\frac{RT}{nF}\log\frac{[\mathrm{Me}]_1^q}{[\mathrm{Me}]_2^q}=\frac{RT}{nF}\log\frac{[\mathrm{Me}_q\mathrm{L}_r]_1}{[\mathrm{Me}_q\mathrm{L}_r]_2}\,.$$

Since $[\mathrm{Me}_q\mathrm{L}_r]=qT_{\mathrm{Me}}$, i.e. the high ligand excess means that practically the total amount of the central ion is present in complex form, the value of q can be calculated; the value of r/q may be determined through variation of the ligand concentration at constant T_{Me}.

Naturally, with this method no information is obtained at all on the composition and stability of the complexes present in solution under different conditions.

It was first pointed out by Jaques [11], in the appendix to a book that appeared in 1914, that the stability constants of the various complexes can in principle be calculated from electrode potential measurements. The total concentration of the central ion is clearly the sum of the concentrations of the free ion and its different complex ions

$$T_{\mathrm{Me}}=[\mathrm{Me}]+[\mathrm{MeL}]+\ldots+[\mathrm{MeL}_N]$$

where N is the maximum number of ligands that can bind to the central ion. Utilizing the equations expressing the dissociation of the complex MeL_n

$$T_{\mathrm{Me}}=[\mathrm{Me}]_1\left(1+\frac{[\mathrm{L}]_1}{K_1}+\frac{[\mathrm{L}]_1^2}{K_1K_2}+\ldots+\frac{[\mathrm{L}]_1^N}{K_1K_2\ldots K_N}\right)$$

$$T_{\mathrm{Me}}=[\mathrm{Me}]_2\left(1+\frac{[\mathrm{L}]_2}{K_1}+\frac{[\mathrm{L}]_2^2}{K_1K_2}+\ldots+\frac{[\mathrm{L}]_2^N}{K_1K_2\ldots K_N}\right)$$

$$\vdots$$

$$T_{\mathrm{Me}}=[\mathrm{Me}]_N\left(1+\frac{[\mathrm{L}]_N}{K_1}+\frac{[\mathrm{L}]_N^2}{K_1K_2}+\ldots+\frac{[\mathrm{L}]_N^N}{K_1K_2\ldots K_N}\right)\,.$$

Thus, to be able to calculate *N* unknown constants, it is sufficient to determine the free central ion concentration at *N* different ligand concentrations. Jaques was aware of the difficulties of the procedure, which are primarily due to the fact that the free ligand concentration is not known; the measurements must therefore be carried out at a high ligand excess, in order that the quantity of ligand bound in the complexes be negligibly small. However, the principle was not applied until the 1940's. Jaques' name did not reappear after 1914. His book was published immediately before the outbreak of the First World War, which may explain why it did not arouse as much interest as it deserved. The stepwise formation of aluminium chloro complexes was observed by Heyrovsky [12] while following the hydrolysis of aluminium chloride potentiometrically. The fact that a whole series of complexes must indeed be considered in the event of stepwise complex formation was first demonstrated with absolute certainty by the experiments of Niels Bjerrum [13]. Bjerrum investigated the thiocyanato complexes of chromium(III). As chromium(III) complexes generally, the thiocyanates are formed and decompose in slow reactions, i.e. they belong in the inert group. If suitable procedures are used, this permits removal of the individual constituents from an equilibrium solution, without any change occurring in the equilibrium concentrations of the other constituents during the time of the experiment. In this exceptional case, therefore, a possibility emerged for direct calculation of the stepwise equilibrium constants from the concentrations of the constituents.

The fundamentally important result from Bjerrum's research was the unambiguous proof of stepwise complex formation. He dealt only briefly with a mathematical description of the equilibrium correlations; since "to him it was quite obvious, that once one knows what the law of mass action is and knows the formation constants for the various complexes, it is a matter of simple algebra to calculate the concentration of each complex in any solution, and it would be a waste of paper, and an insult to the reader to give any detail of the calculations" [14]. After the First World War, however, studies relating to electrolyte solutions were directed primarily to clarification of the activity problem. Here too, Niels Bjerrum took the pioneering steps [15]. These investigations soon led to imposing results, and the success of the Debye–Hückel theory [16] quite overshadowed [17] the study of complex equilibria; it was considered that the latter need be taken into account only exceptionally, and that deviations from the laws for solutions could be interpreted not through the chemical equilibria described by the law of mass action, but in terms of the long-range interactions between the ions. In 1928, however, it was pointed out by McBain and Van Rysselberghe [18] that the primary object of studies on solutions was to determine the natures and concentrations of the ionic species present.

Thus, relatively little quantitative work was reported in the period between the two wars. The most important publications were those of Jannik Bjerrum [19] on copper(II)–ammine complexes, and of Møller [20] on iron(III)–thiocyanate complexes, but even to these there was almost no response.

The discovery of the glass electrode facilitated the measurement of pH substantially, and this gave Jannik Bjerrum the idea of studying complex equilibria pH-metrically [3]. In the same year as Bjerrum's thesis, Leden [21] described a method, based on the measurement of electrode potentials, for determination of the stability constants of halogeno complexes of cadmium(II); this essentially solved the problem raised by Jaques. The significance of the work of Jannik Bjerrum is illustrated by the extremely rare situation that his doctoral thesis was published in a second edition, in 1957.

Following the publications by Jannik Bjerrum and Leden, developments took place at a rate virtually unparalleled in the history of inorganic chemistry. This is at once obvious if the small number of quantitative equilibrium data determined prior to 1941 is compared with the still exponentially growing mass of data relating to a huge number of systems, to be found in the thick volumes of Stability Constants. In this revival of coordination chemistry the discovery of new elements, the preparation of a host of compounds of new types, and, perhaps to the greatest extent, the new and very high demands on analytical chemistry have played an important role. The results achieved during studies on the chemistry of complex equilibria were used productively to develop other fields of coordination chemistry too. This led in turn to important discoveries concerning the structures of complexes, the rates of their reactions, and their reactivities. The present status of coordination chemistry is best illustrated by the dual meaning of coordination. First, coordination refers to the structural arrangement of the atoms in a compound, and it also reflects the connections between the various branches of chemistry. In this latter respect, the role of coordination chemistry is important, indeed.

Finally, it may be mentioned that the chemistry of simultaneous equilibria developed in fact in three independent ways. Practically in parallel with the already outlined development in stepwise complex equilibria, a method was elaborated for treatment of the equilibria of multicomponent gas reactions [22, 23]; mathematically, this is essentially equivalent to the description of simultaneous complex equilibria. As concerns both the mathematical treatment and a number of chemical aspects, work on successive complex equilibria is closely related to studies on the complex equilibria of biopolymers [24].

This three-pronged advance had the obvious consequence that numerous important and mutually valuable results were attained independently of one another. This is yet a further example of the fact that progress in science does not always follow the most economical route.

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Chapter 2

Complex equilibria and equilibrium constants

In the following chapters the different aspects of the chemistry of complex equilibria will be dealt with in detail. It seems appropriate to give first of all a survey of complex equilibria and to treat some fundamental concepts in connection with equilibrium constants.

2.1. Types of complex equilibria in solution

Considering the charge and the size of the metal ions it is obvious that in solution they cannot exist 'freely', but that they are associated with the counter ion(s) or other components of the solution having non-bonding electron pair(s). The term *ligand** refers to any anion or neutral molecules which can be co-ordinated to a metal ion. In nearly all cases the donor property of the solvent itself is considerable. If so, the solvated metal ions are well defined chemical species: *solvo complexes*. If the solvent is water, *aquo complexes* are formed. The number of directly coordinated water molecules is usually equal to the *maximum coordination number N*.

If the solution also contains another ligand, the stepwise substitution of the ligand molecules for the co-ordinated water molecules occurs. If this second ligand is also a neutral molecule, the charge of the successive complexes is the same as that of the central ion. For example, increasing the concentration of ammonia in the solution of cobalt(II) perchlorate causes the following reactions to take place

$$\mathrm{Co(H_2O)_6^{2+} + NH_3 \rightleftharpoons Co(H_2O)_5NH_3^{2+} + H_2O} \tag{2.1}$$

$$\mathrm{Co(H_2O)_5NH_3^{2+} + NH_3 \rightleftharpoons Co(H_2O)_4(NH_3)_2^{2+} + H_2O} \tag{2.2}$$

$$\vdots$$

$$\mathrm{Co(H_2O)(NH_3)_5^{2+} + NH_3 \rightleftharpoons Co(NH_3)_6^{2+} + H_2O\,.} \tag{2.3}$$

---

* For the origin and dissemination of the term see Ref. [1].

The intermediate species $Co(H_2O)_n(NH_3)^{2+}_{(6-n)}$ where $n=1, 2, 3, 4, 5$, are in fact *mixed ligand complexes*. However, as will be pointed out later, in dilute solutions the coordination of the solvent molecules need not be considered, so this type of complex is regarded as a *mononuclear binary complex* and the water molecules are omitted from the formulae. Nevertheless, we have to bear in mind that it means a simplification which cannot always be applied: the coordination of the solvent molecule has always to be considered in the case of inert complexes, but only under certain conditions in the case of labile complexes. It may be mentioned that it is not necessarily true that the binding of *one unidentate* (see later for definition) ligand results in the displacement of *one* solvent molecule. For brevity the mononuclear binary complexes may be termed *parent complexes*; all types of complexes can be derived from these species.

If the ligand is an anion, then during stepwise complex formation the positive charge of the metal ion is gradually neutralized, and it often happens that an overcompensation of the charge of the central ion occurs and complex anions are formed

$$Al^{3+} + F^- \rightleftharpoons AlF^{2+} \tag{2.4}$$

$$AlF^{2+} + F^- \rightleftharpoons AlF_2^+ \tag{2.5}$$

$$\vdots$$

$$AlF_5^{2-} + F^- \rightleftharpoons AlF_6^{3-}\,. \tag{2.6}$$

If the ligand has more than one atom or group with donor properties (*multidentate ligands*), complexes of cyclic structure may be formed. This kind of complex was termed by Morgan and Drew [2] a *chelate* ($\chi\eta\lambda\eta$ = crab's claw). (Originally the term was used for the ring itself *chelate ring*, but soon also to describe the entire structure [*metal chelate* or simply *chelate*]; nowadays it is even used as a verb.) The chelate-forming ligands may be either anions, as for example oxalate, or neutral molecules, e.g. ethylene diamine or may contain both ionic and neutral donor groups as in the case of glycine. Naturally the number of different chelating agents is extremely large, and day by day dozens of new compounds are prepared.

In the case of multidentate ligands the maximum number of ligands which may be co-ordinated is evidently smaller than the maximum co-ordination number. If the number of donor groups is big enough and their steric arrangement is suitable, very stable complexes with 1 : 1 metal : ligand ratio may be formed.

The successive complex formation is quite analogous to the stepwise protonation of the ligands

$$^-OOC{-}COO^- + H^+ \rightleftharpoons HOOC{-}COO^- \tag{2.7}$$

$$HOOC{-}COO^- + H^+ \rightleftharpoons HOOC{-}COOH\,. \tag{2.8}$$

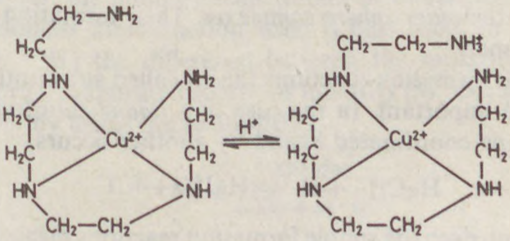
From this fact two important conclusions must be drawn.

(1) The mathematical treatment of the acid–base equilibria is the same as that of the successive complex equilibria.

(2) There is a competition between protons and metal ions for the ligand.

In the case of a few ligands the conjugate acids are so strong (e.g., HCl, HBr, HI) that this competition can be disregarded. In general, however, the dissociation of the conjugate acids of the ligands is of fundamental importance in the treatment of complex equilibria.

The protonation of a co-ordinated ligand does not necessarily mean the breaking of the bond between the metal ion and the ligand. Thus there is a possibility for the formation of *protonated complexes*. For example, the protonation of the complexes of multidentate ligands may take place according to the following reaction



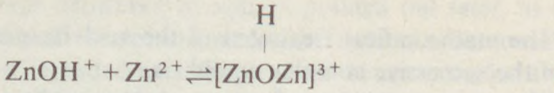
(2.9)

Protonation of complexes of unidentate ligands may also occur. For example, the protonation of hydroxo complexes results in the formation of aquo complexes, because of the donor property of the water — the conjugate acid of the hydroxide ion

$$Fe(H_2O)_5OH^{2+} + H^+ \rightleftharpoons Fe(H_2O)_6^{3+} . \tag{2.10}$$

It follows from this reaction that the aquo complexes (aquo cations) are weak acids. The aquo cations, however, are much stronger acids than the water itself. This increasing acidity is the result of the repulsion between the central ion and the protons of the co-ordinated water.

The donor capacity of the ligand is frequently not exhausted by being co-ordinated to a certain metal ion. Thus, there is a possibility of it forming a co-ordinative bond with another metal ion. The ligand acts as a *bridge* between the two central ions. The complexes having more than one central ion are termed *polynuclear complexes*. (In the most recent literature the term *multicentre* is sometimes used, to avoid the confusion between the atomic nucleus and the central ion of the complex.) Both unidentate and multidentate ligands may serve as bridges in polynuclear complexes



$$ZnOH^+ + Zn^{2+} \rightleftharpoons [Zn\overset{\overset{H}{|}}{O}Zn]^{3+} \qquad (2.11)$$

$$NH_2{-}CH_2{-}CH_2{-}NH_2Ag^+ + Ag^+ \rightleftharpoons [AgNH_2{-}CH_2{-}CH_2{-}NH_2Ag]^{2+}. \qquad (2.12)$$

In naming these polynuclear complexes the Greek letter μ is written before the bridging ligand.

The polynuclear complexes may be *homo-* or *heteropolynuclear* depending on whether the metal centres are the same or different.

Association between a co-ordinatively saturated complex and a ligand may also occur

$$Co(NH_3)_6^{3+} + Cl^- \rightleftharpoons Co(NH_3)_6Cl^{2+} \qquad (2.13)$$

$$Co(en)_3^{3+} + S_2O_3^{2-} \rightleftharpoons Co(en)_3S_2O_3^+ . \qquad (2.14)$$

These species are the *outer sphere complexes*. Their formation also takes place in a stepwise manner.

Besides all these formation reactions the so-called substitution reactions are very frequent and important. In the case of a *ligand substitution reaction* the displacement of one coordinated ligand by another occurs

$$HgCl_4^{2-} + 4I^- \rightleftharpoons HgI_4^{2-} + 4Cl^- . \qquad (2.15)$$

(As was pointed out, even the simple formation reactions mean the displacement of the coordinated solvent molecules.) The central ion may also be displaced by another suitable metal ion

$$CdI^+ + Hg^{2+} \rightleftharpoons HgI^+ + Cd^{2+} . \qquad (2.16)$$

As appears from this brief summary, in a solution of several metal ions and ligands a fairly large number of different species may exist*. As the physical, chemical and biological properties of a given solution are determined by the nature and the quantity of the different constituents, the fundamental importance of reliable methods to establish the composition and the concentration of these species is obvious. The quantitative treatment of these equilibria is based on the law of mass action.

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* Even more equilibria have to be considered if two (or more) phases are involved. This is the case when the ligand is volatile, or one of the complexes forms a solid phase, or ion-exchange resins are applied, or in the case of liquid–liquid distributions. These more complicated systems will be treated in detail in the subsequent chapters.

2.2 Types of complex equilibrium constants

The law of mass action strictly determines the concentration relations of the reactants and products in every reversible chemical reaction. The numerical value of the equilibrium constants depends on the concentration scale applied. Let us regard the simplest complex formation reaction*

$$\mathrm{Me} + \mathrm{L} = \mathrm{MeL}\,. \tag{2.17}$$

According to the law of mass action

$$K = \frac{[\mathrm{MeL}]}{[\mathrm{Me}][\mathrm{L}]}\,. \tag{2.18}$$

The dimensions of the equilibrium constant (K) are therefore the reciprocal of those of the concentration. In complex equilibrium studies the most frequently used concentration scale is the molarity (moles of solute per 1000 ml of solution); sometimes, however, the molality scale (moles of solute per 1000 g of solvent) and the dimensionless mole-fraction scale is also used. In the case of dilute solutions ($< 10^{-1}\ M$) the difference between the molarity and molality is negligible; in more concentrated solutions molarity (M) can be simply obtained from molality (m) by using the relationship

$$M = \frac{1000\ dm}{1000 + m \cdot w} \tag{2.19}$$

where d is the density of the solution and w is the molecular weight of the particular solute. For fairly dilute solutions the mole-fraction of a certain solute can be simply converted into molarity by multiplying the mole-fraction (x) by the molarity of the pure solvent (M_s)

$$M = M_s x\,. \tag{2.20}$$

In dilute aqueous solutions $M = 55.51\ x$.

The interconversion of the equilibrium constants based on different concentration scales can be made accordingly, taking into account the resultant power to which the concentration is raised.

The stepwise formation of parent complexes can be described by the following set of equilibrium constants

$$K_1 = \frac{[\mathrm{Me}]}{[\mathrm{Me}][\mathrm{L}]} \tag{2.21}$$

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* Me is the metal ion, L is the ligand, charges are omitted, and [X] is the concentration of X.

$$K_2 = \frac{[\mathrm{MeL_2}]}{[\mathrm{MeL}][\mathrm{L}]} \tag{2.22}$$

$$K_N = \frac{[\mathrm{MeL}_N]}{[\mathrm{MeL}_{N-1}][\mathrm{L}]}. \tag{2.23}$$

These equilibrium constants characterize the stability of the complexes and are usually called *stability constants.* Sometimes, especially in the older literature, the reciprocal values of these constants are used and these are called instability constants. The products of the individual stability constants also give characteristic constants, called overall or cumulative formation constants or stability products, usually denoted by

$$\beta_1 = K_1 = \frac{[\mathrm{MeL}]}{[\mathrm{Me}][\mathrm{L}]} \tag{2.24}$$

$$\beta_2 = K_1 K_2 = \frac{[\mathrm{MeL_2}]}{[\mathrm{Me}][\mathrm{L}]^2} \tag{2.25}$$

$$\vdots$$

$$\beta_N = K_1 K_2 \ldots K_N = \frac{[\mathrm{MeL}_N]}{[\mathrm{Me}][\mathrm{L}]^N}. \tag{2.26}$$

In general $\beta_n = \prod_{i=1}^{n} K_i$.

Unfortunately, there is no unified symbolism in connection with even these simplest complex equilibrium constants. Instead of K, k or b is also frequently used and the stability product is sometimes denoted by K or κ. Although to the present authors it seems to be more logical to use K and κ for the stability constant and product, respectively, it is proposed to use the symbols recommended by the IUPAC Commission on Equilibrium Data [3]. The meaning of the subscripts and superscripts may differ from author to author and it is always very important to define the symbols used.

For reactions in which the metal ion reacts with the protonated ligand

$$\mathrm{MeL}_{n-1} + \mathrm{HL} \rightleftharpoons \mathrm{MeL}_n + \mathrm{H}^+ \tag{2.27}$$

or

$$\mathrm{Me} + n\mathrm{HL} \rightleftharpoons \mathrm{MeL}_n + n\mathrm{H}^+ \tag{2.28}$$

it is sometimes practical to use the following constants

$$^*K_n = \frac{[\mathrm{MeL}_n][\mathrm{H}^+]}{[\mathrm{MeL}_{n-1}][\mathrm{HL}]} \tag{2.29}$$

and

$$*\beta_n = \frac{[\mathrm{MeL}_n][\mathrm{H}^+]^n}{[\mathrm{Me}][\mathrm{HL}]^n}. \tag{2.30}$$

These constants are composite ones, $*K_n$ being the product of the stability constant and the acidity constant (see later)

$$*K_n = K_n \cdot K_a \tag{2.31}$$

$$*\beta_n = \beta_n \cdot K_a^n. \tag{2.32}$$

The equilibrium constant of the ligand substitution reaction

$$\mathrm{MeL} + \mathrm{X} \rightleftharpoons \mathrm{MeX} + \mathrm{L} \tag{2.33}$$

is evidently the ratio of the corresponding stability constants

$$K = \frac{[\mathrm{MeX}][\mathrm{L}]}{[\mathrm{MeL}][\mathrm{X}]} = \frac{K_{\mathrm{MeX}}}{K_{\mathrm{MeL}}}. \tag{2.34}$$

Analogously, the equilibrium constant of the central ion exchange reaction

$$\mathrm{MeL} + \mathrm{M} \rightleftharpoons \mathrm{ML} + \mathrm{Me} \tag{2.35}$$

is the ratio of the stability constants of the complexes in question

$$K = \frac{[\mathrm{ML}][\mathrm{Me}]}{[\mathrm{MeL}][\mathrm{M}]} = \frac{K_{\mathrm{ML}}}{K_{\mathrm{MeL}}}. \tag{2.36}$$

Just as complex equilibria can be characterized by stability and instability constants, the acid-base equilibria of the ligands can be treated by *protonation* and *acidity constants*, respectively. The *acidity constant* ($K_{a,n}$) is the equilibrium constant for the splitting off the *n*th proton from a charged or uncharged acid, to be defined. The *protonation constant* ($K_{\mathrm{H},n}$) is the equilibrium constant for the addition of the *n*th proton to a charged or uncharged ligand, to be defined. The following equations define these constants and show their interrelation

$$K_{a,1} = \frac{[\mathrm{H}_{Z-1}\mathrm{L}][\mathrm{H}]}{[\mathrm{H}_Z\mathrm{L}]} = \frac{1}{K_{\mathrm{H},Z}} \tag{2.37}$$

$$\vdots$$

$$K_{a,2} = \frac{[\mathrm{H}_{Z-2}\mathrm{L}][\mathrm{H}]}{[\mathrm{H}_{Z-1}\mathrm{L}]} = \frac{1}{K_{\mathrm{H},Z-1}} \tag{2.38}$$

$$\vdots$$

$$K_{a,Z+1-n} = \frac{[\mathrm{H}_{n-1}\mathrm{L}][\mathrm{H}]}{[\mathrm{H}_n\mathrm{L}]} = \frac{1}{K_{\mathrm{H},n}} \tag{2.39}$$

$$\vdots$$

$$K_{a,Z} = \frac{[L][H]}{[HL]} = \frac{1}{K_{H,1}}. \qquad (2.40)$$

The value of Z, the number of dissociable protons, is not free from some ambiguity. For example, tartaric acid has two carboxyl and two alcoholic hydroxyl groups. These latter groups are such weak acids that their acidic character is usually not considered. In complex formation reactions, however, they play an important role, so it is not permitted to disregard these equilibria. The following abbreviations are variously used for the tartrate ion as ligand and for its conjugate acid

$$T^{2-},\ T^{4-},\ H_2T,\ H_2T^{2-},\ H_4T\ .$$

The interrelation between the acidity and protonation constant depends on the value of Z. If tartaric acid is defined as H_4T, the relations are as follows

$$K_{a,1} = \frac{1}{K_{H,4}};\quad K_{a,2} = \frac{1}{K_{H,3}};\quad K_{a,3} = \frac{1}{K_{H,2}};\quad K_{a,4} = \frac{1}{K_{H,1}}. \qquad (2.41)$$

However, if tartaric acid is defined as H_2T, the following relations are valid

$$K_{a,1} = \frac{1}{K_{H,2}};\quad K_{a,2} = \frac{1}{K_{H,1}}. \qquad (2.42)$$

To avoid confusion it is imperative to define the formula of the ligand and its conjugate acid unambiguously.

2.3. Equilibrium constants involving concentrations and activities

The law of mass action is strictly valid only when activities are used instead of concentrations. Because the activity of a species is equal to the product of its concentration and its activity coefficient, there is a simple relationship between the stoichiometric equilibrium constants (involving concentrations) and the thermodynamic equilibrium constants (involving activites), K_n°

$$K_n^\circ = \frac{\{MeL_n\}}{\{MeL_{n-1}\}\{L\}} = K_n \frac{f_{MeL_n}}{f_{MeL_{n-1}} \cdot f_L} \qquad (2.43)$$

where the activities are written in { } brackets, and f denotes an activity coefficient. The activity of a particular solute approaches the concentration as the system approaches a certain limiting state chosen arbitrarily. In the case of the standard activity scale this limiting state is the pure solvent. Thermodynamically, equally well defined and useful activity scales can be obtained by choosing a mixed solvent or a solution of a salt as the limiting state. Of course, only equilibrium constants referring to the same activity scale can be directly compared.

The different experimental methods provide information on either concentration or activities. In general it can be said that electrochemical methods give activities, while optical methods give concentrations. In the evaluation of the results the conversion between activities and concentrations has to be carried out by means of the activity coefficients. Sometimes it is useful to apply mixed equilibrium constants, which were first recommended by Brønsted. In this case the concentration of one of the species is replaced by its activity. This species is most frequently the proton because its activity can be directly obtained from potentiometric pH determination.

It is evident that the calculation of thermodynamic equilibrium constants requires either the knowledge of the activity coefficients or at least that they should be kept constant. If the constancy of the activity coefficients, or more correctly the constancy of their combination written in Eq. (2.43), is secured, $K_n^\ominus$ is proportional to K_n.

Thermodynamic equilibrium constants referring to the standard activity scale can be obtained by (1) studying very dilute solutions (total electrolyte concentrations less than 10^{-3} M) in which the combinations of the activity coefficients are practically equal to unity; (2) studying fairly dilute solutions where the activity coefficients can be obtained theoretically or semiempirically; (3) determining the equilibrium constants at different ionic strengths and then extrapolating to infinite dilution.

The applicability of the first method is evidently limited to the investigation of very stable complexes. The basis of the second and third methods is the Lewis–Randall principle [4] according to which in dilute solutions the activity coefficient of a given solute is the same in all solutions of the same ionic strength. The ionic strength is defined by the equation

$$I = \frac{1}{2} \sum c_i z_i^2 \tag{2.44}$$

(where c_i is the concentration and z_i the charge of the ith species). This principle was later theoretically corroborated by the Debye–Hückel theory. If the concentration of the complexes in the system is not negligible in comparison with the concentration of the inert electrolyte, the change of the ionic strength due to complex formation has to be considered. This change may be quite large. For example, in a 0.1 M solution of cadmium chloride the ionic strength calculated by assuming total dissociation is 0.3, whereas if complex formation is taken into account the value is only 0.11.

When the value of $K_n^\ominus$ is obtained by extrapolation of a series of K_n values determined at different ionic strengths, the problem arises as to which function of the ionic strength should be used in the extrapolation, that is, are the log K_n

values to be plotted against I, $I^{1/2}$ or $I^{1/3}$ etc*. The deviation of the values of $K_n^\ominus$ obtained by different extrapolation methods may amount to several hundred per cent [5]!

The validity of the original and of the different extended forms of the Debye–Hückel equation is fairly limited. The most frequently applied formulae are summarized in Table 2.1. High ligand concentrations must be used when

Table 2.1 Equations for the calculation of mean activity coefficients*

Equation	Range of validity	Author	Ref.
$-\log f_\pm = A\lvert Z_+Z_-\rvert\sqrt{I}$	$<10^{-3}\,M$	Debye and Hückel	[6]†
$-\log f_\pm = A\lvert Z_+Z_-\rvert\dfrac{\sqrt{I}}{1+B\mathring{a}\sqrt{I}}$	$<10^{-2}\,M$	Debye and Hückel	[6]§
$-\log f_\pm = A\lvert Z_+Z_-\rvert\dfrac{\sqrt{I}}{1+B\mathring{a}\sqrt{I}}+B'I$	up to a few molar	Hückel	[8]‡
$-\log f_\pm = A\lvert Z_+Z_-\rvert\dfrac{\sqrt{I}}{1+\sqrt{I}}$	<0.1	Güntelberg	[9]
$-\log f_\pm = A\lvert Z_+Z_-\rvert\dfrac{\sqrt{I}}{1+\sqrt{I}}+B'I$	<0.5	Guggenheim	[10]‡
$-\log f_\pm = A\lvert Z_+Z_-\rvert\left(\dfrac{\sqrt{I}}{1+\sqrt{I}}-0.2\,I\right)$	<0.2	Davies	[11, 12]
$-\log f_\pm = A\lvert Z_+Z_-\rvert\dfrac{\sqrt{I}}{1+1.5\sqrt{I}}$	<0.2	Scatchard	[13]
$-\log f_\pm = A\lvert Z_+Z_-\rvert\dfrac{\sqrt{I}}{1+\sqrt{I}}+B'I+C'I^{3/2}$	<0.2	Datta and Grzybowski	[14]‡

* $f_\pm$ is the geometric mean of the thermodynamically indeterminate individual ionic activity coefficients.

† A is a constant. $A=(2N\pi e^6)^{1/2}/2.3026\,(10\mathrm{k}\,\varepsilon T)^{3/2}$ where N is Avogadro's number. For aqueous solutions at 25 °C, $A=0.509$.

§ B is a constant. $B=50.3\,(\varepsilon T)^{-1/2}$. For aqueous solutions at 25 °C $B=0.328$. å an adjustable parameter, and represents the mean effective diameter of the hydrated ions in Ångström units. The value of å was estimated by Kielland [7] for 130 ions.

‡ B' and C' are adjustable parameters. The values of B' and C' are different in the different equations.

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* Evidently, in the case of uncharged ligands $\log K_n$ must be plotted against I.

working with weak or moderately stable complexes and so reliable activity coefficients cannot be calculated. It is frequently necessary to work with a high concentration of an inert electrolyte present, i.e., to use another activity scale. Moreover, this is the only effective method for the majority of complex systems, and in principle, if the necessary precautions are taken, it is as sound theoretically as the study of dilute solutions where the standard activity is applied. The basis of the constant ionic medium method (first used by Bodländer) is Brønsted's principle of the constant ionic environment [15], which states that the activity coefficient of all solutes present as small fractions of the total electrolyte concentration is constant at constant total electrolyte concentration. For the development and detailed analysis of the constant ionic medium method the fundamental paper by Biedermann and Sillén [16] should be consulted. The inert electrolyte has to meet the following requirements:

(1) it must be a strong electrolyte;

(2) its cation must not associate with the ligand and with the complex species;

(3) its anion must not associate with the central metal ion and with the complex species;

(4) redox reaction must not occur between the constituents of the inert electrolyte and the central ion or ligand;

(5) its solubility has to be large enough;

(6) its contribution to the measured physical or chemical property must be negligible.

Among the very few salts which satisfy these demands sodium perchlorate is most frequently used. According to experiments, up to 20% of the sodium perchlorate may be replaced by the salt (or the conjugate acid) of the ligand anion without considerable change in the activity coefficients, if the total electrolyte concentration is kept at 3 *M*. The potential oxidizing property of the perchlorate ion has always to be borne in mind. For a while it was thought that perchlorate is not co-ordinated by any metal ion at all. However, it was found that Fe(III) [17], Ce(III) [18], Hg(I) and Hg(II) [19], Nd(III) [20], La(III), Tl(I), Cd(II), Mg(II) and Mn(II) [21] form weak complexes with perchlorate ions. The interaction is, however, so small that even in the case of most of the metal ions mentioned above there is no appreciable complex formation in a 3 *M* sodium perchlorate solution. In the evaluation of results obtained with such concentrated solutions it must be reckoned that not only the sodium perchlorate present in high concentration is responsible for the observed effect, but also some of its impurities. In sodium perchlorate 'low in chloride', produced by BDH, the maximum amount of chloride is less than 0.002% [22]. This means, that in a 3 *M* sodium perchlorate solution the chloride ion concentration may amount to 2.4×10^{-4} *M*, and the concentration of sulphate may be much higher. These concentrations are not always negligible, especially considering the increase of the stability of complexes in highly concentrated solutions, due to the much lower water activity [23].

Just as the study of dilute solutions cannot furnish data on the water content of the species, the constant ionic medium method cannot provide any information on the number of units of either constituent of the medium associated with the complex species [24, 25]. In equilibrium analysis the concentration of MeL_n is the sum of the concentrations of all the mononuclear species in which the ratio L : Me equals n. For example, the concentration of the copper(II) diammine complex in a sodium perchlorate medium is as follows

$$[Cu(NH_3)_2^{2+}] = \sum\sum\sum [Cu(NH_3)_3(H_2O)_x(Na^+)_y(ClO_4^-)_z^{2+y-z}]. \quad (2.45)$$

There are two immediate consequences of this situation: (1) the equilibrium constants (K_n) determined in different ionic media do not refer to the same chemical species MeL_n; (2) the relation of the different ligands and the corresponding conjugate acids, i.e., the distribution of the protons among the different constituents associated with the metal ion, is not exactly defined. For example, the quantity $Hg(NH_3)_2^{2+}$ in the equilibrium analysis made in a constant concentration ammonium nitrate medium in fact includes the whole group of species $Hg(NH_3)_2(H_2O)_x(NH_4^+)_y(NO_3^-)_z$. By choosing $z=0$, and $(x, y)=(2, -2), (1, -1)$ or $(0, -1)$ one finds that such different species as $Hg(OH)_2$, $HgNH_3OH^+$ and $HgNH_2^+$ cannot be distinguished on the basis of a study performed in a single ionic medium [25, 26].

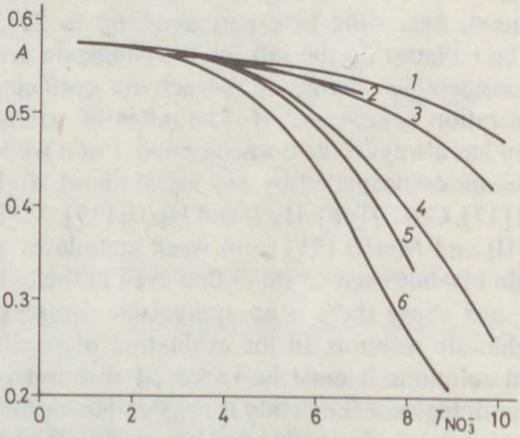


Fig. 2.1. The absorbance of Pu(VI) at 948 mμ as a function of nitrate concentration for several aqueous nitrate salt solutions.

Curve *1* — $Ca(NO_3)_2$; Curve *2* — $NaNO_3$; Curve *3* — NH_4NO_3; Curve *4* — $LiNO_3$; Curve *5* — $Al(NO_3)_3$; Curve *6* — HNO_3 [28]

(Reproduced with permission from *J. Phys. Chem.*, **65**, 1099 (1961))

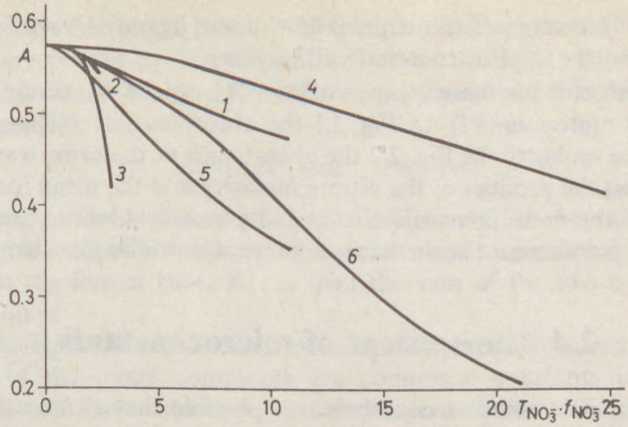


Fig. 2.2. The absorbances of Fig. 2.1 plotted as a function of $T_{NO_3^-} \cdot f_{NO_3^-}$.
Curve *1* — $Ca(NO_3)_2$; Curve *2* — $NaNO_3$; Curve *3* — NH_4NO_3; Curve *4* — $LiNO_3$; Curve *5* — $Al(NO_3)_3$; Curve *6* — HNO_3 [28]
(Reproduced with permission from *J. Phys. Chem.*, **65**, 1099 (1961))

The complexes to be studied are sometimes so weak that is not possible to work with a constant ionic medium. In such cases the introduction of the *effective activity coefficient quotient* and the *effective stability constant* may be expedient [27]. The thermodynamic stability constant is the product of a concentration quotient (K_n) and of an activity coefficient quotient (F_n)

$$K_n^{\ominus} = K_n F_n. \tag{2.46}$$

The effective activity coefficient (F'_n) is the product of the activity quotient and the mean ionic activity coefficient of the salt of the ligand (CL)

$$F'_n = F_n \cdot f_{\pm CL}. \tag{2.47}$$

Marcus [27], who developed the concept of the effective stability constant, suggested calculating F'_n by using Hückel's equation, and derived the following approximate equation

$$\log F'_n = -[2(n-m)-1]\frac{A\sqrt{C_{CL}}}{1+B_a^0\sqrt{C_{CL}}} + C_{CL}\sum b_i z_i \tag{2.48}$$

where m is the charge on the metal ion, C_{CL} is the concentration of the ligand and b is the adjustable parameter of Hückel's equation. This method was successfully applied in a number of cases. Nevertheless, the chemical meaning of the constants obtained by this method is not clear and these constants may be regarded as apparent ones which allow description of the behaviour of a given system. However, if the counter ion of the ligand is varied, the same function cannot be applied to describe the system.

This is evident from Ryan's experiments [28] on the formation of nitrate complexes of plutonium(VI). In Fig. 2.1 the absorbance at 948 mμ is plotted against nitrate molarity. In Fig. 2.2 the absorbance at the same wavelength is plotted against the product of the nitrate molarity and the mean ionic activity coefficient. If the concept of effective stability constant were correct all the experimental points would be on the same curve, which is far from being the case.

2.4 The concept of microconstants

In many types of complex equilibria it is possible that chemically different species of the same composition are formed. The equilibrium analysis cannot distinguish between isomeric species and in such cases some of the equilibrium constants are, in fact, composite constants and their resolution into constants characterizing a single species requires always some extrathermodynamical data. There are many types of systems where the formation of isomeric species should be considered:

(1) the simultaneous formation of inner and outer sphere complexes;
(2) complex formation involving ambidentate ligands;
(3) complex formation involving ligands occurring as different conformers;
(4) the stepwise complex formation involving geometrical isomers;
(5) protonation of multidentate ligands;
(6) protonation of metal complexes.

Strictly speaking, the inner and outer sphere complexes $Me(H_2O)_5L$ and $Me(H_2O)_6L$ are not isomeric species, but since water is in high excess they cannot be distinguished by equilibrium analysis. Therefore the equilibrium constant K_1 is in fact the sum of the stability constants of the inner sphere and outer sphere species

$$K_1 = K_o + K_i.$$

If the isomerization reaction is considered between the two species

$$Me(H_2O)_6L_{(aq)} \rightleftharpoons Me(H_2O)_5L_{(aq)}$$

one can introduce the isomerization constant which is the ratio of the two stability constants

$$K_{i,o} = \frac{K_o}{K_i}.$$

A system where $Me(H_2O)_6L$ and $Me(H_2O)_5L$ are simultaneously formed can be fully characterized by any pair of the four constants K_1, K_o, K_i, $K_{i,o}$.

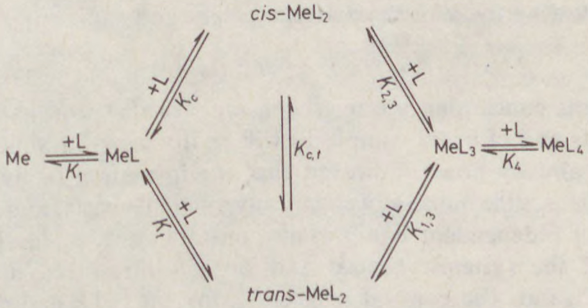
If an ambivalent ligand, e.g. CN^-, forms a complex two different 1 : 1 species can be formed

$$\text{Me—CN} \quad \text{and} \quad \text{Me—NC}.$$

In most cases the carbon complex is formed exclusively, but there are indications that in certain cases both species are present in comparable concentrations [29]. As in the former case, K_1, is then the sum of the two corresponding microconstants.

When the ligand, e.g. *β*-alanine, exists in different conformers, the stability constants of the metal complexes are composite constants involving the corresponding microconstants. Some comparative studies with ligands of fixed conformation can give information which conformer is dominating, but so far no microconstants could be evaluated [30].

The simplest case of the formation of *cis* and *trans* isomers is provided by the stepwise formation of a series of square planar complexes.



This is a two component system consisting of *five complex species* and the complete equilibrium characterization requires *five independent constants.* K_c and K_t are the microconstants

$$K_c = \frac{[cis\text{-}MeL_2]}{[MeL]\,[L]}; \quad K_t = \frac{[trans\text{-}MeL_2]}{[MeL]\,[L]}$$

K_2, the constant obtained by the equilibrium analysis, is the sum of the two microconstants, while the relation between K_3 and the corresponding microconstants $K_{2,3}$ and $K_{1,3}$

$$K_{2,3} = \frac{[MeL_3]}{[cis\text{-}MeL_2]\,[L]}; \quad K_{1,3} = \frac{[MeL_3]}{[trans\text{-}MeL_2]\,[L]}$$

is as follows

$$\frac{1}{K_3}=\frac{1}{K_{2,3}}+\frac{1}{K_{1,3}}.$$

Introducing the isomerization constant, $K_{c,t}$

$$K_{c,t}=\frac{[cis\text{-MeL}_2]}{[trans\text{-MeL}_2]}$$

the following relations can be written

$$K_{c,t}=\frac{K_c}{K_t}=\frac{K_{1,3}}{K_{2,3}}$$

$$K_c=\frac{K_2\cdot K_{c,t}}{1+K_{c,t}};\quad K_t=\frac{K_2}{1+K_{c,t}}$$

$$K_{1,3}=K_3(1+K_{c,t});\quad K_{2,3}=K_3\left(1+\frac{1}{K_{2,3}}\right).$$

For the complete description of the equilibria in the system the first four and any of the following five constants are necessary and sufficient

$$K_1, K_2, K_3, K_4, K_c, K_t, K_{1,3}, K_{2,3}, K_{c,t}.$$

The problems concerning the microconstants of the protonation of multidentate ligands and of metal complexes will be discussed in Subchapters 5.2.5 and 6.8. It is already noted, however, that the formation of hydrogen bond formation decreases the number of chemically different species and consequently the number of independent equilibrium constants needed for the complete description of the systems. Noszál and Burger introduced in the case of multidentate ligands the concept of group constant [31], assuming that the only reason of the difference of the macroconstants referring to the same functional group is statistical. This assumption decreases the number of the equilibrium constants needed to describe the system and, in favourable cases, this approach permits the estimation of number of hydrogen bridges of the ligand.

2.5 The lower and upper limits of stability constants

The lower and upper limits of stability constants are important both conceptually and practically. From the definition of an equilibrium constant it follows only that its value is a positive number

$$0<K<\infty.$$

It is obvious, however, that the Gibbs energy change of any chemical reaction must be in the range of chemical energies and since the relation between ΔG and K

$$\Delta G = -RT \ln \mathrm{K},$$

the Gibbs energy of any complex formation reaction and the corresponding stability constant must be between two limiting values

$$-\Delta G^{\circ}_{\min} < -\Delta G^{\circ} < -\Delta G^{\circ}_{\max}$$

$$K_{\min} < K < K_{\max}.$$

For the limiting values of Gibbs energies and thus those of the stability constants one can make a reasonable assumption by considering, what was mentioned at the beginning, that any complex formations in fact are substitution reactions. In an aqueous solution coordinated water molecules are successively substituted by other ligands and the Gibbs energy change per substituted water molecule is given by the difference of the Gibbs energy of a given Me—OH$_2$ bond and that of a Me—L bond. An approximate value can be obtained by neglecting the entropy changes and considering the enthalpy changes only. By considering the available bond energies, for the minimum value $-\Delta G_{\min} \sim 40$ kJ/mole/bond, while for the maximum value $-\Delta G_{\max} \sim 150$ kJ/mole/bond are obtained and thus for the stability constants defined by Eq. (2.21) the limiting values of K_1 are as follows

$$K_{\min} \sim 10^{-8} - 10^{-9}\ M$$

$$K_{\max} \sim 10^{25} - 10^{26}\ M.$$

The smallest experimentally determined stability constant has been determined by Swaddle and Guastalla [32]

$$K_1 = \frac{[\mathrm{Cr(H_2O)_5I^{2+}}]}{[\mathrm{Cr(H_2O)_6^{3+}}][\mathrm{I^-}]} = 7 \times 10^{-5}\ M.$$

Some of the highest published values of K_1 referring to a single bond formation approach this upper limit.

Table 2.2 The lower and upper limits of stability constants determined by different methods

Measured property	$K_{\min}/M$	$K_{\max}/M$
Colligative properties	10	10^4
Absorbance	1	10^6
EMF	1	10^{22}

It should be borne in mind, however, that different methods applied for the determination of stability constants usually impose much more severe limitations, as shown by Table 2.2.

These limiting values refer to labile complexes. In case of inert complexes extrathermodynamic data, e.g. molar absorbance of some species, are independently available. In such cases stability constants of much less stable complexes can be reliably determined. This is the case with the extreme small stability constant of the monoiodochromium(III) complex.

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Chapter 3

General characterization of complex equilibrium systems

3.1 Introduction

The mathematical description of complex equilibrium systems is based on equations derived from the law of mass action and from the mass balances. Even in the simplest case, however, this is a rather complicated procedure, requiring the solution of a non-linear equation or system of equations.

As an example, let us consider the aqueous solution of a weak acid (HL). From the law of mass action we have

$$K_D = \frac{[\mathrm{H}][\mathrm{L}]}{[\mathrm{HL}]} \tag{3.1}$$

$$K_w = [\mathrm{H}][\mathrm{OH}] \tag{3.2}$$

and for the mass balance

$$T_\mathrm{H} = T_\mathrm{L} = [\mathrm{L}] + [\mathrm{HL}] = [\mathrm{H}] + [\mathrm{HL}] - [\mathrm{OH}]. \tag{3.3}$$

Rearrangement of (3.1)–(3.3) leads to

$$[\mathrm{H}]^3 + K_D[\mathrm{H}]^2 - (K_D T_\mathrm{L} + K_w)[\mathrm{H}] - K_D K_w = 0. \tag{3.4}$$

Exact calculation of the equilibrium hydrogen ion concentration necessitates the solution of cubic equation (3.4). The calculation may be simplified if certain terms are neglected, considering chemical conditions, such as the actual value of T_L, and the ratios of T_L and K_D and of K_D and K_w. Nevertheless, this relationship draws attention to the relative complexity of calculation of the concentrations (or constants) in equilibrium systems.

If the law of mass action and the mass balances are applied to systems containing several components, together with various associations formed, a system of nonlinear equations is unavoidable.

Attempts have been made to simplify the calculations by using specific correlations for equilibrium systems of various types. This has led to the introduction of various auxiliary functions, application of which has appreciably facilitated the description of equilibrium systems and the evaluation of the experimental results. The most important of these auxiliary functions is the formation function introduced by N. Bjerrum [1]. This assumed a particularly momentous role in equilibrium chemistry when J. Bjerrum [2] developed a pH-metric experimental procedure for determination of the formation function. (A detailed analysis of the function is given in Section 3.5.)

The advent of computers resulted in huge changes in the evaluation of the experimental data. One essential consequence was that the auxiliary functions were replaced by the original correlations, and numerous programs are now available [3–9] for calculations on equilibrium systems of any arbitrary complexity, without the need for correlations specifically characterizing the individual systems.

In this chapter we discuss the basic correlations for equilibrium systems, and present a general description. It should be noted that numerous authors have given general descriptions of equilibrium systems, in connection with the development of the various computerized evaluation methods. Such a description of the gaseous equilibrium systems is also to be found in a handbook [10]. It is worth mentioning, however, that, despite the complete identity of the thermodynamic and mathematical bases, the computational method relating to gas-phase and solution-phase equilibrium systems developed virtually independently of each other. The computational methods used to describe the equilibrium conditions in biological systems developed very similarly, but again practically independently [11]. A mutual application of the results that have been attained would certainly be fruitful in all three fields.

The present analysis begins with an account of the definitions and basic equations, and examples are then given to illustrate the various possibilities for the mathematical description of equilibrium systems. A detailed treatment is presented on the interactions between the components, the functions describing the interactions, and their differential connections.

The formation function provides such illustrative information in equilibrium chemistry that it has remained an important auxiliary function, even in the age of the computer. Accordingly in Section 3.5 it is presented and analysed. The connection between the formation function and the functions generally describing the interactions of the components is also discussed. Section 3.6 deals with the general rules governing the concentration distribution in complex equilibrium systems.

The discussion necessitated a notational system suitable alike for descriptions of the equilibrium systems, the interactions of the components, and the rules of concentration distribution. None of the previous notations were completely appropriate for this purpose, and we have therefore developed a new system, which naturally contains the elements of the earlier ones. The chemical aspects of the characterization of equilibrium systems are stressed in the present chapter, some of the more complicated mathematical derivations are given in the Appendix.

3.2 Definitions, basic equations

The first step in the description of equilibrium systems is the definition of the components. In the chemistry of complex equilibria, it is obvious to choose the free ligand(s) and species (proton, metal ion(s)) not capable of further dissociation as the components.

The components of some *m*-component equilibrium system are denoted by $k_1, \ldots, k_i, \ldots, k_m$, and their total concentrations by $T_1, \ldots, T_i, \ldots, T_m$. The number of species (metal ions(s), ligand(s), proton, proton complexes, mononuclear and polynuclear complexes, etc.) is n, and they are denoted by $A_1, \ldots, A_i, \ldots, A_n$. In a species A_j, the number of component i is given by the *stoichiometric number* α_{ji}. The series $A_1, \ldots, A_i, \ldots, A_n$ is chosen so that its first m members are the same as the components $k_1, \ldots, k_m$, i.e. $A_i = k_i$ if $i \leq m$. The stoichiometric numbers for the components are therefore 1 if $j = i$, and 0 if $j \neq i$.

To illustrate the notations, let us consider a system containing a metal ion Me, a ligand L, H^+ and OH^- ions, proton complexes HL and H_2L, parent complexes MeL and MeL_2, a protonated complex MeLH, and a mixed hydroxo complex MeL(OH). The compositions of the species $A_1, \ldots, A_{10}$ in this three-component system are given by the α_{ji} values in Table 3.1.

The arrangement of the α_{ji} data in Table 3.1 is termed the *composition matrix* of the equilibrium system. The first m rows of the composition matrix contain the m-order unit matrix relating to the components, while the other rows refer to the associations in the system, in an arbitrary arrangement. For ease of

Table 3.1 α_{ji} values for an equilibrium system containing components H, L, M and the associations HL, H_2L, MeL, MeL_2, MeLH and $MeL(OH) = MeLH_{-1}$

Species	Components		
	k_1	k_2	k_3
	H	L	Me
	α_{ji}		
$k_1 \equiv A_1 = H$	1	0	0
$k_2 \equiv A_2 = L$	0	1	0
$k_3 \equiv A_3 = Me$	0	0	1
$A_4 = HL$	1	1	0
$A_5 = H_2L$	2	1	0
$A_6 = MeL$	0	1	1
$A_7 = MeL_2$	0	2	1
$A_8 = MeLH$	1	1	1
$A_9 = MeL(OH) \equiv MeLH_{-1}$	−1	1	1
$A_{10} \equiv OH^-$	−1	0	0

survey, however, it is advisable to follow some definite sequence. Since the components of the system are given in the title of the Table, it is not necessary to reiterate them among the species. Their repetition is merely justified by the fact that the mathematical description of the system then becomes simpler.

The complex $MeLH_{-1}$ is given as species A_9 in Table 3.1. The negative sign of the stoichiometric number for the proton in this complex indicates that, when the complex is formed from Me and L, the coordination causes one of the protons of the molecule to become free; this proton does not dissociate in the absence of the metal ion or the ligand. The proton in question may be associated with the ligand, e.g. in the case of certain ligands containing —OH, —$CONH_2$ or —CONH— groups. Frequently, however, a proton is lost by a water molecule remaining in the coordination sphere of the complex MeL, and thus the notation $MeLH_{-1}$ may also refer to a mixed hydroxo complex MeL(OH). In effect, therefore, the negative stoichiometric number stems from the fact that the solvent molecules are not shown in the composition matrix, even for solvents tending to undergo autoprotolysis. Consequently, the OH^- ion too features in Table 3.1; its stoichiometric number with respect to the proton is -1.

With the exception of the first m rows and the final row relating to OH^-, each row of the composition matrix corresponds to a chemical reaction. The stoichiometric numbers give the numbers of the various components in the composition of the given species. Thus, the equilibrium reaction describing the formation of the individual associations may be written in the form

$$\alpha_{j1}k_1 + \alpha_{j2}k_2 + \ldots + \alpha_{jm}k_m \rightleftharpoons A_j. \tag{3.5}$$

As an example, for MeLH in Table 3.1

$$H + L + Me \rightleftharpoons MeLH.$$

On application of the law of mass action to the individual formation processes, the *formation constant* of some species A_j is defined by

$$\beta_j = \frac{[A_j]}{[k_1]^{\alpha_{j1}}[k_2]^{\alpha_{j2}} \ldots [k_m]^{\alpha_{jm}}}. \tag{3.6}$$

In the sense of this definition, the value of the formation constant relating to the components of the system is unity. Hence, for a full description of the equilibrium system, a knowledge of $n-m$ formation constants is necessary.

If Eq. (3.6) is applied to the OH^- ion, characterized by a stoichiometric number of -1 with respect to the proton

$$\beta_{10} = \beta_{OH^-} = \frac{[OH]}{[H^+]^{-1}} = [H^+][OH^-] = K_w. \tag{3.7}$$

It thus emerges that in this concept the formation constant of the OH^- ion corresponds to the ionic product of water.

For the association $MeLH_{-1}$, the definition equation is

$$\beta_9 = \beta_{MeLH_{-1}} = \frac{[MeLH_{-1}]}{[Me][L][H]^{-1}} = \frac{[MeLH_{-1}][H]}{[Me][L]}. \tag{3.8}$$

However, the composition $MeLH_{-1}$ may also denote a mixed hydroxo complex. A more illustrative datum on the stability of the association is obtained if the formation constant is given in the form

$$\beta_{MeL(OH)} = \frac{[MeL(OH)]}{[Me][L][OH]} \tag{3.9}$$

corresponding to the process

$$Me + L + OH \rightleftharpoons MeL(OH).$$

A comparison of Eq. (3.8) and Eq. (3.9) reveals that the equilibrium constants defined in these two ways are connected by the ionic product of water

$$\beta_{MeLH_{-1}} = \beta_{MeL(OH)}[H][OH] = \beta_{MeL(OH)}K_w \tag{3.10}$$

$$\log \beta_{MeLH_{-1}} = \log \beta_{MeL(OH)} - pK_w. \tag{3.11}$$

The notations used so far provide a simple possibility for expressing the total concentrations of the components $k_1, \ldots, k_n$. Since the number of component i in some optional species A_j is α_{ji}, A_j contributes to the total concentration of component i with α_{ji}-times of its own concentration, i.e.

$$T_i = \sum_{j=1}^{n} \alpha_{ji}[A_j]. \tag{3.12}$$

Expressing the concentration of A_j from Eq. (3.6), substituting into Eq. (3.12), and considering every component, we obtain the following system of equations

$$\begin{aligned} T_1 &= \sum_{j=1}^{n} \alpha_{j1}\beta_j[k_1]^{\alpha_{j1}} \ldots [k_i]^{\alpha_{ji}} \ldots [k_m]^{\alpha_{jm}} \\ T_i &= \sum_{j=1}^{n} \alpha_{ji}\beta_j[k_1]^{\alpha_{j1}} \ldots [k_i]^{\alpha_{ji}} \ldots [k_m]^{\alpha_{jm}} \\ T_m &= \sum_{j=1}^{n} \alpha_{jm}\beta_j[k_1]^{\alpha_{j1}} \ldots [k_i]^{\alpha_{ji}} \ldots [k_m]^{\alpha_{jm}}. \end{aligned} \tag{3.13}$$

Equation (3.13) is the most important in describing complex equilibrium systems. It is essentially the mass balance expressed in terms of the concentrations of the components, the formation constants of the associations, and the stoichiometric numbers.

For the descriptions of special equilibrium systems, use is frequently made of the charge balance too, which reflects the principle of electroneutrality. However, the charge balance is always applied *instead of* the mass balance for some component. Supplementation of Eq. (3.13) with the charge balance would lead to a redundant equation system.

The left-hand side of Eq. (3.13) features the total concentrations; these are usually termed the analytical concentrations. However, the total and analytical concentrations relating to the proton are not identical concepts, though they are often confused. In the subsequent discussion, the analytical concentration of the proton refers to the proton concentration *added* to the system, and the total concentration is the quantity defined by Eq. (3.13). Therefore, the total proton concentration may be negative as a result of the negative stoichiometric numbers.

A similar procedure is advisable in all cases when the solvent undergoes autoprotolysis, and the ions formed take part in the equilibrium processes.

If the Equations (3.6) and (3.13) are used for the full description of the system in Table 3.1, we obtain the expressions given in Table 3.2.

Table 3.2 Complete characterization of the system containing the components H, L and Me, the associations HL, H_2L, MeL, MeL_2, MeLH and $MeLH_{-1}$

	Components			
	k_1	k_2	k_3	
	H	L	Me	
Species	Composition matrix			Formation constants
$k_1 = A_1 = H$	1	0	0	$\beta_1 = 1$
$k_2 = A_2 = L$	0	1	0	$\beta_2 = 1$
$k_3 = A_3 = Me$	0	0	1	$\beta_3 = 1$
$A_4 = HL$	1	1	0	$\beta_4 = [HL]/[H][L]$
$A_5 = H_2L$	2	1	0	$\beta_5 = [H_2L]/[H]^2[L]$
$A_6 = MeL$	0	1	1	$\beta_6 = [MeL]/[Me][L]$
$A_7 = MeL_2$	0	2	1	$\beta_7 = [MeL_2]/[Me][L]^2$
$A_8 = MeLH$	1	1	1	$\beta_8 = [MeLH]/[Me][L][H]$
$A_9 = MeLH_{-1}$	−1	1	1	$\beta_9 = [MeLH_{-1}]/[Me][L][H]^{-1}$
$A_{10} = OH$	−1	0	0	$\beta_{10} = [OH][H] = K_w$

$$T_1 = T_H = \sum \alpha_{j1}[A_j] = [H] + [HL] + 2[H_2L] + [MeLH] - [MeLH_{-1}] - [OH]$$

$$T_2 = T_L = \sum \alpha_{j2}[A_j] = [L] + [HL] + [H_2L] + [MeL] + 2[MeL_2] + [MeLH] + [MeLH_{-1}]$$

$$T_3 = T_{Me} = \sum \alpha_{j3}[A_j] = [Me] + [MeL] + [MeL_2] + [MeLH] + [MeLH_{-1}]$$

3.3 Transformation of the composition matrix

The starting-point for the considerations in the previous section was to regard the components of the system as species not capable of further dissociation. This manner of selecting the components corresponds to the chemical viewpoint, i.e. the resulting total concentrations are the same as the concentrations found with the appropriate analytical methods. (See the previous section for considerations on the total concentration of the proton.)

From the thermodynamic interpretation of the concept of the components, however, it is clear that the components may be chosen in many other ways. *m* species can be selected from a total of *n* such species in

$$\binom{n}{m} = \frac{n!}{m!(n-m)!} \tag{3.14}$$

different ways. However the number of combinations in Eq. (3.14) is the number of possible component series only if species with linearly independent compositions are obtained in every case.

The mathematical criterion of linear independence is that the determinant of the composition matrix relating to the *m* species in question should not be zero. For the equilibrium system described by the correlations in Table 3.2 (disregarding the OH^- ion), the number of combinations is $\binom{9}{3} = 84$. The corresponding determinants, however, reveal that 13 species-triplets from among these can not be components of the system, for the determinant of the matrix is zero.

The chemical meaning of a zero determinant is that, as a result of some equilibrium reaction, there is a definite fixed correlation between the concentrations of the species concerned, and accordingly they can not assume optional concentrations relative to one another. Table 3.3 lists those species which cannot be components of the model system. Table 3.3 also gives the equilibrium reactions through which two of the concentrations of the species unambiguously define the third.

Apart from the 13 triplets in Table 3.3, all the other combinations are suitable, i.e. there are $84 - 13 = 71$ different possibilities for the mathematical descriptions of the given system.

The right-hand column in this Table gives the correlations between the various concentrations. These equations obviously always hold, independently of the values of the total concentrations. This provides a possibility for establishment of the correlations relating to the individual points of the concentration distribution curves, without a knowledge of the actual concentration distribution. The correlations in Table 3.3 lead to the following findings:

Table 3.3 Species-triplets with interdependent concentrations

	Species triplet		Equilibrium	Concentration correlation
1.	A_1, A_2, A_4	H, L, HL	$H+L \rightleftharpoons HL$	$[HL] = \beta_4 [H][L]$
2.	A_1, A_2, A_5	H, L, H_2L	$2H+L \rightleftharpoons H_2L$	$[H_2L] = \beta_5 [H]^2 [L]$
3.	A_1, A_4, A_5	H, HL, H_2L	$H+HL \rightleftharpoons H_2L$	$[H_2L] = (\beta_5/\beta_4)[H][HL]$
4.	A_1, A_6, A_8	H, MeL, MeLH	$H+MeL \rightleftharpoons MeLH$	$[MeLH] = (\beta_8/\beta_6)[MeL][H]$
5.	A_1, A_6, A_9	H, MeL, $MeLH_{-1}$	$MeL \rightleftharpoons MeLH_{-1}+H$	$[MeLH_{-1}] = (\beta_9/\beta_6)[MeL][H]^{-1}$
6.	A_1, A_8, A_9	H, MeLH, $MeLH_{-1}$	$MeLH \rightleftharpoons MeLH_{-1}+2H$	$[MeLH_{-1}] = (\beta_9/\beta_8)[MeLH][H]^{-2}$
7.	A_2, A_3, A_6	L, Me, MeL	$Me+L \rightleftharpoons MeL$	$[MeL] = \beta_6 [Me][L]$
8.	A_2, A_3, A_7	L, Me, MeL_2	$Me+2L \rightleftharpoons MeL_2$	$[MeL_2] = \beta_7 [Me][L]^2$
9.	A_2, A_4, A_5	L, HL, H_2L	$H_2L+L \rightleftharpoons 2HL$	$[HL] = \sqrt{(\beta_4^2/\beta_5)[H_2L][L]}$
10.	A_2, A_6, A_7	L, MeL, MeL_2	$MeL+L \rightleftharpoons MeL_2$	$[MeL_2] = (\beta_7/\beta_6)[MeL][L]$
11.	A_3, A_4, A_8	Me, HL, MeLH	$Me+HL \rightleftharpoons MeHL$	$[MeHL] = (\beta_8/\beta_4)[Me][HL]$
12.	A_3, A_6, A_7	Me, MeL, MeL_2	$MeL_2+Me \rightleftharpoons 2MeL$	$[MeL] = \sqrt{(\beta_6^2/\beta_7)[MeL_2][Me]}$
13.	A_6, A_8, A_9	MeL, MeLH, $MeLH_{-1}$	$MeLH_{-1}+MeLH \rightleftharpoons 2MeL$	$[MeL] = \sqrt{(\beta_6^2/\beta_8\beta_9)[MeLH_{-1}][MeLH]}$

(1) The concentrations of HL and L are equal at $pH = \log \beta_4 = \log \beta_{HL}$.

(2) The concentrations of H_2L and L are equal at $pH = 0.5 \log \beta_5 = 0.5 \log \beta_{H_2L}$.

(3) The concentrations of H_2L and HL are equal at $pH = \log(\beta_5/\beta_4)$.

(4) If MeLH is regarded as a weak acid, its dissociation constant is β_6/β_8. Therefore the concentrations of MeL and MeLH are equal at $pH = -\log(\beta_6/\beta_8)$.

(5) The acidic dissociation constant of the complex MeL is β_9/β_6. Therefore the concentrations of MeL and $MeLH_{-1}$ are equal at $pH = -\log(\beta_9/\beta_6)$.

(6) The concentrations of MeLH and $MeLH_{-1}$ are equal at $pH = 0.5 \log(\beta_8/\beta_9)$.

(7) At the point of intersection of the concentration distribution curves for Me and MeL, we have $pL = -\log[L] = \log \beta_6$.

(8) At the point of intersection of the concentration distribution curves for Me and MeL_2, we have $pL = -\log[L] = 0.5 \log \beta_7$.

(9) The constant for the equilibrium process $H_2L + L \rightleftharpoons 2HL$ expresses the stability of the proton complex HL against its rearrangement into the species H_2L and L. This stability is the higher, the larger the value of β_4^2/β_5. Since β_4 is the constant for the protonation process $H + L \rightleftharpoons HL$, while β_5/β_4 is the corresponding constant for $H + HL \rightleftharpoons H_2L$, it follows that the *relative stability* of HL against the species L and H_2L is governed by the ratio of the equilibrium constants of the two processes, i.e. β_4^2/β_5.

This draws attention to the fact that the formation of some species in appreciable concentration depends not only on its formation constant, but also on its stability against various 'disproportionation' reactions.

(10) The concentrations of the complexes MeL and MeL_2 are equal at the free ligand concentration corresponding to $pL = 0.5 \log(\beta_7/\beta_6)$.

(11) The affinity of the metal ion Me for the monoprotonated ligand is characterized by the constant β_8/β_4. The concentrations of Me and MeLH are equal at $[HL] = \beta_4/\beta_8$.

(12) From an analogous analysis to that in point 9, it emerges that the stability of the complex MeL against the "disproportionation" reaction $2MeL \rightleftharpoons Me + ML_2$ is governed by the ratio of the constants for the equilibrium processes $Me + L \rightleftharpoons MeL$ and $MeL + L \rightleftharpoons MeL_2$.

(13) Similarly, its stability against the 'disproportionation' $2MeL \rightleftharpoons MeLH_{-1} + MeLH$ is governed by the ratio of the constants for the equilibrium processes $MeLH_{-1} + H \rightleftharpoons MeL$ and $MeL + H \rightleftharpoons MeLH$. The formation of ML in appreciable concentration is therefore to be expected only if the formation constant β_6 *and* the reciprocals of the constants for the equilibrium processes discussed in points 12 and 13 are relatively large.

In practice, the compositions and stabilities of the associations formed in complex equilibrium systems are studied in a definite interval of total concentrations. It is not sure (and in general it is not even probable) that the compositions of the main associations in the system will remain unchanged at concentration ratios considerably different from those studied experimentally. The change of the concentration range may mean that species which were not detected under the experimentally studied conditions will now be present in significant concentration. However, the above findings (which can also be derived for any optional system) still hold true. In other words, no matter what equilibrium system is involved, if any of the species-triplets listed in Table 3.3 are present, then the given correlations hold between their concentrations.

We have seen that 13 of the 84 possible species-triplets can not be components of the system. The other 71 triplets can be components, i.e. the concentrations of any three of them (together with the formation constants) are sufficient for a complete mathematical description of the system. If the choice of components differs from the customary one, there will naturally be modifications in the composition matrix for the system, and also in the formation constants and the expression for the mass balance. An example is given in the Appendix of the matrix algebraic operations for the transformation between two different component series, and they are presented in connection with the model system in Table 3.2.

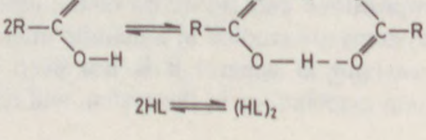
3.4 Description of interactions of components

We have already presented general correlations suitable for a description of equilibrium systems, together with the conclusions drawn from an analysis of the composition matrix. We shall now examine the basic correlations from the aspect of a description of the interactions between the components.

3.4.1 One-component systems

The study of one-component equilibrium systems is of minor importance in the chemistry of complex equilibria. The only justification for its treatment is that the correlations and functions introduced also prove valuable in the description of systems of two or more components.

In one-component homogeneous equilibrium systems, only the dimerization, trimerization, . . ., polymerization of the component need be considered. This situation is encountered in concentrated solutions of certain organic acids, for instance, where the molecules are linked by hydrogen-bonds:



$$2HL \rightleftharpoons (HL)_2$$

Two remarks must be made in connection with the above process:

Processes of this type are generally studied in some solvent present in great excess. In the strict thermodynamic sense of the concept of components, therefore, these systems are at least two-component ones. The solvent naturally interacts with both the monomer and the dimer, while the dimerization automatically involves a transformation of the solvation sphere. However, this is neglected during the mathematical description of the system, and no attention is paid to the solvent molecules that play a fundamental chemical role in the equilibrium. By virtue of this simplification, such systems are characterized as one-component systems.

The process $2HL \rightleftharpoons (HL)_2$ can be conceived of as a dimerization in a one-component system only in the concentration interval where the dissociation of HL may be neglected. If there is an overlap of the concentration intervals for the dimerization and the dissociation process $HL \rightleftharpoons H + L$, these systems too must be treated as two-component systems. The system is naturally also regarded as a two-component one if only the dissociation is studied: in the sense of the Brønsted theory, one condition of dissociation is that there should be an independent proton acceptor in the system.

It follows that, in the strict thermodynamic sense, a one-component homogeneous equilibrium system can occur only in the gas phase. A classical example is the gas-phase dimerization of NO_2; $2NO_2 \rightleftharpoons N_2O_4$.

From the aspect of the mathematical description of equilibrium systems, however, those systems may be regarded as one-component ones in which the composition of the species can be given by a column vector. Since i (the index of the component) is always 1 in this case, α_{ji} is replaced by α_j.

As customary in the chemistry of polymers, the species not capable of further dissociation in a one-component system will be termed a monomer, while the associations formed from this will be termed dimers, trimers, etc.

A single equation defining the total concentration describes the one-component systems

$$T = \sum \alpha_j [A_j] = \sum \alpha_j \beta_j [k]^{\alpha_j} . \tag{3.15}$$

A good choice for the description of the degree of dissociation is the ratio of the free and total concentrations of the component (r), which may be expressed as follows

$$r = \frac{[k]}{T} = \frac{[k]}{\sum \alpha_j \beta_j [k]^{\alpha_j}} \tag{3.16}$$

As [k] decreases, the value of r tends to a limiting value of 1; as [k] increases, r tends to 0. It is recommended to plot the value of r as a function of the logarithm (or the negative logarithm) of the free monomer concentration. We first consider the case when we are concerned only with dimerization in the system, i.e. the maximum degree of association is 2.

3.4.1.1 Dimerization of one component

For the dimerization of one component, the r function may be written as

$$r = \frac{[\mathrm{k}]}{T} = \frac{[\mathrm{k}]}{[\mathrm{k}] + 2\beta_2[\mathrm{k}]^2} = \frac{1}{1 + 2\beta_2[\mathrm{k}]}. \tag{3.17}$$

It follows immediately from Eq. (3.17) that if $r = 0.5$, $2\beta_2[\mathrm{k}] = 1$, i.e.

$$\beta_2 = \frac{1}{2[\mathrm{k}]_{r=0.5}}. \tag{3.18}$$

Equation (3.17) may be differentiated with respect to log [k]

$$\frac{\mathrm{d}r}{\mathrm{dlog}\,[\mathrm{k}]} = 2.303\frac{\mathrm{d}r}{\mathrm{dln}\,[\mathrm{k}]} = 2.303\frac{\mathrm{d}r}{\mathrm{d}[\mathrm{k}]}[\mathrm{k}] \tag{3.19}$$

$$\frac{\mathrm{d}r}{\mathrm{d}[\mathrm{k}]} = \frac{2\beta_2}{(1 + 2\beta_2[\mathrm{k}])^2} \tag{3.20}$$

Substitution of Eq. (3.20) into Eq. (3.19) gives

$$\frac{\mathrm{d}r}{\mathrm{dlog}\,[\mathrm{k}]} = -2.303\frac{2\beta_2[\mathrm{k}]}{(1 + 2\beta_2[\mathrm{k}])^2} = -2.303 \cdot r \cdot (1 - r) \tag{3.21}$$

It can be seen from Eq. (3.21) that this differential quotient depends only on the value of r. It follows directly from this that all systems in which only the

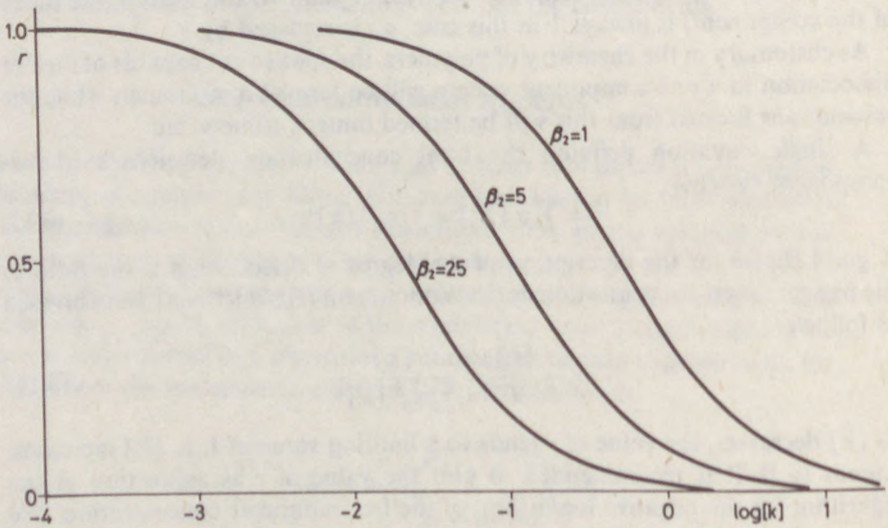


Fig. 3.1 $r = f(\log[\mathrm{k}])$ functions at various β_2 values for the dimerization of one component

dimerization of one component need be considered, are described by curves of the same shape. The position of the curve on the log [k] scale naturally depends on the dimerization constant β_2, but its shape is independent of this. It is also evident from Eq. (3.21) that the curve is symmetrical about its mid-point ($r=0.5$), the differential quotients at identical distances from the mid-point being the same. Figure 3.1 shows the theoretically calculated $r=f(\log[\mathrm{k}])$ curves for various β_2 values to illustrate the above statements.

3.4.1.2 Di- and trimerization of one component

When both di- and trimerization of one component are considered, the r function can be given by

$$r=\frac{[\mathrm{k}]}{T}=\frac{1}{1+2\beta_2[\mathrm{k}]+3\beta_3[\mathrm{k}]^2} \tag{3.22}$$

Differentiating

$$\frac{\mathrm{d}r}{\mathrm{d}\log[\mathrm{k}]}=2.303\frac{\mathrm{d}r}{\mathrm{d}[\mathrm{k}]}[\mathrm{k}]=$$
$$=-2.303\frac{2\beta_2[\mathrm{k}]+6\beta_3[\mathrm{k}]^2}{(1+2\beta_2[\mathrm{k}]+3\beta_3[\mathrm{k}]^2)^2}\,. \tag{3.23}$$

This may be rearranged to

$$\frac{\mathrm{d}r}{\mathrm{d}\log[\mathrm{k}]}=-2.303\cdot r\cdot(1-r+r\cdot 3\beta_3[\mathrm{k}]^2)\,. \tag{3.24}$$

In order to rearrange the final term, [k] is expressed as the solution of the quadratic equation (3.22)

$$[\mathrm{k}]=\frac{\sqrt{4\beta_2^2+12\beta_3\dfrac{1-r}{r}}-2\beta_2}{6\beta_3}\,. \tag{3.25}$$

Substitution of Eq. (3.25) into Eq. (3.24) gives

$$\frac{\mathrm{d}r}{\mathrm{d}\log[\mathrm{k}]}=-2.303r\left\{1-r+r\left(\frac{2}{3}\frac{\beta_2^2}{3}+\frac{1-r}{r}-\sqrt{\frac{4}{9}\cdot\frac{\beta_2^4}{\beta_3^2}+\frac{4}{3}\cdot\frac{\beta_2^2}{\beta_3}\cdot\frac{1-r}{r}}\right)\right\}. \tag{3.26}$$

If β_2^2/β_3 is denoted by x, after simplification Eq. (3.26) becomes

$$\frac{\mathrm{d}r}{\mathrm{d}\log[\mathrm{k}]}=-2.303r\left(2-2r+\frac{2}{3}rx-\sqrt{\frac{4}{9}x^2r^2+\frac{4}{3}xr(1-r)}\right). \tag{3.27}$$

This equation shows that at a given r value the shape of the function $r=f(\log[\mathrm{k}])$ depends only on the value of x, i.e. it is a function only of the quotient β_2^2/β_3.

For an explanation of the chemical meaning of this result, let us consider first the equations defining β_2 and β_3

$$2\mathrm{k} \rightleftharpoons \mathrm{k}_2 \quad \beta_2=\frac{[\mathrm{k}_2]}{[\mathrm{k}]^2} \tag{3.28}$$

$$3\mathrm{k} \rightleftharpoons \mathrm{k}_3 \quad \beta_3=\frac{[\mathrm{k}_3]}{[\mathrm{k}]^3}. \tag{3.29}$$

For the quotient, therefore, we have

$$x=\frac{[\mathrm{k}_2]^2[\mathrm{k}]^3}{[\mathrm{k}_3][\mathrm{k}]^4}=\frac{[\mathrm{k}_2]^2}{[\mathrm{k}_3][\mathrm{k}]}. \tag{3.30}$$

The expression on the right-hand side of Eq. (3.30) is the equilibrium constant of the 'disproportionation' process $\mathrm{k}_3+\mathrm{k} \rightleftharpoons 2\mathrm{k}_2$. Thus, x expresses the stability of the dimer against transformation into the monomer and the trimer. Accordingly, a high x value means that a dimer is first formed as the concentration of the component is increased, this association being stable in a relatively broad concentration interval. Transformation of the dimer to the trimer occurs only if [k] (and T) is elevated considerably. A low x value, however, means that no matter how large β_2 is, only a slight amount of dimer is formed, and the elevation of [k] is accompanied by conversion to the trimer in a narrow concentration interval.

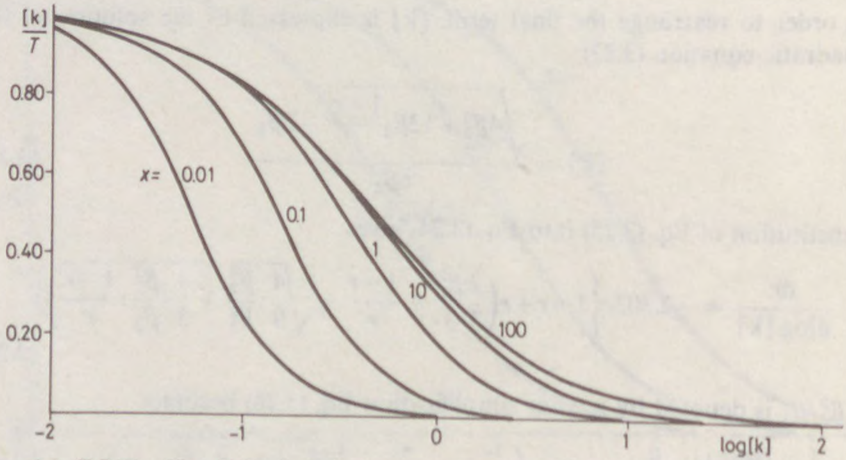


Fig. 3.2 $[\mathrm{k}]/T=f(\log[\mathrm{k}])$ functions at various $x=\beta_2^2/\beta_3$ values for the di- and trimerization of one component

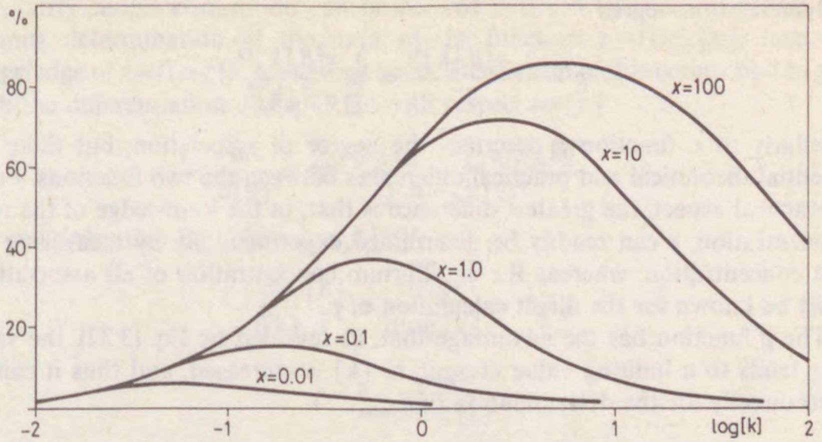


Fig. 3.3 Partial molar percentage of the dimeric species as a function of log [k] at various $x=\beta_2^2/\beta_3$ values for the di- and trimerization of one component

To illustrate all this, Fig. 3.2 presents the function $[\mathrm{k}]/T=f(\log[\mathrm{k}])$ at various x values, the value of β_2 being chosen as 1. Figure 3.3 shows the percentage concentration distribution of the dimer molecule as a function of log [k], at various x values.

3.4.1.3 Polymerization of one component

In one-component systems containing associations with a polymerization degree of more than three, the function $[\mathrm{k}]/T=f(\log[\mathrm{k}])$ becomes more complicated. However, the considerations in the preceding point can be generalized to these more complex systems. The concentration of any member of the series can be expected to be the higher, the greater its stability against disproportionation into the two neighbours, i.e. the greater the value of the $\mathrm{k}_{n-1}+\mathrm{k}_{n+1}\rightleftharpoons 2\mathrm{k}_n$ equilibrium constant

$$\frac{[\mathrm{k}_n]^2}{[\mathrm{k}_{n-1}][\mathrm{k}_{n+1}]}=\frac{\beta_n^2}{\beta_{n-1}\beta_{n+1}}. \tag{3.31}$$

One of the important questions in equilibrium chemical studies on polymerization processes is the establishment of the composition of the association with the maximum polymerization degree, i.e. the value of $\alpha_{j\max}$. The previously defined and analysed function $r=f(\log[\mathrm{k}])$ can not be used directly for this purpose, for the limiting value of r is always 1 or 0, independently of the maximum polymerization degree. Therefore the following function is defined for establishment of the composition of the association with maximum polymerization degree

$$p = \frac{\sum \alpha_j^2 \beta_j [\mathrm{k}]^{\alpha_j}}{T} = \frac{\sum \alpha_j^2 \beta_j [\mathrm{k}]^{\alpha_j}}{\sum \alpha_j \beta_j [\mathrm{k}]^{\alpha_j}} . \tag{3.32}$$

Similarly to *r*, function *p* describes the degree of association, but there are essential theoretical and practical differences between the two functions. From a practical aspect, the greatest difference is that, in the knowledge of the total concentration, *r* can readily be determined experimentally by measuring the free concentration, whereas the equilibrium concentration of all associations must be known for the direct calculation of *p*.

The *p* function has the advantage that, as revealed by Eq. (3.32), the value of *p* tends to a limiting value of $\alpha_{j\max}$ as [k] is increased, and thus it can be used directly for the determination of $\alpha_{j\max}$.

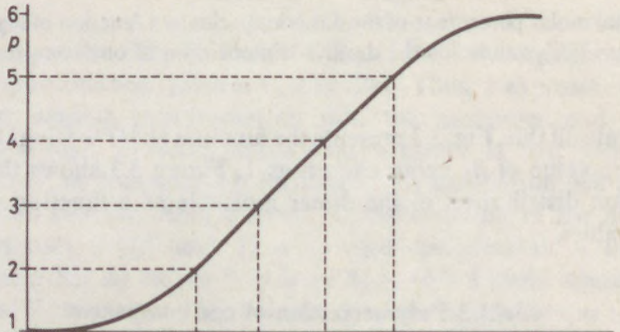


Fig. 3.4 Differential connection of the *r* and *p* functions describing the polymerization of one-component systems

A fairly simple connection can be derived between the two functions; this permits determination of the data of the function $p = f(\log[\mathrm{k}])$ into the knowledge of $r = f(\log[\mathrm{k}])$, and vice versa. Derivation of this connection begins with the differentiation of Eq. (3.16) with respect to [k]

$$\frac{\mathrm{d}r}{\mathrm{d}[\mathrm{k}]} = \frac{\sum \alpha_j \beta_j [\mathrm{k}]^{\alpha_j} - \sum \alpha_j^2 \beta_j [\mathrm{k}]^{\alpha_j}}{(\sum \alpha_j \beta_j [\mathrm{k}]^{\alpha_j})^2}. \tag{3.33}$$

On multiplication by $[\mathrm{k}]/r = \sum \alpha_j \beta_j [\mathrm{k}]^{\alpha_j}$

$$\frac{\mathrm{d}r}{\mathrm{d}[\mathrm{k}]} \frac{[\mathrm{k}]}{r} = \frac{\mathrm{d}\log r}{\mathrm{d}\log[\mathrm{k}]} = 1 - p \tag{3.34}$$

or

$$p = 1 - \frac{\mathrm{d}\log r}{\mathrm{d}\log[\mathrm{k}]}. \tag{3.35}$$

Thus, on the basis of Eq. (3.35), the value of p can be calculated directly from the differential quotients at various points of the plotted curve $\log r = f(\log[\mathrm{k}])$. The desired value of $\alpha_{j\max}$ is the upper limiting value of p.

This is illustrated in Fig. 3.4, which presents the transformation $r = f(\log[\mathrm{k}]) \rightarrow p = f(\log[\mathrm{k}])$, for a model system with $\alpha_{j\max} = 6$.

3.4.2 Two- and multicomponent systems

Two-component equilibrium systems are investigated most frequently in solution chemistry. This is readily understandable: the study of the pair-wise interactions of the ligand(s), the metal ion(s) and the proton (i.e. the study of the protonation of the ligands, the hydrolysis of the metal ion and the formation of metal complexes with non-protonating ligands) is itself a very important field, but such studies must also be carried out if the equilibrium constants are required as auxiliary data in studies of more complicated equilibrium systems.

The r function can be applied to describe the interactions of the components in two-component equilibrium systems, in much the same way as discussed earlier. There is an essential difference, however: the r function must be defined for both components, and a two-variable function is obtained in both cases

$$r_1 = \frac{[\mathrm{k}_1]}{T_1} = \frac{[\mathrm{k}_1]}{\sum \alpha_{j1} \beta_j [\mathrm{k}_1]^{\alpha_{j1}} [\mathrm{k}_2]^{\alpha_{j2}}} \tag{3.36}$$

$$r_2 = \frac{[\mathrm{k}_2]}{T_2} = \frac{[\mathrm{k}_2]}{\sum \alpha_{j2} \beta_j [\mathrm{k}_1]^{\alpha_{j1}} [\mathrm{k}_2]^{\alpha_{j2}}}. \tag{3.37}$$

The r function is characteristic of self-association in one-component systems. This is also true for two-component systems, but with a modified chemical content. In one-component systems, the association means the formation of a chemical bond between two molecules (ions) of component k. In contrast, in two-component systems the 'self-association' generally occurs through the binding of more than one ion (molecule) of one component to the other component. In an aqueous solution of phosphoric acid, for instance, a trimeric proton species H_3^{3+} is not formed, whereas the species H_3PO_4 predominates in the phosphate–proton equilibrium system, at appropriately low pH. Accordingly, although Eqs (3.36) and (3.37) suggest that r_1 and r_2 express merely the self-association of k_1 and k_2, respectively, they are in fact functions which also characterize the *interaction between the two components.*

The new p functions are defined similarly to that for one-component systems

$$p_{11}=\frac{\sum\alpha_{j1}^2\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}}}{T_1}=\frac{\sum\alpha_{j1}^2\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}}}{\sum\alpha_{j1}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}}} \tag{3.38}$$

$$p_{22}=\frac{\alpha_{j2}^2\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}}}{T_2}=\frac{\sum\alpha_{j2}^2\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}}}{\sum\alpha_{j2}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}}}. \tag{3.39}$$

Like the r functions, the p_{11} and p_{22} function are characteristic not only of self-association, but also of the interaction of the two components. The interaction of the two components alone is expressed by the function in the numerator of which the associations containing both components feature. The weighted sums of the concentrations of these can also be referred to the total concentrations T_1 and T_2, leading to the definitions

$$\begin{aligned}p_{12}&=\frac{\sum\alpha_{j1}\alpha_{j2}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}}}{T_1}=\\&=\frac{\sum\alpha_{j1}\alpha_{j2}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}}}{\sum\alpha_{j1}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}}}\end{aligned} \tag{3.40}$$

$$\begin{aligned}p_{21}&=\frac{\sum\alpha_{j1}\alpha_{j2}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}}}{T_2}=\\&=\frac{\alpha_{j1}\alpha_{j2}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}}}{\alpha_{j2}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}}}.\end{aligned} \tag{3.41}$$

It follows from Eqs (3.40) and (3.41) that there is a simple connection between p_{12} and p_{21}

$$p_{12}/p_{21}=T_2/T_1\,. \tag{3.42}$$

In order to demonstrate some of the details of the chemical meaning of Eqs (3.36)–(3.41), we shall discuss some examples.

During the study of proton – ligand and ligand – metal ion interactions, the case is frequently encountered where the column vector relating to one of the components can only be 0 or 1. In the case of the protonation processes of ligands containing several functional groups (e.g. ethylenediamine or ethylenediaminetetraacetate) or the conjugate base ligands of weak acids, capable of the uptake of several protons (e.g. CO_3^{2-} or PO_4^{3-}), associations containing more than one ligand are not formed at all, or at extremely high concentrations only. In the composition matrix describing the protonation processes, therefore, every element of the column vector relating to the ligand as component (with the exception of the zero element for the proton) is 1.

A similar situation is encountered with the halo complexes of certain metal ions, for instance, in the concentration range where associations containing more than one metal ion (polynuclear complexes) are not yet formed. In these systems, the stoichiometric numbers for the metal ions as components are always 1, with the exception of 0 for the halide ion. The processes taking place in systems of the above two types are termed stepwise association. The numerator and denominator of the r and p functions relating to the ligand in such systems, and to the metal ion in the case of metal complexes, can be divided by the equilibrium concentration of the ligand or the metal ion. If the row number of these components is 1, Eqs (3.36), (3.38) and (3.40) are modified to

$$r_1 = \frac{[\mathrm{k}_1]}{T_1} = \frac{1}{\sum \alpha_{j1}\beta_j[\mathrm{k}_2]^{\alpha_{j2}}} \tag{3.43}$$

$$p_{11} = 1 \tag{3.44}$$

$$p_{12} = \frac{\sum \alpha_{j1}\alpha_{j2}\beta_j[k_2]^{\alpha_{j2}}}{\sum \alpha_{j1}\beta_j[k_2]^{\alpha_{j2}}}. \tag{3.45}$$

It is clear from Eqs (3.43) and (3.45) that in these cases r_1 depends only on the proton concentration in the case of ligand protonation processes, and only on the ligand concentration in the case of stepwise complex formation. Equation (3.44) means that an association containing more than one ligand is not formed even in the presence of protons, and an association containing more than one metal ion is not formed even in the presence of halide ligands. (Stepwise metal complex formation occurs not only with halides, but also in those systems where the ligand is the conjugate base of an acid. In the latter case, however, the systems are three-component ones, which will be dealt with in the following section. It will be seen in Section 3.5 that in these systems p_{12} corresponds to the formation function.)

If the conditions of stepwise association (stepwise protonation or stepwise complex formation) do not hold then r_1, r_2, p_{11}, p_{21} and p_{22} are real two-variable functions. In this case a three-dimensional plot of the functions would be necessary for a complete picture of the equilibrium system. In practice, however, the equilibrium or total concentration of one of the components being fixed. The fixed concentration is indicated in brackets after the lower index of the functions. $r_{1(T_1)}$ therefore means the r_1 function at fixed T_1 concentration. In this case the variation of $[\mathrm{k}_1]$ (or r_1) is possible only with the variation of $[\mathrm{k}_2]$ and the closely connected T_2. Since any of the r functions may be defined by fixing four different quantities ($[k_1]$, $[k_2]$, T_1 and T_2), a total of eight r functions may be given.

The independent variable of the r functions may be one of the three non-fixed total or equilibrium concentrations. This means a total of $3 \times 8 = 24$ different functions, characterizing the two-component systems. The functions and their differential correlations are illustrated in the Appendix on the H^+–$B(OH)_4^-$ polynuclear two-component system [12].

In systems, containing more than two components, the r and p functions describing the interaction of the components can be given as follows

$$r_i = \frac{[k_i]}{T_i} \tag{3.46}$$

$$p_{ik} = \frac{\sum \alpha_{ji}\alpha_{jk}\beta_j[k_1]^{\alpha_{j1}} \ldots [k_m]^{\alpha_{jm}}}{T_i}. \tag{3.47}$$

The number of the possibility of the different plotting modes (functions) increases enormously with the increase of the number of components. The differential connections between these functions [13–18], however, can be relatively easily derived as it is illustrated in the Appendix. The examples in the Appendix have been selected as to pertain to the principles of the various experimental and computational procedures applied in the study of equilibrium systems.

3.5 The complex formation function

3.5.1 The formation function for stepwise association

3.5.1.1 Definitions, basic equations

The phenomenon of stepwise association was touched on in Section 3.4. We speak of stepwise association in an equilibrium system containing a metal ion and a ligand, Me and L, when the interaction between them can be characterized by the following series of equilibrium processes and the corresponding series of equilibrium constants

$$\mathrm{Me} + \mathrm{L} \rightleftharpoons \mathrm{MeL} \quad K_1 = \frac{[\mathrm{MeL}]}{[\mathrm{Me}][\mathrm{L}]} \tag{3.48}$$

$$\mathrm{MeL} + \mathrm{L} \rightleftharpoons \mathrm{MeL}_2 \quad K_2 = \frac{[\mathrm{MeL}_2]}{[\mathrm{MeL}][\mathrm{L}]} \tag{3.49}$$

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

$$\mathrm{MeL}_{N-1} + \mathrm{L} \rightleftharpoons \mathrm{MeL}_N \quad K_N = \frac{[\mathrm{MeL}_N]}{[\mathrm{MeL}_{N-1}][\mathrm{L}]}. \tag{3.50}$$

These equilibrium constants are termed *stepwise stability constants*. In Eq. (3.50), N is the maximum number of ligand that can be taken up by a metal ion.

In the case of stepwise association, the composition matrix introduced in Section 3.2 can be given as in Table 3.4.

$$T_{\mathrm{Me}} = [\mathrm{Me}] + [\mathrm{MeL}] + [\mathrm{MeL}_2] + \ldots + [\mathrm{MeL}_N] = \sum \beta_{\mathrm{MeL}_j}[\mathrm{Me}]\,[\mathrm{L}]^j =$$
$$= [\mathrm{Me}] \sum \beta_{\mathrm{MeL}_j}[\mathrm{L}]^j$$

$$T_{\mathrm{L}} = [\mathrm{L}] + [\mathrm{MeL}] + 2[\mathrm{MeL}_2] + \ldots N[\mathrm{MeL}_N] =$$
$$= [\mathrm{L}] + \sum j\beta_{\mathrm{MeL}_j}[\mathrm{Me}]\,[\mathrm{L}]^j = [\mathrm{L}] + [\mathrm{Me}] \sum j\beta_{\mathrm{MeL}_j}[\mathrm{L}]^j.$$

Niels Bjerrum [1] introduced the concept of the average ligand number to characterize the extent of complex formation; this is the average number of ligands coordinated to one metal ion in a system containing the series of complexes Me, MeL, ..., MeL_N. Accordingly, the defining equation is

Table 3.4 Composition matrix describing stepwise complex formation, with equations defining formation constants, stepwise stability constants and total concentrations

	Components			
Species	Me	L	Formation constants	Stepwise stability constants
Me	1	0	$\beta_{\mathrm{Me}} = 1$	$K_0 = 1$
L	0	1	$\beta_{\mathrm{L}} = 1$	—
MeL	1	1	$\beta_{\mathrm{MeL}} = [\mathrm{MeL}]/[\mathrm{Me}]\,[\mathrm{L}]$	$K_1 = K_{\mathrm{MeL}} = \beta_{\mathrm{MeL}}$
MeL_2	1	2	$\beta_{\mathrm{MeL}_2} = [\mathrm{MeL}_2]/[\mathrm{Me}]\,[\mathrm{L}]^2$	$K_2 = K_{\mathrm{MeL}_2} = \beta_{\mathrm{MeL}_2}/\beta_{\mathrm{MeL}}$
⋮			⋮	⋮
MeL_j	1	j	$\beta_{\mathrm{MeL}_j} = [\mathrm{MeL}_j]/[\mathrm{Me}]\,[\mathrm{L}]^j$	$K_j = K_{\mathrm{MeL}_j} = \beta_{\mathrm{MeL}_j}/\beta_{\mathrm{MeL}_{j-1}}$
⋮			⋮	⋮
MeL_N	1	N	$\beta_{\mathrm{MeL}_N} = [\mathrm{MeL}_N]/[\mathrm{Me}]\,[\mathrm{L}]^N$	$K_N = K_{\mathrm{MeL}_N} = \beta_{\mathrm{MeL}_N}/\beta_{\mathrm{MeL}_{N-1}}$

$$\bar{n} = \frac{T_{\mathrm{L}} - [\mathrm{L}]}{T_{\mathrm{Me}}} = \frac{[\mathrm{MeL}] + 2[\mathrm{MeL}_2] + 3[\mathrm{MeL}_3] + \ldots + N[\mathrm{MeL}_N]}{[\mathrm{Me}] + [\mathrm{MeL}] + [\mathrm{MeL}_2] + \ldots + [\mathrm{MeL}_N]} \tag{3.51}$$

where T_{L} and T_{Me} are the total concentrations of ligand and metal ion, respectively, and [L] is the equilibrium concentration of the ligand. The difference between T_{L} and [L] is therefore the concentration of bound ligand. In a discussion of the stepwise complex formation processes, the constants β_{Me}, β_{MeL}, β_{MeL_j} ..., β_{MeL_N} describing the series of complexes Me, MeL, ..., MeL_j, ..., MeL_N are denoted by $\beta_0, \beta_1, \ldots, \beta_j, \ldots, \beta_N$.

Using the equations for the total ligand and total metal ion concentrations $\bar{n}$ can be expressed by means of the formation constants or the stepwise stability constants

$$\bar{n}=\frac{\sum\limits_{j=1}^{N} j\beta_j[\mathrm{L}]^j}{\sum\limits_{j=0}^{N} \beta_j[\mathrm{L}]^j} \tag{3.52}$$

$$\bar{n}=\frac{\sum\limits_{j=1}^{N} j\prod\limits_{i=1}^{j} K_i[\mathrm{L}]^j}{\sum\limits_{j=0}^{N} \prod\limits_{i=0}^{j} K_i[\mathrm{L}]^j} \tag{3.53}$$

where

$$\prod_{i=0}^{j} K_i=K_0K_1K_2\ldots K_j=\beta_j \quad \text{and} \quad K_0\equiv\beta_0\equiv 1.$$

Equations (3.52) and (3.53) lead to two important consequences. It may be seen that there is a possibility for the calculation of the values of the formation constants through the experimental determination of at least N different $\bar{n}$ and [L] data pairs. It is also clear that the average ligand number is independent of both the total concentration of the ligand and the total concentration of the metal ion, and depends only on the equilibrium concentration of the ligand. Solutions in which the values of T_{L} and T_{Me} differ, but [L] and consequently $\bar{n}$ are the same, are known as *corresponding solutions* [19].

Another concept used to describe an equilibrium system in the case of stepwise complex formation is the degree of formation of the system of compounds; this is defined by

$$\alpha=\frac{\bar{n}}{N}. \tag{3.54}$$

The degree of formation of the individual members in the series of complexes Me, MeL, ..., MeL$_N$ can be given by

$$\alpha_{\mathrm{MeL}_j}=\alpha_j=\frac{\beta_j[\mathrm{L}]^j}{\sum\limits_{k=0}^{N} \beta_k[\mathrm{L}]^k}. \tag{3.55}$$

α_{MeL_j} is generally called the mole fraction of the complex MeL$_j$. This name is ambiguous, however, for it does not have the same meaning as mole fraction in the strict thermodynamic sense. In the present book, α_{MeL_j} and similar quantities will be named *partial mole fractions*, the word partial indicating that the reference basis is not the total number of moles, but the total concentration of the metal ion. It may be seen from Eq. (3.55) that the partial mole fraction of the complex MeL$_j$ is also dependent on the equilibrium concentration of the ligand only.

At the same time, it is also clear that α_{MeL_j} is a function of all the formation constants; thus, if the partial mole fraction of any of the member of the series Me, MeL, . . ., MeL_N is measured for at least N different [L] values, the β_j values can be calculated.

The partial mole fraction relating to the metal ion can be given by

$$\alpha_{\mathrm{Me}} = \alpha_0 = \frac{1}{\sum_{j=0}^{N} \beta_j [\mathrm{L}]^j}. \tag{3.56}$$

Some remarks were made in connection with stepwise association in Section 3.4, during the discussion of the interactions of the components. It was seen that the r_1 and p_{12} functions (among others) are applicable to describe the degree of association. A comparison of Eqs (3.43) and (3.45) with Eqs (3.53) and (3.56) demonstrates that for stepwise complex formation $p_{12} = \bar{n}$ and $r_1 = \alpha_{\mathrm{Me}}$. The differential connection of p_{12} and r_1 is derived in the Appendix. This correlation can be written as

$$\frac{\mathrm{d}\log \alpha_{\mathrm{Me}}}{\mathrm{d}\log [\mathrm{L}]} = -\bar{n}. \tag{3.57}$$

The significance of Eq. (3.57) is that it creates a link between the two characteristic functions of stepwise complex formation. Thus, in the knowledge of the data on one of these functions, the data on the other can readily be calculated (by means of appropriate numerical of graphical integration or differentiation).

The correlations describing stepwise association, and their connections with one another, have been presented through the series of formation of the complexes Me, MeL, . . ., MeL_N. A phenomenon that is chemically basically

Table 3.5 Formation constants and stepwise protonation constants describing the stepwise protonation processes of ethylenediaminetetraacetate, and the equations defining the total concentrations

	Components			
Species	L	H	Formation constants	Stepwise stability constants
L	1	0	$\beta_{\mathrm{L}} = 1$	$K_0^{\mathrm{H}} = \mathrm{L} = 1$
H	0	1	$\beta_{\mathrm{H}} = 1$	—
HL	1	1	$\beta_{\mathrm{HL}} = [\mathrm{HL}]/[\mathrm{H}][\mathrm{L}]$	$K_1^{\mathrm{H}} = K_{\mathrm{HL}} = \beta_{\mathrm{HL}}$
$\mathrm{H_2L}$	1	2	$\beta_{\mathrm{H_2L}} = [\mathrm{H_2L}]/[\mathrm{H}]^2[\mathrm{L}]$	$K_2^{\mathrm{H}} = K_{\mathrm{H_2L}} = \beta_{\mathrm{H_2L}}/\beta_{\mathrm{HL}}$
$\mathrm{H_3L}$	1	3	$\beta_{\mathrm{H_3L}} = [\mathrm{H_3L}]/[\mathrm{H}]^3[\mathrm{L}]$	$K_3^{\mathrm{H}} = K_{\mathrm{H_3L}} = \beta_{\mathrm{H_3L}}/\beta_{\mathrm{H_2L}}$
$\mathrm{H_4L}$	1	4	$\beta_{\mathrm{H_4L}} = [\mathrm{H_4L}]/[\mathrm{H}]^4[\mathrm{L}]$	$K_4^{\mathrm{H}} = K_{\mathrm{H_4L}} = \beta_{\mathrm{H_4L}}/\beta_{\mathrm{H_3L}}$
$\mathrm{H_5L}$	1	5	$\beta_{\mathrm{H_5L}} = [\mathrm{H_5L}]/[\mathrm{H}]^5[\mathrm{L}]$	$K_5^{\mathrm{H}} = K_{\mathrm{H_5L}} = \beta_{\mathrm{H_5L}}/\beta_{\mathrm{H_4L}}$
$\mathrm{H_6L}$	1	6	$\beta_{\mathrm{H_6L}} = [\mathrm{H_6L}]/[\mathrm{H}]^6[\mathrm{L}]$	$K_6^{\mathrm{H}} = K_{\mathrm{H_6L}} = \beta_{\mathrm{H_6L}}/\beta_{\mathrm{H_6L}}$

different, but which is formally identical, is encountered in the protonation of ligands capable of taking up more than one proton. To illustrate this formal identity, Table 3.5 presents a composition matrix describing the protonation processes for a ligand (e.g. ethylenediaminetetraacetate) capable to take up 6 protons, with the formation constants of the proton complexes H_jL, the corresponding stepwise stability constants of the proton complexes, and the equations defining the total concentrations

$$T_L = [L]+[HL]+[H_2L]+[H_3L]+[H_4L]+[H_5L]+[H_6L] = \sum_{j=0}^{6} \beta_{H_jL}[H]^j[L] = [L]\sum_{j=0}^{6} \beta_{H_jL}[H]^j$$

$$T_H = [H]+[HL]+2[H_2L]+3[H_3L]+4[H_4L]+5[H_5L]+6[H_6L] = [H]+\sum_{j=0}^{6} j\beta_{H_jL}[L][H]^j = [H]+[L]\sum_{j=0}^{6} \beta_{H_jL}[H]^j$$

$$\bar{n}_H = \frac{T_H-[H]}{T_L} = \frac{\sum_{j=0}^{6} j\beta_{H_jL}[H]^j}{\sum_{j=0}^{6} \beta_{H_jL}[H]^j}.$$

The formal identity is seen strikingly if Tables 3.4 and 3.5 are compared; the only differences are that H takes the place of L, and L takes the place of Me. Accordingly, with these same substitutions, Eqs (3.48)–(3.57) are suitable for the description of stepwise protonation too.

To differentiate between the parameters in these two types of systems, the constants K_j and β_j are replaced by K_j^H and β_j^H, $\bar{n}$ by $\bar{n}_H$, and α_{MeL_j} by α_{H_jL} in the case of protonation processes.

3.5.1.2 Statistical considerations

The complex formation function was analysed in detail by Jannik Bjerrum [2]. His considerations were extended by Sen [20], who took into account the properties of the chelate-forming ligands and the various geometrical arrangements of the coordination sites of the metal ions. The values of the formation constants and the ratios of the stepwise constants depend on numerous factors. However, if it is assumed that the coordination sites are strictly equivalent, and that this equivalence is maintained during stepwise complex formation, then the ratios of the stepwise stability constants are governed only by the statistical laws. This means that the probability of release of a monodentate ligand L from the complex MeL_j is proportional to the number of occupied coordination sites (j), while the probability of uptake of a ligand L is proportional to the number of available coordination sites $(N-j)$. Under these conditions, the following equation holds

$$K_1 : K_2 = \frac{N}{1} : \frac{N-1}{2}; \qquad K_j : K_{j+1} = \frac{(N-j+1)(j+1)}{j(N-j)} \tag{3.58}$$

In the case of multidentate ligands, these ratios will naturally be different. For bidentate ligands, with the assumption of an octahedral configuration, the following expression arises for the ratio of the three stepwise stability constants

$$K_1 : K_2 : K_3 = \frac{12}{5} : \frac{5}{2} : \frac{4}{15}. \tag{3.59}$$

Table 3.6 gives the quotients of the stepwise stability constants, calculated with Eq. (3.58) for various N values. The final column of the Table contains the quotients of the stability constants K_1 and K_N. It is interesting to observe that the value of K_1/K_N calculated on a statistical basis coincides with N^2.

It can be seen that the statistical values of K_j/K_{j+1} vary regularly, in an interval with almost the same order of magnitude. Table 3.7 lists the ratios of some stepwise stability constants in the equilibrium systems of certain metal complexes.

Table 3.6 Statistically calculated ratios of stepwise stability constants

N	K_1/K_2	K_2/K_3	K_3/K_4	K_4/K_5	K_5/K_6	K_1/K_N
2	4	—	—	—	—	4
3	3	3	—	—	—	9
4	2.67	2.25	2.67	—	—	16
5	2.50	2	2	2.50	—	25
6	2.40	1.88	1.78	1.88	2.40	36

Table 3.7 Stepwise stability constant ratios in the equilibrium systems of some complexes

	N	K_1/K_2	K_2/K_3	K_3/K_4	K_4/K_5	K_5/K_6
Ag^+-NH_3	2	0.23	—	—	—	—
$Ag^+-SO_4^{2-}$	2	1.51	—	—	—	—
$Hg^{2+}-SO_4^{2-}$	2	1.50	—	—	—	—
$TiO^{2+}-SO_4^{2-}$	2	15.8	—	—	—	—
$Cd^{2+}-I^-$	4	20.4	0.04	4.67	—	—
$Hg^{2+}-I^-$	4	83.5	1.9×10^7	20.0	—	—
$VO^{2+}-F^-$	4	10.5	3.02	29.5	—	—
$Pd^{2+}-Cl^-$	4	6.31	7.24	10.0	—	—
$Al^{3+}-F^-$	6	12.9	14.8	12.9	12.9	14.45
$Zr^{4+}-F^-$	6	30.2	31.6	9.33	1.58	4.67
$Hf^{4+}-F^-$	6	16.6	5.01	1.58	16.6	10.2
$Bi^{3+}-Cl^-$	6	16.6	0.19	12.6	1.35	6.02

Table 3.8 Ratios of stepwise protonation constants of some α, ω-diamines and α, ω-dicarboxylates, as functions of the number of carbon atoms

	K_1^H/K_2^H	
n	Diamines	Dicarboxylates
2	363	275
3	55	339
4	16	16
5	8.7	7.4
6	5.5	5.2

Table 3.8 gives the ratios of the two protonation constants for some α, ω-diamines and α, ω-dicarboxylates. It is clear from the tabulated data that as the number of carbon atoms increases, the value of K_1^H/K_2^H approaches the value of 4 corresponding to the statistical case. (The well-known 'sawtooth' dependence can be seen too for the quotients for the dicarboxylic acids.)

The data in Tables 3.7–3.8 reveal that the ratios of the stepwise stability constants do not agree in general with the statistical values. Thus, besides the statistical effect, other factors too must be considered.

J. Bjerrum took these factors into account by means of the spreading factor x

$$\frac{K_j}{K_{j+1}} = f_j x^2 \tag{3.60}$$

where f_j is the value of the quotient of the constants to be expected on a statistical basis.

The spreading factor may assume a value between 0 and ∞. If the statistical conditions hold, $x = 1$. It may also occur that the value of the distribution factor is constant for all of the constant ratios in a stepwise equilibrium system. Before a discussion of this general case, some considerations will be given on the simplest stepwise complex equilibrium system ($N = 2$). Applying Eq. (3.60) to systems with $N = 2$.

$$\frac{K_1}{K_2} = 4x^2. \tag{3.61}$$

K_1 and K_2 can also be expressed by means of the spreading factor and the average stability constant

$$\log \bar{K} = (\log K_1 + \log K_2)/2 \qquad \bar{K} = \sqrt{K_1 K_2} \tag{3.62}$$

as follows

$$K_1 = 2x\bar{K} \qquad K_2 = \bar{K}/2x. \tag{3.63}$$

From Eqs (3.63) and (3.62)

$$\bar{n}=\frac{2x\bar{K}[\mathrm{L}]+2\bar{K}^2[\mathrm{L}]^2}{1+2x\bar{K}[\mathrm{L}]+\bar{K}^2[\mathrm{L}]^2}. \tag{3.64}$$

It follows from Eq. (3.64) that at $\bar{n}=1$ the product of the equilibrium ligand concentration and the average stability constant has a value of 1, i.e. the average stability constant is the reciprocal of the equilibrium ligand concentration at the point $\bar{n}=1$.

The shape of the complex formation curve $\bar{n}=f(\log \mathrm{L})$ depends on the value of the spreading factor. The connection between the shape of the curve and the spreading factor is illustrated in Fig. 3.5, where $\bar{n}$ is plotted against log [L] at various x values, with $\bar{K}=1$ and $N=2$. At $x>100$, the complexes are formed in two completely separate steps; as x decreases, the separation of the two steps decreases. At $x=4$, the three inflexion points coalesce into one inflexion point. Here, therefore, the separation of the two steps ceases. Then, at $x=0$, where the uptake of the two ligands proceeds in one step, the formation curve attains the limiting value corresponding to the highest possible slope.

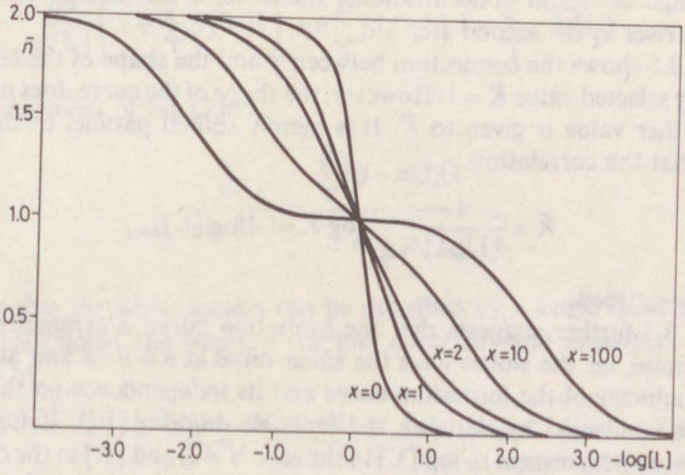


Fig. 3.5 Average ligand number as a function of the negative logarithm of the free ligand concentration, with $\bar{K}=1$, at various values of the spreading factor (x)

The chemical interpretation of the events in Fig. 3.5 is similar to that discussed in connection with di- and trimerization in one-component systems (Section 3.4.1.2). The similarity can be seen well if it is considered that the distribution factor x is directly proportional to the stability of the complex MeL against "disproportionation" into the metal ion Me and the complex $\mathrm{MeL_2}$. The equilibrium constant of the process

$$\mathrm{Me} + \mathrm{MeL}_2 \rightleftharpoons 2\mathrm{MeL} \qquad K^* = \frac{[\mathrm{MeL}]^2}{[\mathrm{Me}]\,[\mathrm{MeL}_2]}$$

can be given by means of the appropriate formation constants, stepwise stability constants and spreading factor

$$K^* = \frac{\beta_1^2}{\beta_2} = \frac{K_1}{K_2} = 4x^2. \tag{3.65}$$

A high value of x therefore means that as the ligand concentration is increased, the complex MeL is formed, $\bar{n}$ assuming a value of 1. Conversion of MeL into MeL_2 occurs only if the ligand concentration is elevated considerably. In a broad range of ligand concentrations, therefore, $\bar{n}$ remains at around 1; it gradually rises in the second step.

Figure 3.5 shows the connection between x and the shape of the curve at an arbitrarily selected value $\bar{K} = 1$. However, the shape of the curve does not change if some other value is given to $\bar{K}$. It is merely shifted parallel to the log [L] axis, so that the correlation

$$\bar{K} = \frac{1}{[\mathrm{L}]_{\bar{n}=1}} \qquad \log \bar{K} = -\log [\mathrm{L}]_{\bar{n}=1} \tag{3.66}$$

should be satisfied.

Figure 3.5 further suggests that the formation curve is symmetrical about the mid-point, i.e. the slopes have the same value at $\bar{n} = 1 - d$ and at $\bar{n} = 1 + d$.

The symmetry of the formation curve and its independence on the value of $\bar{K}$ can be confirmed by deriving the function $\mathrm{d}\bar{n}/\mathrm{d}(\log [\mathrm{L}])$. If Eq. (3.53) is differentiated with respect to log [L] in the case $N = 2$, and [L] in the differential function is replaced by the inverse function of Eq. (3.53), together with the substitutions $\bar{n} = 1 + d$ and $\bar{n} = 1 - d$, the following equation is obtained in both cases

$$\frac{\mathrm{d}\bar{n}}{\mathrm{dlog}\,[\mathrm{L}]} = 2.303 \cdot \frac{1 - d^2 + x^2 d^2 - \sqrt{x^4 d^2 + (1 - d^2) x^2}}{1 - x^2}. \tag{3.67}$$

Equation (3.67) demonstrates that the slopes at distances d in both directions from the mid-point are the same, i.e. the function is symmetrical. At the same time, the value of the slope does not depend on the value of $\bar{K}$, but merely on the spreading factor x. Thus, a variation in $\bar{K}$ results in a parallel shift only At $d = 0$, i.e. at the mid-point of the curve, Eq. (3.67) simplifies to the correlation derived by Bjerrum

$$\frac{\mathrm{d}\bar{n}}{\mathrm{dlog}\,[\mathrm{L}]} = 2.303 \frac{1 - x}{1 - x^2} = \frac{2.303}{1 + x}. \tag{3.68}$$

Accordingly, it appears that the position of the formation curve on the log [L] scale depends on the value of $\bar{K}$, and its shape on the value of x, i.e. K_1/K_2. Hence, all those parameters of the experimentally determined formation curve which are connected with the position on the log [L] scale or with the shape, can be utilized to determine the numerical values of the constants. At the beginning of the 1950's, a number of graphical procedures were developed on this basis, for calculation of the stability constants. The most significant of these were the correction term [21], projection strip [22] and curve fitting [23] methods.

For systems with $N>2$, the correlation between the slope of the formation curve and the spreading factor can be obtained from the rearranged and differentiated form of (3.52)

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}[\mathrm{L}]}\left(1+\sum_1^N \beta_j[\mathrm{L}]^j\right)+\bar{n}\sum_1^N j\beta_j[\mathrm{L}]^{j-1}=\sum_1^N j^2\beta_j[\mathrm{L}]^{j-1}. \tag{3.69}$$

By rearrangement of Eq. (3.69)

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}\ln[\mathrm{L}]}=\frac{\sum_1^N j(j-\bar{n})\beta_j[\mathrm{L}]^j}{1+\sum_1^N \beta_j[\mathrm{L}]^j}. \tag{3.70}$$

Assuming that the whole system can be described by a single spreading factor, i.e. Eq. (3.60) holds, the stepwise stability constants and formation constants are given by

$$K_j=\frac{(N-j+1)}{j}\bar{K}\cdot x^{(N+1-2j)} \tag{3.71}$$

$$\beta_j=\frac{N!}{j!(N-j)!}\bar{K}^j\cdot x^{j(N-j)}=\binom{N}{j}\bar{K}^j x^{j(N-j)}. \tag{3.72}$$

If Eq. (3.72) is substituted into Eq. (3.53), the formation function is as follows

$$\bar{n}=\frac{\sum_1^N j\frac{N!}{(N-j)!j!}\bar{K}^j[\mathrm{L}]^j x^{j(N-j)}}{\sum_1^N \frac{N!}{(N-j)!j!}\bar{K}^j[\mathrm{L}]^j x^{j(N-j)}}. \tag{3.73}$$

Analysis of Eq. (3.73) reveals that at the mid-point of the formation curve ($\bar{n}=N/2$) the product of the free ligand concentration and the average stability constant is 1, just as for systems with $N=2$. Consequently, the following equation is obtained for the slope at the mid-point

$$\Delta = \frac{\sum_{1}^{N} j\left(j-\frac{N}{2}\right)\binom{N}{j}x^{j(N-j)}}{1+\sum_{1}^{N}\binom{N}{j}x^{j(N-j)}}. \tag{3.74}$$

3.5.1.3 Characteristic points of the formation curve

3.5.1.3.1 Half-value points of the formation curve

If two consecutive steps of the complex formation process are separated, i.e. if $x \geqq 100$, then only two complexes can exist in significant concentration in the presence of each other

$$T_{\mathrm{Me}} = \mathrm{MeL}_{j-1} + \mathrm{MeL}_j . \tag{3.75}$$

If

$$\bar{n} = j - \frac{1}{2} = \bar{n}^x \tag{3.76}$$

i.e. the average ligand number has its half-value, then

$$[\mathrm{MeL}_{j-1}] = [\mathrm{MeL}_j] \tag{3.77}$$

i.e.

$$K_j = \frac{1}{[\mathrm{L}]_{\bar{n}^x}}. \tag{3.78}$$

It can readily be seen that Eq. (3.77) will also hold if the distribution factor is not too large, but the value of the average ligand number for the other complexes at the half-value point is also $j - \frac{1}{2}$

$$\frac{\sum\limits_{j-1 \neq i \neq j}^{N} i[\mathrm{MeL}_i]}{\sum\limits_{j-1 \neq i \neq j}^{N} [\mathrm{MeL}_i]} = j - \frac{1}{2}. \tag{3.79}$$

The following two correlations must then hold

$$\beta_j[\mathrm{L}]_{\bar{n}^x}^{j} = \beta_{j-1}[\mathrm{L}]_{\bar{n}^x}^{(j-1)} \tag{3.80}$$

$$\frac{\sum\limits_{j-1 \neq i \neq j}^{N} j\beta_j[\mathrm{L}]_{\bar{n}^x}^{j}}{\sum\limits_{j-1 \neq i \neq j}^{N} j[\mathrm{L}]_{\bar{n}^x}^{j}} = j - \frac{1}{2}. \tag{3.81}$$

Consequently, for all j values $1/K_j$ is the root of the equation

$$\sum_{i=0}^{N}(2j-1-2i)\beta_i[\mathrm{L}]^{i}_{\bar{n}^{*}}=0. \tag{3.82}$$

From Eqs (3.82) and (3.78)

$$\sum_{i=0}^{N}(2j-1-2i)\frac{\beta_i}{K_j^{i}}=0. \tag{3.83}$$

Thus, Eq. (3.78) will hold if the spreading factor is very large, or if there is a definite correlation between the stability constants. This correlation is particularly simple if $\bar{n}^*$ is the same as $\bar{n}$ for the complexes MeL_{j-1-i} and MeL_{j+1}. This means that the stepwise stability constants form a geometric series

$$\begin{gathered}\beta_j[\mathrm{L}]^{j}_{\bar{n}^{*}}=\beta_{j-1}[\mathrm{L}]^{j-1}_{\bar{n}^{*}}\\ \beta_{j+1}[\mathrm{L}]^{j+1}_{\bar{n}^{*}}=\beta_{j-2}[\mathrm{L}]^{j-2}_{\bar{n}^{*}}\end{gathered} \tag{3.84}$$

i.e.

$$\beta_{j+1}[\mathrm{L}]^{j+1}_{\bar{n}^{*}}=\beta_{j-1-i}[\mathrm{L}]^{j-1-i}_{\bar{n}^{*}}$$

$$\left(\frac{\beta_j}{\beta_{j-1}}\right)^{3}=\frac{\beta_{j+1}}{\beta_{j-2}} \tag{3.85}$$

and

$$\left(\frac{\beta_j}{\beta_{j-1}}\right)^{2i+1}=\frac{\beta_{i+j}}{\beta_{j-1-i}} \tag{3.86}$$

which are equivalent to

$$K_j^{2}=K_{j-1}\cdot K_{j+1} \tag{3.87}$$

and

$$K_j^{(2i+1)}=\prod K_{j-1}\cdot\ldots\cdot K_{j+i}\,. \tag{3.88}$$

The meaning of these equations is that the ratio of the stepwise constants is constant for the whole system. Instead of the usual N, such systems can be described by two constants: one of the stepwise constants, and the quotient of the constants. This condition is the basis of the Dyrssen–Sillén two-parameter equation [24] and some other methods used for calculation of the stepwise constants. Van Panthaleon van Eck [25] found that the following correlation holds for a number of complex equilibrium systems

$$\log K_j=\log K_1-2\lambda(j-1)\,. \tag{3.89}$$

Equation (3.89) expresses the constancy of the quotient of the stepwise constants

$$\frac{K_j}{K_{j+1}}=10^{2\lambda}, \tag{3.90}$$

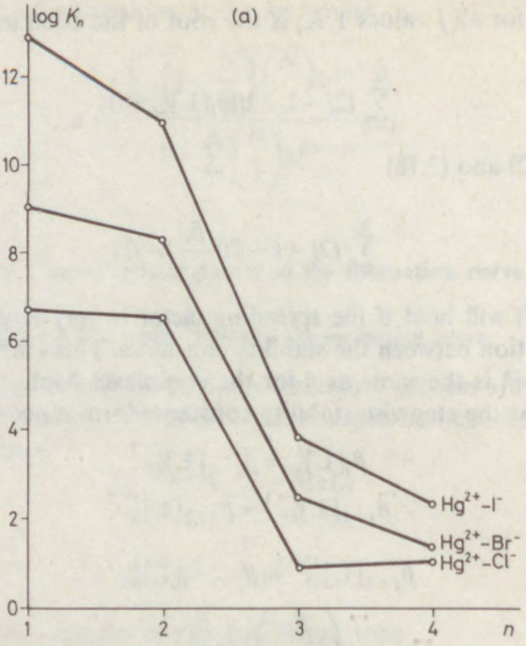


Fig. 3.6 (a) log K_n as a function of n in various Hg^{2+}–halide systems; (b) log β_n/n as a function of n in various Hg^{2+}–halide systems →

If Eq. (3.58) held, then the value of log K_j would be given by the following equation

$$\log K_j = \log K_1 - \log N \cdot j + \log (N - j + 1) . \tag{3.91}$$

It is clear from Figs 3.6 (a) and 3.6 (b) that the Van Panthaleon van Eck equation holds instead of Eq. (3.91) for the systems depicted. This means that in these and similar systems the statistical factors are compensated by other effects, the product of the corresponding statistical factor and the spreading factor remaining constant

$$\frac{K_j}{K_{j+1}} = f_j x_j^2 = 10^{2\lambda} . \tag{3.92}$$

Equation (3.89) generally holds only when the polarization effects are not too significant. Even in these systems, however, the correlation may in part be true, as can be seen for the mercury(II)–halide systems in Figs 3.6 (a) and 3.6 (b). These Figures depict the correlations corresponding to both Eqs (3.89) and (3.93). The latter can be derived from Eq. (3.89) by taking into consideration the formation constants

$$\frac{\log \beta_j}{j} = \log \beta_1 - (j - 1) . \tag{3.93}$$

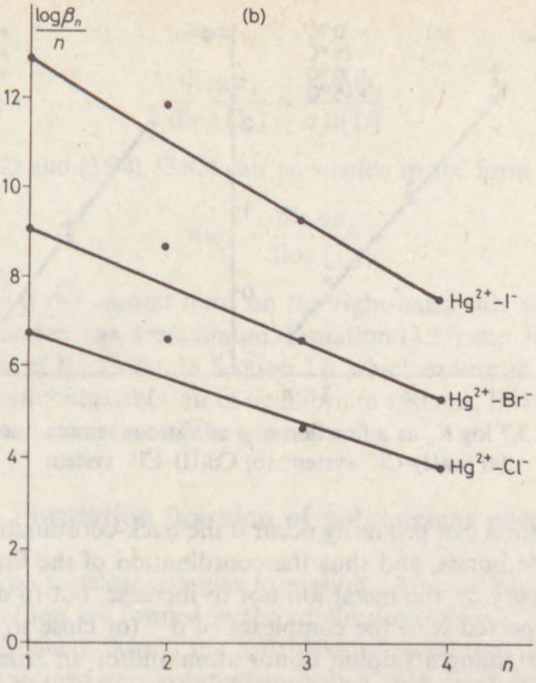


Fig. 3.6 (b)

It is worthwhile mentioning that in systems where Eqs (3.89) and (3.91) do not hold, i.e. where covalent bonding predominates, the ratio K_j/K_{j+1} varies much more with temperature than in systems where the coordinate bonds are mainly electrostatic in nature. Figures 3.7 (a) and 3.7 (b) demonstrate that in the tin(II)–chloride and cadmium(II)–chloride systems the correlation holds only at certain temperatures. The number of systems satisfying the relation $K_j < K_{j+1}$ is fairly small. This sequence generally holds for the silver-ammine complexes [26–29], and it has also been reported to hold for Hg(II)–OH^- [30], Zn(II)–NH_3 [31], Co(II)–thioglycollic acid [32], Cu(II)–diethylbiguanidine [33], Cd(II), Mg(II) and Ni(II)–*o*-ethylthiobenzoic acid [34], Co(II)–1-nitroso-2-naphthol [35], and in the equilibrium systems of divalent transition metal ions with certain pyrazolone derivatives [36–38], Fe(II)–1,10-phenanthroline [39–40], Fe(II)–1,10-phenanthroline derivatives [41–42], Cu(II)–dimethylglyoxime [43–44] and Cu(II)–dimethylglyoxime derivatives [45].

Experimental data smaller than the statistically calculated K_j/K_{j+1} value have recently been found in a number of equilibrium systems [46–61]. A constant ratio smaller than the statistical value means that the filling of some coordination site of the metal ion increases the possibility of incorporation of the next ligand.

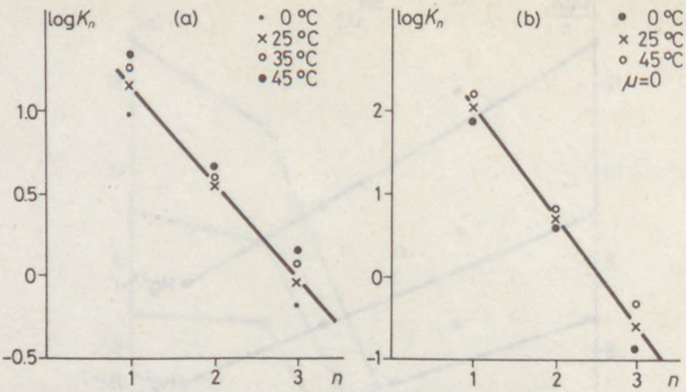


Fig. 3.7 log K_n as a function of n at various temperatures.
(a) Sn(II)–Cl$^-$ system; (b) Cd(II)–Cl$^-$ system

This phenomenon can primarily occur if the back-coordination is important in the coordinate bonds, and thus the coordination of the first ligand causes the electron density on the metal ion not to increase, but to decrease. This is mainly to be expected with the complexes of d^{10} (or close to d^{10}) metal ions with ligands containing a sulphur donor atom and/or an aromatic π-system.

A constant quotient smaller than statistical is also found if the coordination of the first ligand alters the geometry of the coordination sphere of the metal ion, thereby facilitating the entry of the next ligand.

This phenomenon is observed with complexes of Ag^+ and Hg^{2+}. A similar consideration relates to stepwise protonation processes [55].

It should be noted that if the value of K_1/K_2 is small, the complex MeL is formed only in low concentration and consequently the stepwise constants K_1 and K_2 can generally be determined only with appreciable inaccuracy [62]; the value of β_2 can only be calculated accurately.

3.5.1.3.2 Integer points of the formation curve

We have seen that the chemical meaning of the half-value points on the formation curve depends on the ratio of the stability constants.

The integer points, however, always have a definite physical content, independently of the quotient of the constants: at the integer points $j=\bar{n}$, the partial mole fraction of the complex MeL_j always has a maximum. This can readily be seen after differentiation and rearrangement of Eq. (3.55)

$$\frac{d\alpha_j}{d[L]}\left(1+\sum_1^N \beta_k[L]^k\right)+\alpha_j\sum_1^N k\beta_k[L]^{k-1}-j\beta_j[L]^{j-1}=0\,. \qquad (3.94)$$

We also have

$$\frac{\mathrm{dlog}\,\alpha_j}{\mathrm{dlog}\,[\mathrm{L}]}=\frac{[\mathrm{L}]\mathrm{d}\alpha_j}{\alpha_j\mathrm{d}[\mathrm{L}]}. \tag{3.95}$$

From Eqs (3.52) and (3.94), (3.95) can be written in the form

$$\bar{n}=j-\frac{\mathrm{dlog}\,\alpha_j}{\mathrm{dlog}\,[\mathrm{L}]}. \tag{3.96}$$

It is obvious that the second term on the right-hand side will be zero if the partial mole fraction has a maximum. Equation (3.57) can readily be seen to be a special case of Eq. (3.96). In Section 3.6, which examines the rules relating to the concentration distribution of equilibrium systems, this same correlation is obtained as a special case of the general rules.

3.5.2 Formation function of polynuclear complexes

We speak of polynuclear complex formation if associations containing more than one central ion are formed in the equilibrium system. This phenomenon is particularly frequent during the hydrolysis of metal ions. The hydrolysis of metal ions was studied very comprehensively and in great detail by Sillén and his coworkers [63], and a large proportion of the findings on the formation functions of polynuclear complexes are due to the Sillén school.

In the course of the discussion on formation curves describing stepwise equilibria, it was seen that $\bar{n}$ is independent of the concentration of the central ion, the corresponding r and p functions are single-variable functions, r coincides with α_{Me} and p with $\bar{n}$. The r and p functions are naturally also suitable for describing polynuclear equilibrium systems. For this purpose, however, use may also be made of the correlations corresponding to the equations defining the formation functions $\bar{n}=(T_{\mathrm{L}}-[\mathrm{L}])/T_{\mathrm{Me}}$ and $\bar{n}_{\mathrm{H}}=(T_{\mathrm{H}}-[\mathrm{H}])/T_{\mathrm{L}}$. By definition, $\bar{n}$ is the average number of ligands (protons) bound to a central ion. If the central ion is chosen as the first component, and the ligand as the second one, the formation function can be given in general by

$$\bar{n}=\frac{\sum\alpha_{j2}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}}-[\mathrm{k}_2]}{\sum\alpha_{j1}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}}}. \tag{3.97}$$

The value of $\bar{n}$ is directly related to r_2

$$\bar{n}=\frac{T_2-[\mathrm{k}_2]}{T_1}=\frac{T_2}{T_1}\left(1-\frac{[\mathrm{k}_2]}{T_2}\right)=\frac{T_2}{T_1}(1-r_2). \tag{3.98}$$

Via Eq. (3.98), therefore, if r_2 is known, $\bar{n}$ can be calculated, and vice versa. If the differential connection of the two functions is derived at $T_2=$constant or

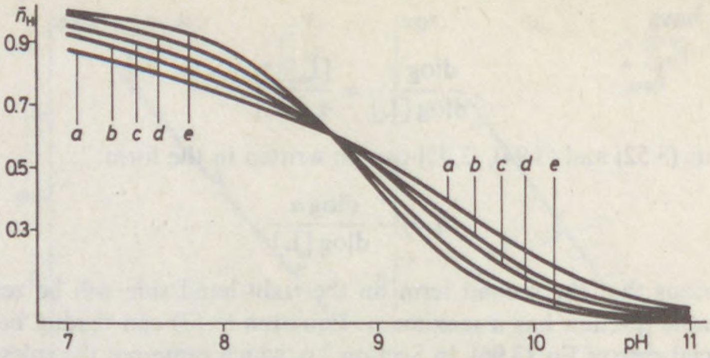


Fig. 3.8 Formation curves in the H^+–$B(OH)_4^-$ system at various total borate concentrations.
a — $T_B = 0.5$, *b* — $T_B = 0.3$; *c* — $T_B = 0.2$; *d* — $T_B = 0.1$; *e* — $T_B = 10^{-5}$ *M*

$T_1 =$ constant, the formation function of polynuclear complexes too can readily be fitted into the overall system of differential connections discussed in the Appendix.

The formation function for polynuclear complexes differs fundamentally from the formation function for stepwise association in that the shape of the curve depends on the total concentration of the central ion too. This is illustrated in Fig. 3.8, which shows the formation curves in the borate–proton equilibrium system at various total borate concentrations. Figure 3.8 reveals that as the total borate concentration decreases, the curves tend towards the formation curve describing the one-step protonation process ($H + B \rightleftharpoons HB$).

The shapes of the formation curves for polynuclear complexes and their dependence on the metal ion concentration are characteristic of the compositions of the associations predominating in the system. Accordingly, the compositions of the predominant associations can be estimated to a good approximation from certain parameters of the curves. This is very important prior to the computer evaluation of the experimental results, during the setting-up of a suitable chemical model. The shapes and concentration-dependences of these curves, the compositions of the main associations, and the correlations between them will therefore be surveyed in Chapter 5.

3.6 Rules of concentration distribution in complex equilibrium systems

3.6.1 Introduction

The equilibria in complex systems are most often illustrated by the concentration distribution curves. These are obtained by plotting the concentrations of the complexes formed as a function of the equilibrium concentration, or of the negative logarithm of the equilibrium concentration of one of the components.

The rules of concentration distribution for the stepwise formation of mononuclear complexes (and the stepwise protonation of ligands not forming polyacids) are well known; they were dealt with in Section 3.5.

The rules of concentration distribution relating to more complicated equilibrium systems (polynuclear complexes, mixed ligand complexes, protonated complexes and hydroxo complexes) have been clarified in recent years [64–71]; primarily these results will be discussed in the following Section.

3.6.2 Two-component systems

3.6.2.1 Concentration distribution during stepwise complex formation

In the case of stepwise complex formation, the increase of the ligand concentration is accompanied by a monotonous decrease of the metal ion concentration and by a monotonous increase of the concentration of the complex containing the maximum number of ligands, while the concentrations of the intermediate complexes vary according to maximum curves. The maximum concentrations of the intermediate complexes are to be found at the integer points on the formation curve. The concentrations of the complexes MeL_{j-1} and MeL_j are equal at the ligand concentration agreeing with the equilibrium constant for the process $\mathrm{MeL}_j \rightleftharpoons \mathrm{MeL}_{j-1} + \mathrm{L}$.

One essential feature of the concentration distribution of complexes formed in a stepwise equilibria is that the partial mole fractions (α_j) referred to the total metal ion concentration depend only on the equilibrium concentration of the ligand. Thus, if the equilibrium concentration of the ligand is known, the concentration distribution can be read off directly at any total metal ion or total ligand concentration. From a practical, and mainly an analytical chemistry aspect, however, a knowledge of the distribution curves is not always sufficient: in general, we know not the equilibrium concentration of the ligand, but the total concentrations of the components. If the concentration distribution is to be calculated, the equations

$$T_{\mathrm{Me}}=\sum_{0}^{N}[\mathrm{MeL}_j]=[\mathrm{Me}]\sum_{0}^{N}\beta_j[\mathrm{L}]^j \tag{3.99}$$

and

$$T_{\mathrm{L}}=[\mathrm{L}]+[\mathrm{Me}]\sum_{0}^{N}j\beta_j[\mathrm{L}]^j=[\mathrm{L}]+\bar{n}T_{\mathrm{Me}} \tag{3.100}$$

must be solved first for [L] and [Me] by some iteration procedure, then the concentration distribution of the complexes can be calculated.

Equations (3.99) and (3.100) also give the possibility for the construction of nomograms from which the equilibrium concentration of the ligand can be read off directly. Figure 3.9 (taken from Butler [77]) depicts a nomogram for the Cd^{2+}–Cl^- system.

The dashed line denotes a 0.1 *M* $CdCl_2$ solution; from this, the equilibrium concentration of the chloride ion can be read off directly as 0.09 *M*. This can

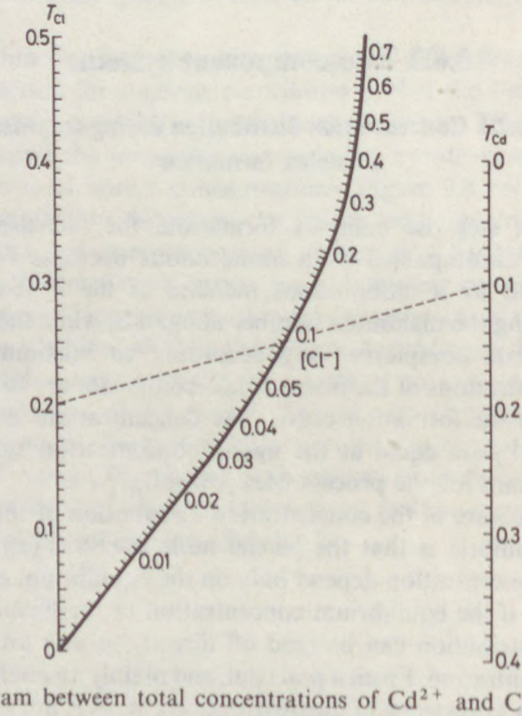


Fig. 3.9 Nomogram between total concentrations of Cd^{2+} and Cl^- and equilibrium concentration of Cl^- [77]
(Reproduced with permission from: Butler, J. N., *Ionic Equilibrium*, Addison-Wesley, Reading, 1964, p. 335)

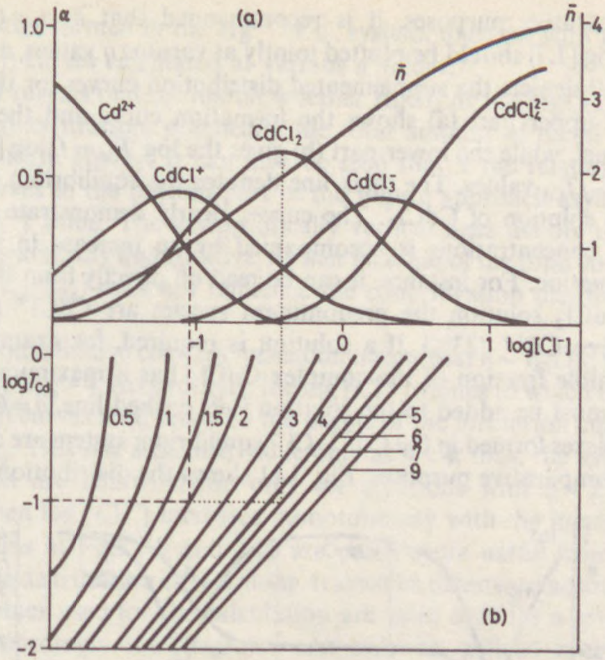


Fig. 3.10 Extended concentration distribution diagram of the Cd^{2+}–Cl^- equilibrium system.
(a) Formation curve and concentration distribution of complexes; (b) $\log T_{Cd} = f(\log[Cl^-])$ functions at various concentration ratios $q = T_{Cl^-}/T_{Cd}$ [64]
(Reproduced with permission from *Talanta*, **29**, 473 (1982))

be used with explicit formulae to calculate the partial mole fractions of the individual complexes.

However, the distribution of the complexes can similarly be read off directly, without separate calculation, if the $\bar{n}, \alpha_j = f(\log[L])$ curves are given supplemented with the total concentrations [64].

One possibility for this supplementation is given by the fact that at the constant concentration ratio $q = T_L/T_{Me}$ the parameter T_{Me} too can be expressed as a function of the equilibrium concentration of the ligand

$$q = \frac{T_L}{T_{Me}} = \frac{[L]}{T_{Me}} + \bar{n}\,. \tag{3.101}$$

Substitution of Eq. (3.52) into Eq. (3.101) gives

$$T_{Me} = \frac{\sum_0^N \beta_j [L]^{j+1}}{\sum_0^N (q-j)\beta_j [L]^j}\,. \tag{3.102}$$

For comparative purposes, it is recommended that $\bar{n}$, $\alpha_j = (\log[\mathrm{L}])$ and $\log T_{\mathrm{Me}} = f(\log[\mathrm{L}])$ should be plotted jointly at various q values, as in Fig. 3.10.

Figure 3.10 depicts the supplemented distribution curves for the $\mathrm{Cd^{2+}}$–$\mathrm{Cl^-}$ system. The upper part (a) shows the formation curve and the distribution curves as usual, while the lower part (b) gives the $\log T_{\mathrm{Cd}} = f(\log[\mathrm{Cl^-}])$ curves at various $T_{\mathrm{Cl}}/T_{\mathrm{Cd}}$ values. The thick line denotes the equilibrium conditions in the aqueous solution of $\mathrm{CdCl_2}$. The curves clearly demonstrate that increase of the total concentrations is accompanied by an increase in the degree of complex formation. For instance, it can be read off directly from the curves that in 0.1 *M* $\mathrm{CdCl_2}$ solution the predominant species are $\mathrm{CdCl^+}$ (44%), $\mathrm{CdCl_2}$ (31%) and free $\mathrm{Cd^{2+}}$ (23%). If a solution is required, for example, in which the partial mole fraction of the complex $\mathrm{CdCl_2}$ has a maximum, then about 0.4 *M* KCl must be added to the solution (see: dashed line, $q = 6$).

The complexes formed in the $\mathrm{Cd^{2+}}$–$\mathrm{Cl^-}$ equilibrium system are comparatively weak. For comparative purposes, Fig. 3.11 shows the distribution curves of the

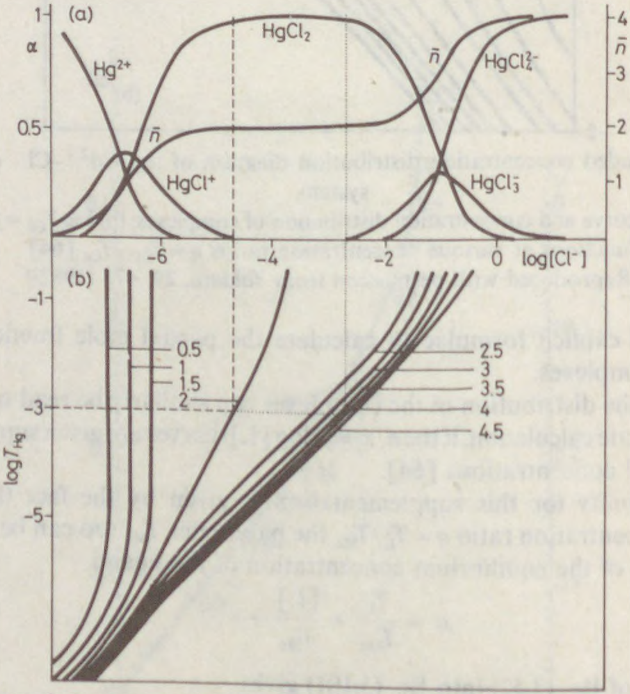


Fig. 3.11 Extended concentration distribution diagram of the $\mathrm{Hg^{2+}}$–$\mathrm{Cl^-}$ equilibrium system.
(a) Formation curve and concentration distribution of complexes; (b) $\log T_{\mathrm{Hg}} = f(\log[\mathrm{Cl^-}])$ functions at various concentration ratios $q = T_{\mathrm{Cl^-}}/T_{\mathrm{Hg}}$ [64]
(Reproduced with permission from *Talanta*, **29**, 473 (1982))

stable complexes formed in the Hg^{2+}–Cl^- system, together with the $\log T_{Hg} = f(\log [Cl^-])$ curves calculated at various q values.

Figure 3.11 reveals that, no matter whether $HgCl_2$ or $K_2[HgCl_4]$ is dissolved in 10^{-3} M concentration, practically the total amount of metal ion is to be found in the form $HgCl_2$. It can also be seen that if the relation $T_{Cl}/T_{Hg} < 4$ holds, the curves in the bottom part of the Figure approach asymptotically a given $\log [Cl^-]$ value. The asymptotically vertical lines denote that complex formation is practically quantitative; further increase of the total concentrations (at constant T_{Cl}/T_{Hg}) does not influence the concentration distribution of the complexes.

The nearly quantitative complex formation means that $\bar{n} \sim T_{Cl}/T_{Hg}$ if $T_{Cl}/T_{Hg} < 4$, and $\bar{n} \sim 4$ if $T_{Cl}/T_{Hg} > 4$. Accordingly, the $\log [Cl^-]$ values to which the $\log T_{Me} = f(\log [Cl^-])$ curves tend relate to the points of the formation curve at which $\bar{n} \sim q = T_{Cl}/T_{Hg}$. This has a defined value only at $\bar{n} < 4$; thus, the asymptotically vertical curves are characteristic only for solutions with $q = T_{Cl}/T_{Hg} < 4$. If $T_{Cl}/T_{Hg} > 4$, then $\log [Cl^-]$ increases monotonously with the increase of T_{Hg}.

The diagrams in Figs 3.9 and 3.10 are much more useful from a practical aspect than the distribution curves alone. It must be taken into account however, that the β_j values used for the calculation are valid only for a given standard state, and accordingly the diagrams can only be utilized under the same conditions. The variation of the total concentrations along the $\log T_{Me} = f(\log [L])$ curves also alters the ionic strength; the curves can therefore be used only in that concentration range in which this change is negligible compared to the concentration of the background electrolyte. This restriction means that the $\log T_M = f(\log [L])$ curves correctly describe the variation in the concentration distribution only in the case of dilution with the background electrolyte; concentration of the solution (evaporation of the solvent) unavoidably alters the standard state too.

It frequently occurs during the stepwise formation of complexes that an electrically neutral member of the series of complexes yields a sparingly soluble precipitate. In this case, the diagrams should be supplemented with the solubility curve. This possibility is dealt with in Section 4.7, in connection with the application of solubility measurements for the determination of equilibrium constants.

The above correlations also hold for the pH-dependent distribution curves in the event of the stepwise protonation of the ligands. However, the shape of the $\log T_L = f(\text{pH})$ curves is different from that of the $\log T_{Me} = f(\log [L])$ curves: on dilution these curves tend to the value $\text{pH} = \text{p}K_w/2$ [65], and in the sense of the definitions discussed in Section 3.2 the concentration ratio $q = T_H/T_L$ may even be negative.

The differences are illustrated in Fig. 3.12, on the example of the distribution curves and $\log T_L = f(\text{pH})$ curves for the citrate–proton equilibrium system.

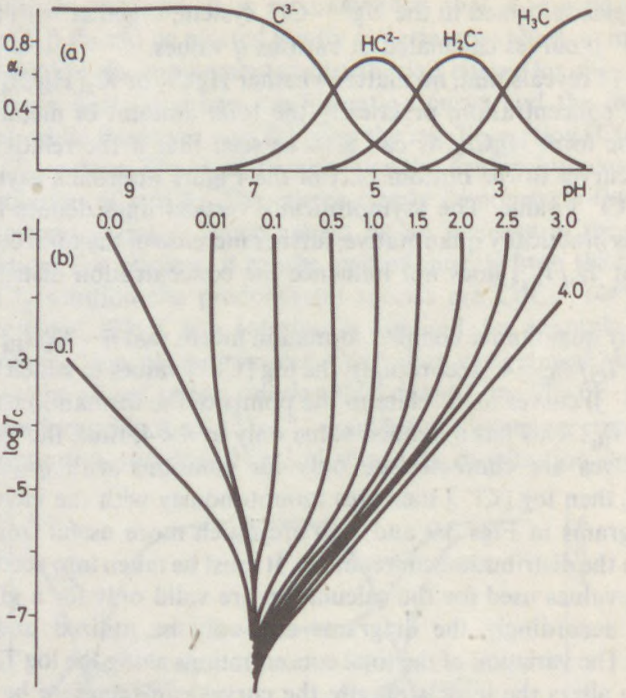


Fig. 3.12 Extended concentration distribution diagram of the citrate–proton equilibrium system.

(a) Concentration distribution of species protonated to various extents; (b) $\log T_H = f(\mathrm{pH})$ functions at various concentration ratios $q = T_H/T_C$ [64]

(Reproduced with permission from *Talanta*, **29**, 473 (1982))

During calculation of the concentration distribution, it must be borne in mind that the formation constants can only be determined with an error of some hundredths, or in some cases some tenths of a logarithmic unit, and this variation of the constants whithin the error may mean a considerable modification of the concentration distribution of the complexes.

This is shown in Figs 3.13 (a)–(d), on the example of the distribution curves for the Cd^{2+}–Cl^- system.

It is apparent from the Figures that an increase in the formation constant of some complex MeL_j leads to increases in the α_j values, primarily at the expense of α_{j-1} and α_{j+1}; however, if there is appreciable overlap of the equilibria, the change may also show up in the concentration distribution curves of the 'more distant' complexes. This effect is an automatic consequence of the fact that an increase in β_j leads to increases in the equilibrium constant of the

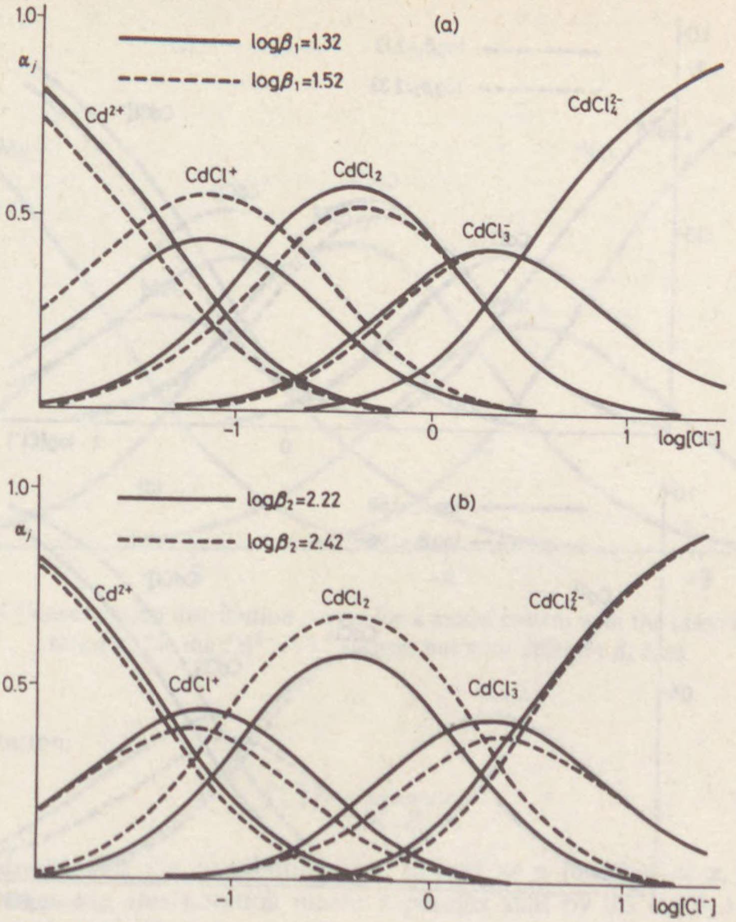


Fig. 3.13 (a) (b) Variation in concentration distribution of complexes formed in the Cd^{2+}–Cl^- system in response to increase of the log β_j values by 0.2 log unit

'reproportionation' reactions $MeL_{j-1} + MeL_{j+1} \rightleftharpoons 2MeL_j$, $MeL_{j-2} + MeL_{j+2} \rightleftharpoons 2MeL_j$, etc.

It is an important feature of the distribution curves that their relative positions are controlled by the quotient of the stepwise constants K_j/K_{j+1}. If all of the K_j/K_{j+1} values are the same in two equilibrium systems, then distribution curves of the same shape are obtained, independently of the value of β_1. This is illustrated in Fig. 3.14, where the distribution curves are plotted for the Cd^{2+}–Cl^- system, the K_j/K_{j+1} values being retained, with the log β'_1 value changed by 4 units. A simple derivation leads to the following correlation between the formation constants for the Cd^{2+}–Cl^- system and those for the

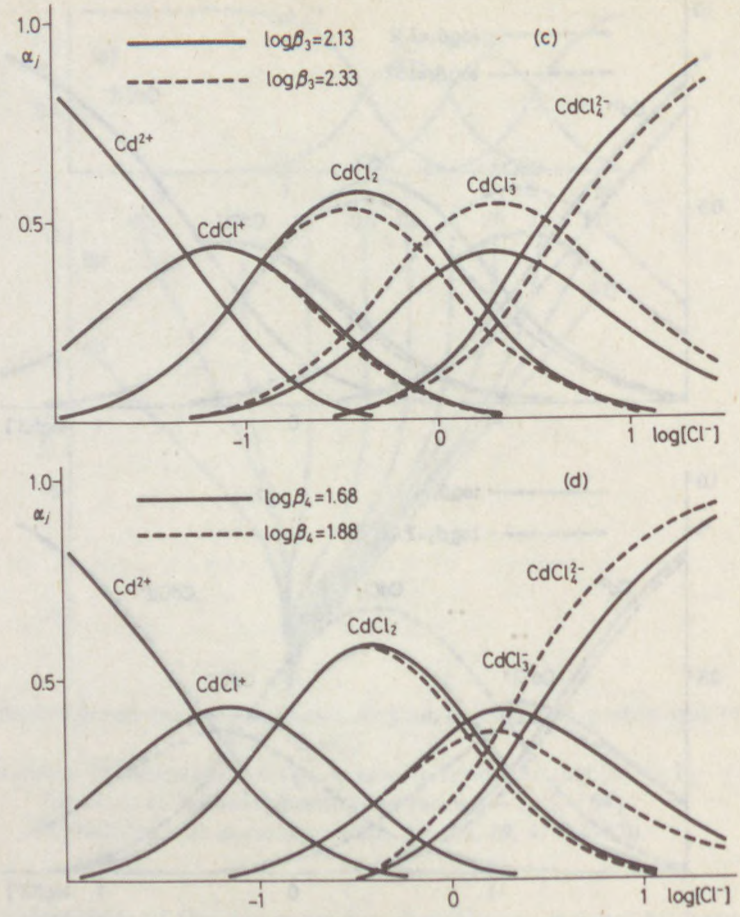


Fig. 13. (c) (d)

model system described by the distribution curves in Fig. 3.14

$$\log \beta'_j = \log \beta_j + j \cdot 4. \tag{3.103}$$

The identity of the K_j/K_{j+1} data means that the equilibrium constants of any of the 'reproportionation' reactions $y\mathrm{MeL}_{j-x} + x\mathrm{MeL}_{j+y} \rightleftharpoons (x+y)\mathrm{MeL}_j$ are also the same; this identity explains the coincidence of the distribution curves.

Let us confirm the coincidence of the distribution curves for identical K_j/K_{j+1} values in the case $N=4$ the α_2 function describing the distribution of MeL_2. The partial mole fraction α_2 is expressed in terms of the stepwise constants

$$\alpha_2 = \frac{K_1K_2[\mathrm{L}]^2}{1 + K_1[\mathrm{L}] + K_1K_2[\mathrm{L}]^2 + K_1K_2K_3[\mathrm{L}]^3 + K_1K_2K_3K_4[\mathrm{L}]^4}. \tag{3.104}$$

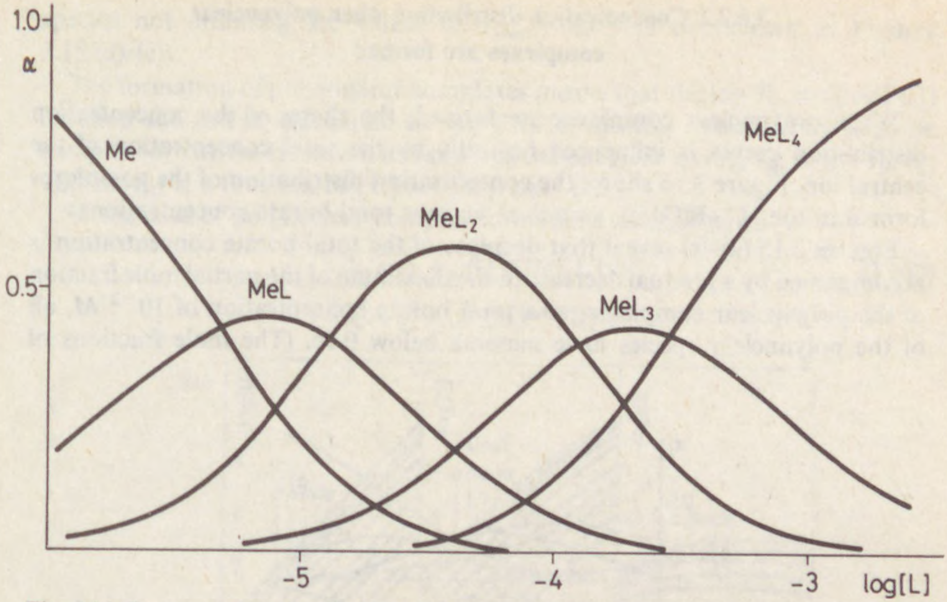


Fig. 3.14 Concentration distribution curves for a model system with the same K_j/K_{j+1} ratios as for the Cd^{2+}–Cl^- system, but with different β_j data

The notation

$$[L]=\frac{1}{\sqrt{K_1K_2}}x \tag{3.105}$$

is introduced, and the distribution is examined as a function of x. (On a logarithmic scale, this notation means a parallel shift by 0.5 $\log\beta_2$.) If Eq. (3.105) is substituted into Eq. (3.104)

$$\alpha_2=\frac{x^2}{1+\left(\frac{K_1}{K_2}\right)^{\frac{1}{2}}x+x^2+\left(\frac{K_2}{K_3}\right)^{-1}\left(\frac{K_1}{K_2}\right)^{\frac{1}{2}}x^3+\left(\frac{K_2}{K_3}\right)^{-2}\left(\frac{K_1}{K_2}\right)^{-1}\left(\frac{K_3}{K_4}\right)^{-1}x^4}. \tag{3.106}$$

Only the ratios of the stepwise constants feature in Eq. (3.106). The identical values of these means that on the $\log x$ scale (by horizontal shifting of the $\log[L]$ scale) the α_2 functions can be made to overlap, i.e. they coincide. The general correlation between the shape of the distribution curves and the ratio K_j/K_{j+1} can be derived in a similar manner, by means of the substitution (parallel shift) $[L]=\beta_j^{(-1/j)}$

3.6.2.2 Concentration distribution when polynuclear complexes are formed

When polynuclear complexes are formed, the shape of the concentration distribution curves is influenced basically by the total concentration of the central ion. Figure 3.15 shows the concentration distribution of the complexes formed in the H^+–$B(OH)_4^-$ system at various total borate concentrations.

Figures 3.15 (a)–(e) reveal that decrease of the total borate concentration is accompanied by a gradual decrease in the maximum of the partial mole fraction of the polynuclear complexes; at a total borate concentration of 10^{-2} *M*, all of the polynuclear species have maxima below 0.05. (The mole fractions of

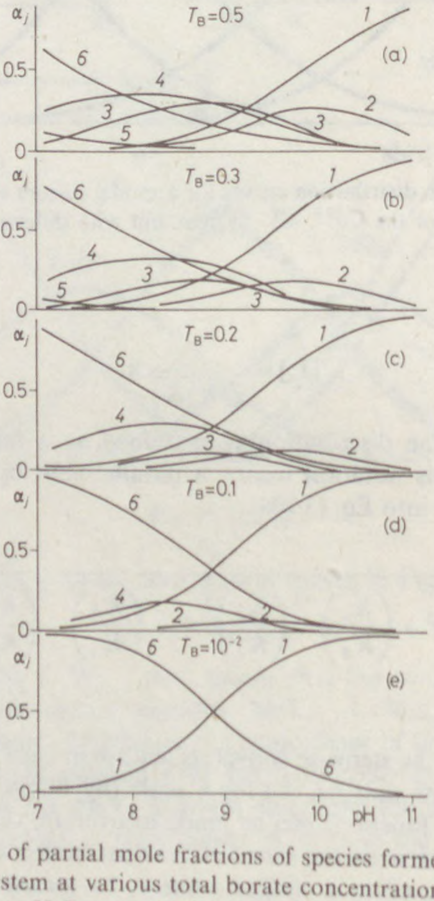


Fig. 3.15 Distribution of partial mole fractions of species formed in the H^+–$B(OH)_4^-$ system at various total borate concentrations.
1 — B; *2* — HB_3; *3* — H_2B_3; *4* — H_3B_5; *5* — H_4B_5; *6* — HB; where $B = B(OH)_4^-$

species not attaining the values of $\alpha_{j\max}=0.05$ are not shown in Figures 3.15 (a)–(e)).

The formation of polynuclear complexes means that the $\log T_{\mathrm{Me}} = f(\log[\mathrm{L}])$ function can not be calculated so easily as for systems described by stepwise complex formation. However, it is still true that, at given $q = T_{\mathrm{L}}/T_{\mathrm{Me}}$ or $q = T_{\mathrm{H}}/T_{\mathrm{L}}$, T_{Me} (or T_{H}) is a function of [L] (or [H]) only [65].

In the case of polynuclear complex formation, we may write

$$T_{\mathrm{H}} = \sum \alpha_{j\mathrm{H}}\beta_j[\mathrm{H}]^{\alpha_{j\mathrm{H}}}[\mathrm{L}]^{\alpha_{j\mathrm{L}}} \tag{3.107}$$

$$T_{\mathrm{L}} = \sum \alpha_{j\mathrm{L}}\beta_j[\mathrm{H}]^{\alpha_{j\mathrm{H}}}[\mathrm{L}]^{\alpha_{j\mathrm{L}}}.$$

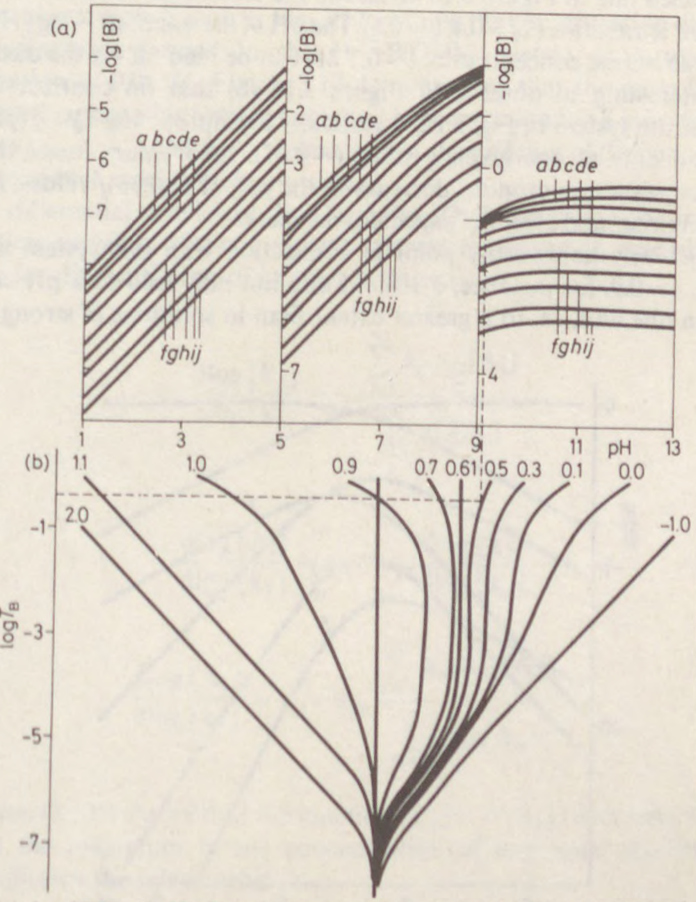


Fig. 3.16 (a) $\log[\mathrm{B}] = f(\mathrm{pH})$ functions at various total borate concentrations. *a* — $T_{\mathrm{B}}=0.5$; *b* — $T_{\mathrm{B}}=0.3$; *c* — $T_{\mathrm{B}}=0.2$; *d* — $T_{\mathrm{B}}=0.1$; *e* — $T_{\mathrm{B}}=0.05$; *f* — $T_{\mathrm{B}}=0.02$; *g* — $T_{\mathrm{B}}=0.01$; *h* — $T_{\mathrm{B}}=0.005$; *i* — $T_{\mathrm{B}}=0.002$; *j* — $T_{\mathrm{B}}=0.001$; (b) $T_{\mathrm{B}} = f(\mathrm{pH})$ functions describing the H^+–$\mathrm{B(OH)}_4^-$ system at various concentration ratios $q = T_{\mathrm{H}}/T_{\mathrm{B}}$

At $q = T_H/T_L$, the following implicit function can be derived between [L] and [H]

$$\sum(\alpha_{jH} - q^{\alpha_{jL}})\beta_j[H]^{\alpha_{jH}}[L]^{\alpha_{jL}} = 0. \tag{3.108}$$

T_L can be calculated by solving Eq. (3.108) for [L] at various hydrogen ion concentrations. Figure 3.16 presents $\log T_B = f(pH)$ curves for the H^+–$B(OH)_4^-$ system at various q values. Figure 3.16 (a) gives the $\log [B] = f(pH)$ functions at various total borate concentrations. In the knowledge of the total concentrations, the equilibrium concentrations of both components (H^+ and $B(OH)_4^-$) can be read off from the Figure. Thus, the concentrations of the different species can be calculated through direct formulae, without an iterative procedure.

The dashed line in Figure 3.16 (a) shows the conditions for a 0.1 *M* solution of disodium tetraborate ($T_B = 0.4$, $q = 0.5$). The pH of the solution ($-\log [H^+] = 9.1$) and the free borate concentration (~0.1 *M*) can be read off via the dashed line.

It is interesting to observe in Figure 3.16 (b) that (in contrast with the proton–citrate system in Fig. 3.12) a vertically asymptotic $\log T_B = f(pH)$ curve is obtained only at one given q value (~0.61). At q values lower than this, dilution causes a monotonous decrease in the pH; at higher q values, however, it first increases, and then (as expected) decreases.

A particularly noteworthy point in connection with this system is that at $q = 0.1$ or $q = 0.9$, for instance, a 10-fold dilution may lead to a pH change of more than one unit, i.e. to a greater extent than in solutions of strong acids or

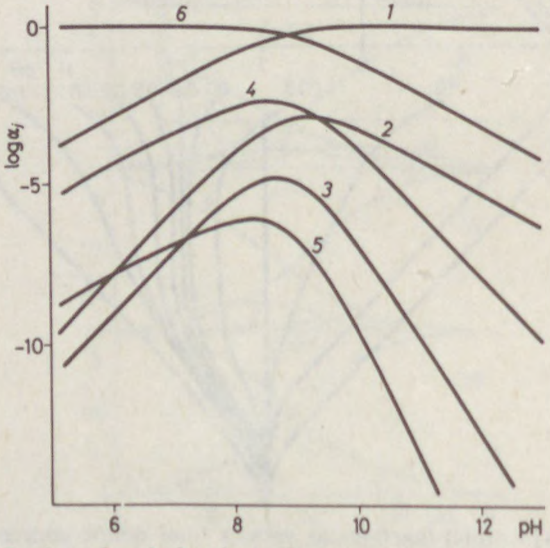


Fig. 3.17 Distribution of mole fractions of species formed in the H^+–$B(OH)_4^-$ system, on the $\log \alpha_j = f(pH)$ scale, at a total borate concentration of 0.01 *M*.
1 — B; *2* — HB_3; *3* — H_2B_3; *4* — H_3B_5; *5* — H_4B_5; *6* — HB; where $B = B(OH)_4^-$

strong bases. (The 10-fold dilution of solutions of weak acids or weak bases means a pH change of 0.5 log unit.) The explanation of the unusual pH change is that the protonation constant of HB_3 ($10^{9.4}$) is larger than that of H_3B_5 ($10^{7.25}$), but smaller than that of the borate ion ($10^{8.87}$).

Dilution is therefore accompanied by a pH increase in the pH interval corresponding to the formation of H_3B_5, and by a pH decrease in the interval corresponding to the formation of HB_3 and H_2B_3.

In order to illustrate the relative concentrations of the species formed in very low concentration, it is useful to plot the $\log \alpha_j = f(\log [L])$ curves: the logarithmic scale allows a concentration change of several orders of magnitude to be followed.

A logarithmic scale is used in Fig. 3.17 to show the concentration distribution of the complexes formed in the H^+–$B(OH)_4^-$ system at a total borate concentration of 0.01 *M*. Figure 3.17 demonstrates that the mole fraction of the polynuclear complex formed in highest concentration has a maximum below 0.01 ($\log \alpha_{j,\max} < -2$), but nevertheless the pH-dependence of the concentrations of the individual species is clearly seen.

If the differential coefficient $\mathrm{d}\log [k_2]/\mathrm{d}\log [k_1]$ describing the logarithmic distribution curves of two-component systems is derived in accordance with the rules for differentiation of implicit functions

$$\frac{\mathrm{d}\log [k_2]}{\mathrm{d}\log [k_1]} = -\frac{\sum\limits_{j=1}^{n} \alpha_{j1}\alpha_{j2}[A_j]}{\sum\limits_{j=1}^{n} \alpha_{j2}^2[A_j]} \tag{3.109}$$

$$\frac{\mathrm{d}\log [A_j]}{\mathrm{d}\log [k_1]} = \alpha_{j1} + \alpha_{j2}\frac{\mathrm{d}\log [k_2]}{\mathrm{d}\log [k_1]}$$

i.e.

$$\frac{\mathrm{d}\log [A_j]}{\mathrm{d}\log [k_1]} = \alpha_{j1} - \alpha_{j2}\frac{\sum\limits_{m=1}^{n} \alpha_{m1}\alpha_{m2}[A_m]}{\sum\limits_{m=1}^{n} \alpha_{m2}^2[A_m]}. \tag{3.110}$$

Equation (3.109) shows that the function $[k_2] = f([k_1])$ decreases monotonously; at the maximum in the concentration of any ionic species A_j, Eq. (3.110) indicates the relationship

$$\left(\frac{\mathrm{d}\log [k_2]}{\mathrm{d}\log [k_1]_{[A_j]=\max}}\right) = -\alpha_{j1}/\alpha_{j2}. \tag{3.111}$$

The validity of Eq. (3.110) is clearly illustrated in Fig. 3.17. At high pH, where the form $B(OH)_4^-$ predominates in the H^+–$B(OH)_4^-$ equilibrium system, and where there is practically no change in its concentration with variation of the pH, slopes $d\log[A_j]/d\log[k_1] = -d\log[B]/dpH$ of the logarithmic distribution curves for the individual species coincide with the corresponding α_{j1} values.

As the pH is decreased, the slope increases; then, after the maximum (since the limiting value of $d\log[B]/d\log[H]$ in the given system is -1) the slope approaches the limiting value $\alpha_{j1}-\alpha_{j2}$. Equation (3.111) shows that the maxima in the concentrations of the individual species follow one another in the sequence of the quotients α_{j1}/α_{j2}, as can be seen in Fig. 3.16.

If Eq. (3.110) is differentiated with respect to $\log[k_1]$

$$\frac{d^2\log[A_j]}{d\log[k_1]^2} = -\alpha_{j2}\frac{\sum\limits_{m=1}^{n}\alpha_{m2}(\alpha_{m1}+\alpha_{m2}x)^2[A_m]}{\sum\limits_{m=1}^{n}\alpha_{m2}^2 A_m} \qquad (3.112)$$

where $x=-d\log[k_2]/d\log[k_1]$. Equation (3.112) reveals that the second derivative is always negative, i.e. the logarithmic concentration distribution curves for two component systems are always concave.

3.6.3 Three-component systems

It was seen in the preceding section that the concentration distribution in two-component systems can be plotted in two dimensions only if mononuclear complexes are formed. The possibility for this is provided by the fact that the partial mole fractions of the complexes are independent of the equilibrium concentration of the metal ion, and depend only on the equilibrium concentration of the ligand.

The formation of polynuclear complexes would necessitate a three-dimensional plot of the complete concentration distribution. Two-dimensional diagrams require that the total or equilibrium concentration of one of the components is fixed. In this case, however, the concentration distribution also depends on the value of the fixed total or equilibrium concentration (see Fig. 3.15).

The complete concentration distribution in three-component systems can in principle be plotted only in four dimensions. If the usual two-dimensional plotting is to be achieved, two total concentration must be fixed. The concentrations of all the species then depend only on the equilibrium concentration of the third component. In some practically important cases, however, there is no need to fix the total concentrations, as the concentration distribution can be illustrated in a simpler way.

In a considerable proportion of three-component systems the ligand is the conjugate base of a weak acid, which does not form a polyacid; at the same time, only mononuclear metal complexes are formed, while the protonation of the complexes and the formation of mixed hydroxo complexes can be neglected. Under such conditions, the relevant equations simplify to

$$T_{\mathrm{H}}-[\mathrm{H}]+[\mathrm{OH}]=[\mathrm{L}]\sum_{i=0}^{Q} i\beta_i^{\mathrm{H}}[\mathrm{H}]^i$$

$$T_{\mathrm{L}}=[\mathrm{L}]\sum_{i=0}^{Q} \beta_i^{\mathrm{H}}[\mathrm{H}]^i+\bar{n}\cdot T_{\mathrm{M}} \tag{3.113}$$

$$T_{\mathrm{Me}}=[\mathrm{Me}]\sum_{j=0}^{N} \beta_j^{\mathrm{H}}[\mathrm{L}]^j.$$

The third equation in this equation system clearly shows that the partial mole fractions of the metal complexes depend on the equilibrium concentration of the ligand only, as if the system were a two-component one. At the same time, the total and equilibrium concentrations of the proton unambiguously govern the equilibrium concentration of the ligand. Systems of this type are generally studied at fixed T_{L} and T_{Me}, through variation of T_{H} (and the pH). However, because of the connection between the equilibrium concentrations, the concentration distribution of the metal complexes is plotted as a function of the equilibrium concentration of the ligand. The correlations discussed in Section 3.6.2.1 naturally apply to these distribution curves.

Another example of the possibilities of simplification is when the mixed ligand complex formation processes $i\,\mathrm{MeX}_N+j\,\mathrm{MeY}_N \rightleftharpoons N\,\mathrm{MeX}_i\mathrm{Y}_j\,(i+j=N)$ are studied at such high ligand concentrations that only the coordinatively saturated complexes are formed. In this case, the stepwise uptake of the ligand Y is accompanied by stepwise dissociation of X.

The rules governing the mole fraction distribution of the complexes are therefore similar to those observed in the analysis of the $\alpha_j=f\,(\log[\mathrm{L}])$ curves for two-component systems; here, however, the independent variable is not the equilibrium concentration of Y, but (because of the dissociation of X) $[\mathrm{Y}]/[\mathrm{X}]$ or $\log([\mathrm{Y}]/[\mathrm{X}])$. A concentration distribution of this type may be seen in the following Chapter, in Fig. 4.15.

If similar possibilities of simplification are not available, the concentration distribution curves are usually calculated and plotted with two fixed total concentrations. In this respect, however, attention must be drawn to the fact that the distribution curves correctly reflect the equilibrium relations only in that total concentration range in which the constants were determined.

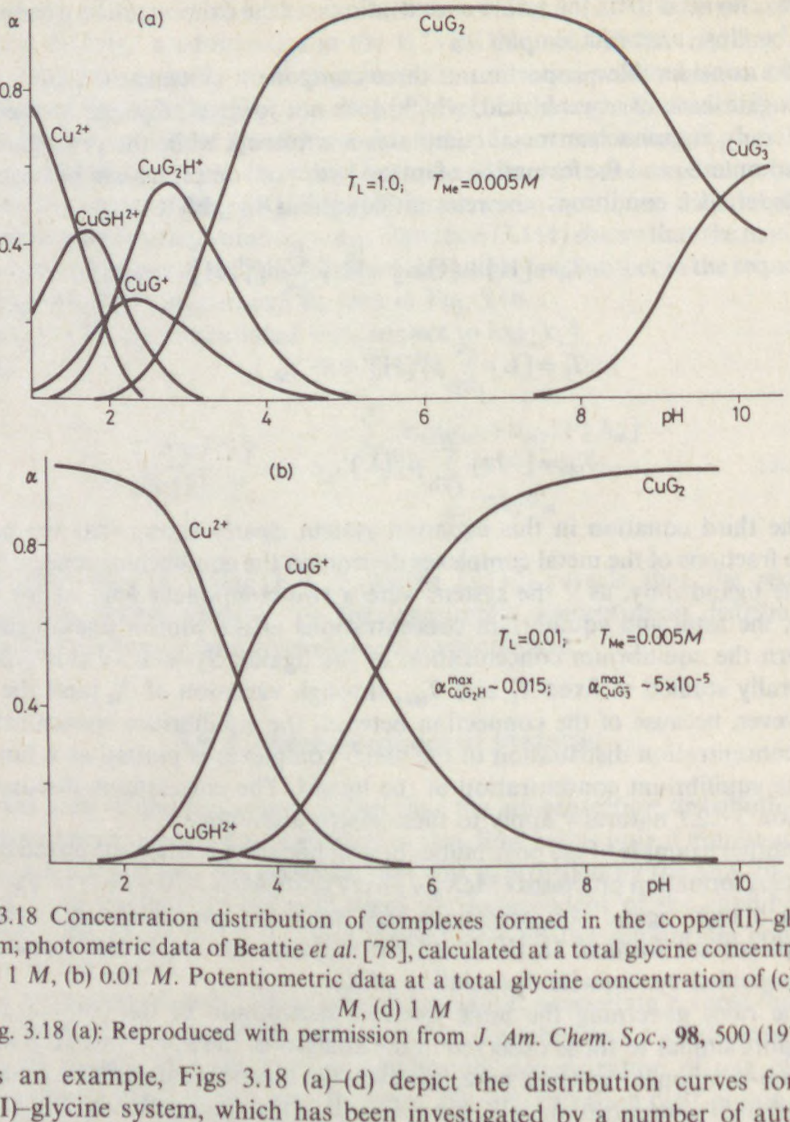


Fig. 3.18 Concentration distribution of complexes formed in the copper(II)–glycine system; photometric data of Beattie *et al.* [78], calculated at a total glycine concentration of (a) 1 *M*, (b) 0.01 *M*. Potentiometric data at a total glycine concentration of (c) 0.01 *M*, (d) 1 *M*

(Fig. 3.18 (a): Reproduced with permission from *J. Am. Chem. Soc.*, **98**, 500 (1976))

As an example, Figs 3.18 (a)–(d) depict the distribution curves for the Cu(II)–glycine system, which has been investigated by a number of authors, including Beattie *et al.* [78].

Figure 3.18 (a) gives the distribution curve calculated with the equilibrium data of Beattie *et al.* [78], obtained photometrically at a total glycine concentration of 1 *M*. If these data are used at a comparable total ligand and total metal ion concentration, the character of the distribution curves changes radically and the partial mole fractions of the protonated complexes become virtually negligible (Fig. 3.18 (b)).

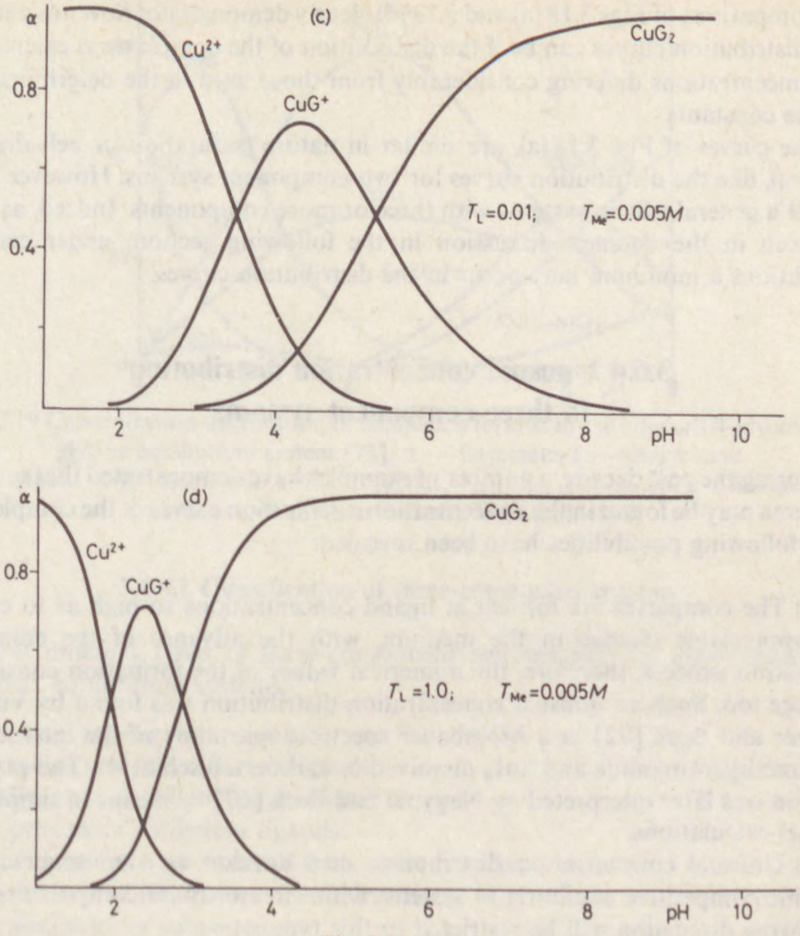


Fig. 3.18 (cont.)

With the pH-potentiometric method most often applied for study of the system (at comparable total concentrations), formation of the protonated complex can not even be detected; only the formation constants of the complexes CuG^+ and CuG_2 can be determined. The distribution curves calculated with the constants obtained with the potentiometric method are presented in Fig. 3.18 (c); there is good agreement with Fig. 3.18 (b), calculated from the photometric data.

Figure 3.18 (d) shows the concentration distribution of the complexes, calculated via the potentiometric data, but at a total glycine concentration of 1 *M*.

Comparison of Figs 3.18 (a) and 3.18 (d) clearly demonstrates how misleading the distribution curves can be if the distribution of the complexes is calculated at concentrations differing considerably from those used in the determination of the constants.

The curves of Fig. 3.18 (a), are similar in nature (saturation or bell-shaped curves), like the distribution curves for two-component systems. However, this is not a general rule in systems with three or more components. Indeed, as will be seen in the detailed discussion in the following section, under certain conditions a minimum may occur in the distribution curves.

3.6.4 Unusual concentration distribution in three-component systems

During the past decade, a number of examples have demonstrated that several extrema may be found in the concentration distribution curves of the complexes. The following possibilities have been revealed:

(1) The complexes are formed at ligand concentrations so high as to cause an appreciable change in the medium; with the advance of the complex formation process, therefore, the numerical values of the formation constants change too. Such an unusual concentration distribution was found by Vértes, Gaizer and Beck [72] in a Mössbauer spectroscopic study of the interaction of dimethylformamide and SnI_4 dissolved in carbon tetrachloride. The phenomenon was later interpreted by Nagypál and Beck [67] by means of simplified model calculations.

(2) Unusual concentration distribution may develop as a consequence of specific competitive equilibria in systems with three or more components; the following discussion will be restricted to this type.

The first distribution curve displaying several extrema was reported by Agarwall and Perrin [73], who found three extrema in the pH-dependent concentration distribution curve of the bis-glycinatocopper(II) complex formed in the copper(II)–glycine–diglycine mixed ligand complex equilibrium system (see Fig. 3.19).

Unusual concentration distributions (with several extrema) have since been observed in other systems. The increasing number of the systems, and the efforts made to establish the rules of concentration distribution, have led to a deeper understanding of the phenomenon, and to a classification of three-component systems (with regard to the nature of the concentration distribution).

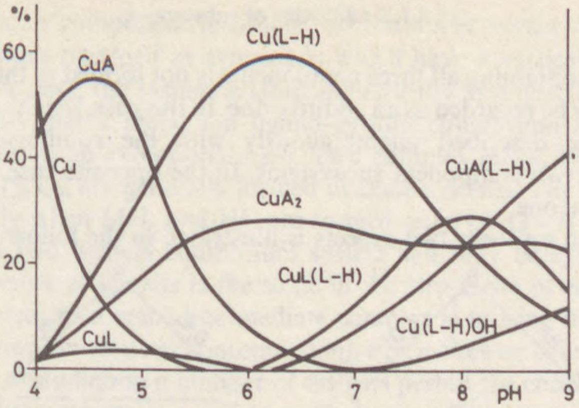


Fig. 3.19 Concentration distribution of complexes formed in the copper(II)–glycine–diglycine equilibrium system [73]. A — Glycinate; L — diglycinate (Reproduced with permission from: Högfeldt, E. (Ed.), *Coordination Chemistry in Solutions*, Berlingska Bokrykeriet, Lund, 1972)

3.6.4.1 Classification of three-component systems

Four different types of three-component systems may be encountered in complex equilibrium systems:

(1) metal ion–ligand–proton;
(2) metal ion–two different ligands;
(3) ligand–two different metal ions;
(4) proton–two different ligands.

Any of these may be classified from three aspects:

(1) number of two-component subsystems;
(2) additivity of subsystems;
(3) symmetry–asymmetry.

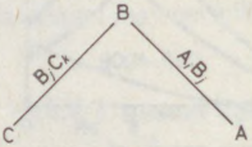
3.6.4.1.1The number of two-component subsystems

Any three-component system may contain two or three two-component subsystems, depending on the number of interacting component pairs. In metal ion–ligand–proton systems, for instance, if complex formation is accompanied by protonation of the ligand and hydrolysis of the metal ion, three two-component subsystems can be distinguished: the ligand–proton, the metal ion–proton (hydroxide ion) and the metal ion–ligand subsystems. If either the hydrolysis of the metal ion or the protonation of the ligand can be disregarded, only two subsystems can be distinguished.

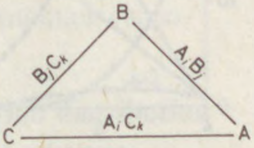
3.6.4.1.2 Additivity of subsystems

If a species containing all three components is not formed in the system, then the system may be regarded as an additive one. In this case, the three-component system can be described unambiguously with the equilibrium constants describing the two-component subsystems. In the opposite case, the system is not an additive one.

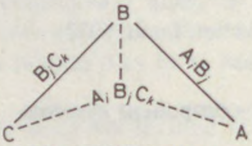
Classification on these two aspects is illustrated in the following scheme



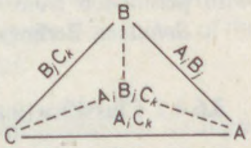
Additive system
Two subsystems



Additive system
Three subsystems



Non-additive system
Two subsystems



Non-additive system
Three subsystems

3.6.4.1.3 Symmetry and asymmetry

The triangles in the foregoing scheme can also be used to characterize the compositions of the species formed in the system. Each of the species $A_iB_jC_k$ is represented by a point with coordinates i/m, j/m, and k/m, where $m=i+j+k$. Thus, the components are situated at the vertices of the triangle, the species containing two components on the sides, and the species containing three components inside the triangle. The coordinates of the individual points give the ratios of the stoichiometric numbers, and accordingly the species and their polymeric forms are denoted by points with the same coordinates.

The concept of symmetry–asymmetry refers to the locations of the points on the triangle diagram. In case of the highest possible symmetry, the diagram has three twofold axes, i.e. it may be denoted by the symbol D_{3h}. However, such a degree of symmetry can rarely be attained. From the aspect of the concentration distribution, it is sufficient to examine the possibility of C_{2v} symmetry. Only one common component is to be found in the majority of three-component systems. As a consequence of complex formation, hydrolysis of the metal ion may be disregarded in most metal ion–ligand–proton systems, and hence the ligand is the common component. The metal ion is the common component in equilibrium systems of mixed ligand complexes.

If the common component is situated at the upper vertex of the triangle, those systems are regarded as symmetric which have a vertical twofold axis. In the opposite case, the system is stoichiometrically asymmetric.

It is obvious that a metal ion–ligand–proton equilibrium system can be symmetric only in an exceptional case. Two complex series, MeL_i $(0<i\leqq N)$ and $\mathrm{H}_j\mathrm{L}$ $(0<j\leqq \mathrm{Q})$, are generally formed in these systems. The system can be symmetric only when MeL and HL are formed only, i.e. $\mathrm{Q}=N=1$. Similarly, the metal ion–two ligands equilibrium system can only be symmetric if the maximum number of ligands is the same in the two series of complexes. It is possible, however, that some intermediate complex is missing from one of the series (or is formed in very low concentration), which likewise causes asymmetry.

The results of studies on a number of systems permit the conclusion that the asymmetry of the system is a necessary (but not sufficient) condition for the occurrence of several extrema.

3.6.4.2 Mathematical considerations

The derivation of the $\mathrm{dlog}\,[\mathrm{k}_3]/\mathrm{dlog}\,[\mathrm{k}_1]$ functions describing three-component systems is given in the Appendix. The products of various concentration sums feature in both the numerator and the denominator of Eq. (A.22). With a view to further transformation of this equation, we take two species, $\mathrm{A_p}$ and $\mathrm{A_q}$, and denote their stoichiometric numbers by p_1, p_2, p_3 and q_1, q_2, q_3. Their roles in the numerator and denominator may be given as

$$((p_2)^2[\mathrm{A}_p]+(q_2)^2[\mathrm{A}_q])(p_1p_3[\mathrm{A}_p]+q_1q_3[\mathrm{A}_q])-$$

$$-(p_1p_2[\mathrm{A}_p]+q_1q_2[\mathrm{A}_q])(p_2p_3[\mathrm{A}_p]+q_2q_3[\mathrm{A}_q])=$$

$$=-(p_1q_2-q_1p_2)(p_2q_3-q_2p_3)[\mathrm{A}_p][\mathrm{A}_q] \tag{3.114}$$

and

$$((p_2)^2[\mathrm{A}_p]+(q_2)^2[\mathrm{A}_q])((p_3)^2[\mathrm{A}_p]+(q_3)^2[\mathrm{A}_q])-$$

$$-(p_2p_3[\mathrm{A}_p]+q_2q_3[\mathrm{A}_q])^2=(p_2q_3-q_2p_3)^2[\mathrm{A}_p][\mathrm{A}_q]\,. \tag{3.115}$$

It may be seen from Eq. (3.114) that the concentration products in the numerator must be multiplied by the determinant formed from the first and last two columns of the stoichiometric matrix

$$\begin{vmatrix} p_1 & p_2 & p_3 \\ q_1 & q_2 & q_3 \end{vmatrix}.$$

At the same time, the concentration products in the denominator are to be multiplied by the square of the determinant formed from the last two columns of the matrix. If Eqs (3.114) and (3.115) are substituted into Eq. (A.22)

$$\frac{\mathrm{dln}\,[\mathrm{k}_3]}{\mathrm{dln}\,[\mathrm{k}_1]} = \frac{\sum\limits_{p=1}^{n}\sum\limits_{q=p}^{n}(p_1q_2-q_1p_2)(p_2q_3-q_2p_3)[\mathrm{A}_p][\mathrm{A}_q]}{\sum\limits_{p=1}^{n}\sum\limits_{q=p}^{n}(p_2q_3-q_2p_3)^2[\mathrm{A}_p][\mathrm{A}_q]}. \tag{3.116}$$

Through a similar, but much more complicated derivation, it can be demonstrated that similar correlations hold for multicomponent systems

$$\frac{\mathrm{dln}\,[\mathrm{k}_3]}{\mathrm{dln}\,[\mathrm{k}_1]} = \frac{\sum\limits_{p=1}^{n}\sum\limits_{q=p}^{n}\cdot\cdot\sum\limits_{y=x}^{n}\det\begin{vmatrix} p_1p_2\cdots p_{(m-1)} \\ q_1q_2\cdots q_{(m-1)} \\ \vdots \\ x_1x_2\ldots x_{(m-1)} \\ y_1y_2\cdots y_{(m-1)} \end{vmatrix}\det\begin{vmatrix} p_2p_3\cdots p_m \\ q_2q_3\cdots q_m \\ \vdots \\ x_2x_3\ldots x_m \\ y_2y_3\cdots y_m \end{vmatrix}[\mathrm{A}_p][\mathrm{A}_q]\cdot\cdot[\mathrm{A}_x][\mathrm{A}_y]}{\sum\limits_{p=1}^{n}\sum\limits_{q=p}^{n}\cdot\cdot\sum\limits_{y=x}^{n}\det\begin{vmatrix} p_2p_3\cdots p_m \\ q_2q_3\cdots q_m \\ \vdots \\ x_2x_3\cdots x_m \\ y_2y_3\cdots y_m \end{vmatrix}^2[\mathrm{A}_p][\mathrm{A}_q]\cdot\cdot[\mathrm{A}_x][\mathrm{A}_y]}. \tag{3.117}$$

It is clear from Eq. (3.117) that the denominator is always positive. Thus only the signs of the concentration products in the numerator need be considered in order to establish the possible extrema of the distribution curve. If all of the concentration products have the same sign, no extremum is found in the distribution curve of the third component. In the opposite case, there may be an extremum in the curve. At given T_2, T_3 and $\beta_1, \ldots, \beta_n$, the number and positions of the extrema are determined by solving the balance equations for T_2 and T_3, together with the equation $\mathrm{dln}\,[\mathrm{k}_3]/\mathrm{dln}\,[\mathrm{k}_1]=0$, for all the possible positive roots $[\mathrm{k}_1]$, $[\mathrm{k}_2]$ and $[\mathrm{k}_3]$.

No general numerical method is known which gives the number of chemically realistic ($0<[\mathrm{k}_i]<T_i$) solutions. As concerns the present discussion, however, it is sufficient to examine whether there is a minimum in the distribution curve. In other words, it is sufficient to establish whether the sign of the second

derivative can be positive at the zero-point of the first derivative. Since the second derivative is required at the zero point of the first derivative, it is sufficient to differentiate only the numerator of Eq. (3.116) with respect to ln $[k_1]$, the denominator remaining unchanged

$$\left(\frac{d^2\ln[k_3]}{d\ln[k_1]^2}\right)_{\frac{d\ln[k_3]}{d\ln[k_1]}=0} =$$

$$= \frac{\sum_{p=1}^{n}\sum_{q=p}^{n}(p_1q_2-q_1p_2)(p_2q_3-q_2p_3)[A_q][A_p]\left(\frac{d\ln[A_p]}{d\ln[k_1]}+\frac{d\ln[A_q]}{d\ln[k_1]}\right)}{\sum_{p=1}^{n}\sum_{q=p}^{n}(p_2q_3-q_2p_3)^2[A_p][A_q]}. \tag{3.118}$$

It follows from the equation defining the equilibrium constants that, at the point $d\ln[k_3]/d\ln[k_1]=0$

$$\frac{d\ln[A_p]}{d\ln[k_1]} = p_1 + p_2\frac{d\ln[k_2]}{d\ln[k_1]}$$
$$\frac{d\ln[A_q]}{d\ln[k_1]} = q_1 + q_2\frac{d\ln[k_2]}{d\ln[k_1]}. \tag{3.119}$$

At the same point, from Eq. (A.20) we have

$$\left(\frac{d\ln[k_2]}{d\ln[k_1]}\right)_{\frac{d\ln[k_3]}{d\ln[k_1]}=0} = -\frac{\sum_{j=1}^{n}\alpha_{j1}\alpha_{j2}[A_j]}{\sum_{j=1}^{n}\alpha_{j2}^2[A_j]}. \tag{3.120}$$

Substitution of Eqs (3.119) and (3.120) into Eq. (3.118), followed by rearrangement, leads to

$$\left(\frac{d^2\ln[k_3]}{d\ln[k_1]^2}\right)_{\frac{d\ln[k_3]}{d\ln[k_1]}=0} =$$

$$= \frac{\sum_{p=1}^{n}\sum_{q=p}^{n}\sum_{j=1}^{n}(p_1q_2-q_1p_2)(p_2q_3-q_2p_3)(p_1+q_1)\alpha_{j2}^2-(p_2+q_2)\alpha_{j1}\alpha_{j2}[A_p][A_q][A_j]}{\sum_{j=1}^{n}\alpha_{j2}^2[A_j]\sum_{p=1}^{n}\sum_{q=p}^{n}(p_2q_3-q_2p_3)^2[A_p][A_q]}. \tag{3.121}$$

According to (3.121), the second derivative can be given in a table form at the zero-point of the first derivative. The left-hand column of this table contains the concentration products $[A_p][A_q]$ multipled by $(p_1q_2-q_1p_2)(p_2q_3-q_2p_3)$.

The heading of Table 3.11 contains the concentrations $[A_j]$ for which $\alpha_{j2} \neq 0$; the corresponding $(q_1+p_1)\alpha_{j2}^2(p_2+q_2)\alpha_{j1}\alpha_{j2}$ data are in the Table.

The numerator of Eq. (3.121) is obtained by summing the left-hand concentration products multiplied by the numbers in the Tables and by the concentrations in the heading. Some examples of the application of Eqs (3.116) and (3.121) will be given in Section 3.6.4.3. To facilitate the chemical interpretation of the results for the various systems, we shall examine the signs of the concentration products in the numerator of Eq. (3.116).

It was seen earlier that the denominator contains only those concentration products for which a non-singular 3 × 3 matrix is obtained if the stoichiometric numbers of the species are supplemented with the vector formed from the stoichiometric numbers of component k_1. Similarly, the numerator contains only those concentration products for which a non-singular matrix is obtained if the stoichiometric numbers are supplemented with the stoichiometric numbers of either the first (1, 0, 0) or the third (0, 0, 1) component. This means that an equilibrium process can be written between the species k_1, k_3, A_p and A_q: $x(1,0,0)+(0,0,1)+y(p_1p_2p_3)+z(q_1q_2q_3)=0$. The corresponding equilibrium constant is

$$K=[k_1]^x[k_3][A_p]^y[A_q]^z\,. \tag{3.122}$$

The unknown parameters x, y and z can readily be expressed by means of the linear equations resulting from the mass balances

$$\begin{aligned}
&x+yp_1+zq_1=0\\
&0+yp_2+zq_2=0\\
&0+yp_3+zq_3=-1\\
&z=-p_2/(p_2q_3-q_2p_3)\\
&y=q_2/(p_2q_3-q_2p_3)\\
&x=-(p_1q_2-q_1p_2)/(p_2q_3-q_2p_3)\,.
\end{aligned}$$

Let us assume that, apart from the components, the system contains only the species A_p and A_q. In this case, we have directly from Eq. (3.122) that the value of $\mathrm{dln}\,[k_3]/\mathrm{dln}\,[k_1]$ is $x=-(p_1q_2-q_1p_2)/(p_2q_3-q_2p_3)$.

If several species are formed, these effects are summed as in Eq. (3.116).

The above considerations clearly show the chemical meaning of Eq. (3.116). The value of $\mathrm{dln}\,[k_3]/\mathrm{dln}\,[k_1]$ is influenced by all of the equilibrium processes that can be written between the species k_1, k_3, A_p and A_q. The stoichiometric numbers of the species govern whether the increase of $[k_1]$ increases or decreases the value of $[k_3]$ via the given equilibrium process.

As concerns the possibility of more than one extremum, the important points are the signs of the x values and the sequence of the various processes of the log [k_1] scale. If the x values have the same sign, the extrema can not appear; in the opposite case they can. If the equilibrium processes follow one another on the log [k_1] scale in such a sequence that the sign changes more than once, there will then be a possibility for more than one extremum (i.e. a minimum too can arise) in the distribution curve of the third component.

The considerations so far have deliberately been restricted to the $\log [k_3] = f(\log [k_1])$ curves. However, the considerations on the transformation of the composition matrix in the Appendix show that in fact this is not a restriction, as any of the species in an equilibrium system (with the exception of k_1) can be selected as the third component. The above correlations and chemical considerations apply without any change to the systems transformed on that basis.

3.6.4.3 Further analysis of rules of unusual concentration distribution

3.6.4.3.1 Stoichiometric asymmetry in mixed ligand equilibrium systems

Schippert [66] used ^{27}Al NMR to study the system Al^{3+} (dissolved in nitromethane)–Cl^-–dimethylformamide. He showed that the concentration of $Al(DMFA)_6^{3+}$ assumes two extrema as a function of the DMFA concentration, and the two extrema can be explained by the difference between the maximum coordination numbers for the subsystems Al^{3+}–Cl^- and Al^{3+}–DMFA.

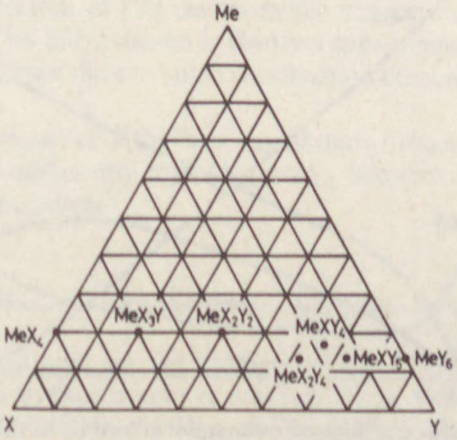


Fig. 3.20 Compositions of complexes formed in the Al^{3+}–Cl^-–dimethylformamide system. M = Al^{3+}, X = Cl^-, Y = DMFA [66]
(Reproduced with permission from *Inorg. Chim. Acta*, **21**, 35 (1977))

In agreement with Schippert's findings, the principles of classification of equilibrium systems indicate that the two extrema are a consequence of the asymmetry depicted in Fig. 3.20.

The concentration distributions of the complexes are illustrated in Fig. 3.21 as functions of the total concentration ratios of the two ligands, and in Fig. 3.22 as functions of the logarithm of the dimethylformamide equilibrium concentration.

In Fig. 3.21, the very sharp maxima in the concentrations of the complexes $AlCl_4^-$ and $Al(DMFA)_6^{3+}$ may be unusual, but a comparison of the two Figures reveals that this phenomenon is a consequence of the significant change of log [DMFA] at around $T_{Cl^-}/T_{DMFA} \sim 0.5$.

A full analysis of the system demonstrates that the concentration of $Al(DMFA)_6^{3+}$ is influenced by 23 concentration products. The most important three equilibrium processes responsible for the unusual concentration distribution are as follows

Equilibrium	Concentration product
(1) $MeX_3Y + 5Y = MeY_6 + 3X$	$[MeX_3Y][X]$
(2) $3MeY_6 + 2Y + MeX_4 = 4MeXY_5$	$[MeX_4][MeXY_5]$
(3) $MeXY_5 + Y = MeY_6 + X$	$[MeXY_5][X]$

It may be observed in the Figures that the effects of the individual equilibrium processes appear practically completely separated.

In the T_Y/T_X interval between 1/3 and 1/2, MeY_6 is mainly formed from MeX_3Y via the first equilibrium process. Since MeY_6 and Y appear on opposite

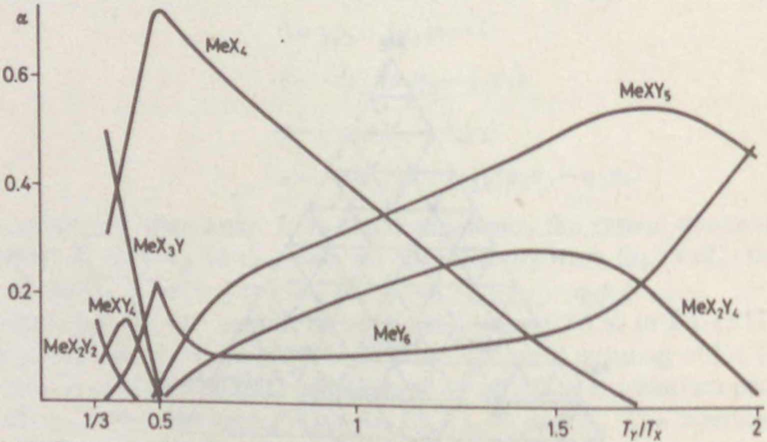


Fig. 3.21 Concentration distribution of complexes formed in the Al^{3+}–Cl^-–dimethylformamide (DMFA) system as a function of the concentration ratio T_{DMFA}/T_{Cl} [66]. $Me = Al^{3+}$, $X = Cl^-$, $Y = DMFA$ [66]
(Reproduced with permission from *Inorg. Chim. Acta*, **21**, 35 (1977))

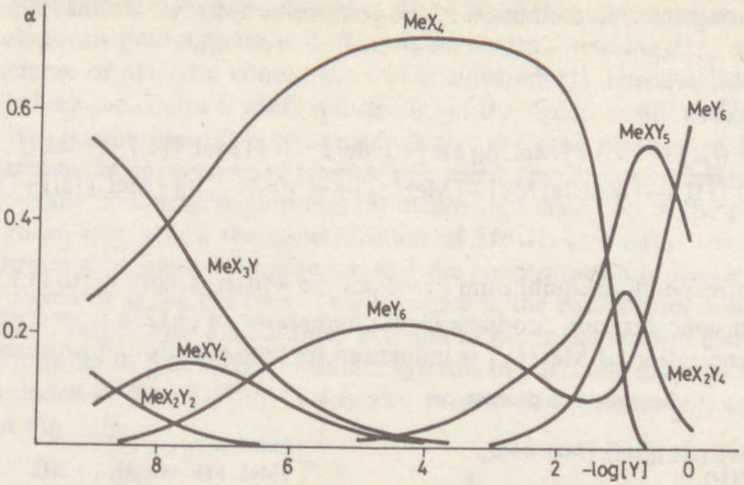


Fig. 3.22 Concentration distribution of complexes formed in the Al^{3+}–Cl^-–dimethylformamide (DMFA) system as a function of $-\log[Y]$. Me = Al^{3+}, X = Cl^-, Y = DMFA (Reproduced with permission from *Inorg. Chim. Acta*, **21**, 35 (1977)

sides of the equilibrium reaction, the elevation of [Y] increases the concentration of MeY_6.

In the T_X/T_Y interval between 0.5 and 0.7, the second equilibrium predominates. It is interesting to observe that the coordinatively saturated MeY_6 reacts with further Y (and with MeX_4), the two featuring on the same side of the equilibrium reaction. Thus, elevation of [Y] decreases the concentration of coordinately saturated MeY_6. This phenomenon is clearly a consequence of the asymmetry, i.e. the difference between the maximum coordination numbers for the subsystems Me–X and Me–Y.

Finally, as a consequence of the third equilibrium, the concentration of MeY_6 again increases. At sufficiently high [Y], MeY_6 becomes the species with the predominant concentration.

3.6.4.3.2 Stoichiometric asymmetry due to polynuclear complex formation

This effect is illustrated on the example of the CH_3Hg^+–acetate–proton system investigated by Rabenstein *et al.* [74]. These authors found that the hydroxo complexes $Me(OH) = MeH_{-1}$ and $Me_2(OH) = Me_2H_{-1}$ are formed in an aqueous solution of methylmercury; in the presence of acetate ion, the complex MeL is formed, too. As illustrated in Fig. 3.23, there are three extrema in the pH-dependent concentration distribution curve for Me_2H_{-1}.

Following the transformation of the composition matrix, we may derive

$$\frac{\mathrm{d}\log[\mathrm{Me_2H_{-1}}]}{\mathrm{dpH}} =$$

$$= \frac{([\mathrm{L}]+[\mathrm{HL}]+[\mathrm{MeL}])([\mathrm{Me}]-[\mathrm{MeH_{-1}}])+[\mathrm{MeL}]([\mathrm{L}]-[\mathrm{MeL}])}{([\mathrm{L}]+[\mathrm{HL}]+[\mathrm{MeL}])([\mathrm{Me}]+[\mathrm{MeH_{-1}}]+4[\mathrm{Me_2H_{-1}}])+[\mathrm{MeL}]([\mathrm{L}]+[\mathrm{HL}])}. \tag{3.123}$$

If the corresponding equilibrium processes are written according to (3.122) for the eight concentration products in the numerator of (3.123), it emerges that the concentration of $\mathrm{Me_2H_{-1}}$ is influenced by four equilibrium processes

Concentration product	Equilibrium	
(1) [L][Me], [HL][Me], [MeL][Me]	$2\mathrm{Me} \rightleftharpoons \mathrm{Me_2H_{-1}} + \mathrm{H}$	1
(2) [MeL][HL]	$2\mathrm{MeL} + \mathrm{H} \rightleftharpoons \mathrm{Me_2H_{-1}} + 2\mathrm{HL}$	−1
(3) [MeL][L]	$2\mathrm{MeL} \rightleftharpoons \mathrm{Me_2H_{-1}} + 2\mathrm{L} + \mathrm{H}$	1
(4) $[\mathrm{L}][\mathrm{MeH_{-1}}]$, $[\mathrm{HL}][\mathrm{MeH_{-1}}]$, $[\mathrm{MeL}][\mathrm{MeH_{-1}}]$	$2\mathrm{MeH_{-1}} + \mathrm{H} \rightleftharpoons \mathrm{Me_2H_{-1}}$	−1

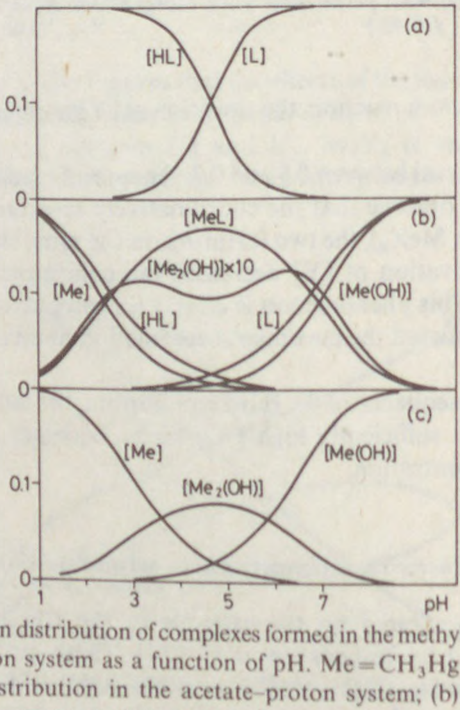


Fig. 3.23 Concentration distribution of complexes formed in the methylmercury–acetate–proton system as a function of pH. $\mathrm{Me} = \mathrm{CH_3Hg^+}$.
(a) Concentration distribution in the acetate–proton system; (b) concentration distribution in the methylmercury–acetate–proton three-component system; (c) concentration distribution in the methylmercury–proton system [70]
(Reproduced with permission from *Coord. Chem. Rev.*, **43**, 233 (1982))

At low pH values, the concentrations of acetic acid (HL) and free methylmercury (Me) obviously predominate, and thus the concentration of Me_2H_{-1} rises with the increase of pH, as a consequence of equilibrium (1). However, in the pH range where the complex MeL is formed, but the ligand is still mainly in the form HL, equilibrium (2) becomes significant; the concentration of Me_2H_{-1} decreases as the pH is raised. At higher pH, where the dissociation $HL \rightleftharpoons L + H$ is practically complete, equilibrium (3) means that elevation of the pH again leads to an increase in the concentration of Me_2H_{-1}. Finally, the effect of equilibrium 4 becomes predominant, and the concentration of Me_2H_{-1} once more decreases as the pH rises. This sequence of the equilibrium processes in question is responsible for the three extrema in the concentration distribution curve. In order to plot such and similar systems in a triangle diagram, the axes are extended so that OH^- (H_{-1}) is also present as a component, as can be seen in Fig. 3.24.

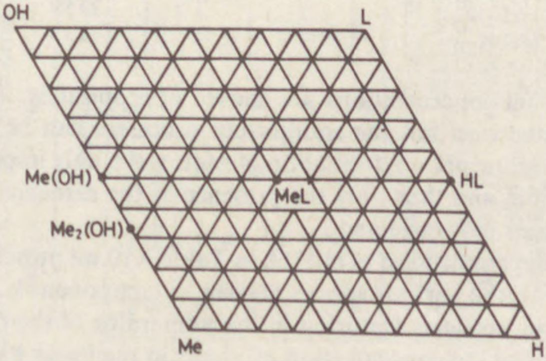


Fig. 3.24 Compositions of complexes formed in the methylmercury–acetate–proton system, in an extended triangle diagram [70]
(Reproduced with permission from *Coord. Chem. Rev.*, **43**, 233 (1982))

3.6.4.3.3 General asymmetry of H–L–Me systems

It was mentioned in Section 3.6.4.1.3 that the proton–ligand–metal ion systems can be symmetric in exceptional cases only. These systems are generally asymmetric. As an example of the analysis of the distributions in systems of this type, we shall present results obtained on the copper(II)–diethylenetriamine–proton system.

This system has been studied among others by Kaden and Zuberbühler [75]; the formation constants they found are listed in Table 3.9. The results of Nagypál, Beck and Zuberbühler [71] showed that a concentration minimum may appear in the concentration distribution curves of the species H_2L and

Table 3.9 Compositions and formation constants of species formed in the copper(II)–diethylenetriamine–proton system [75]

	Components			
	k_1 H	k_2 L	k_3 Me	
Species	Stoichiometric numbers			$\log \beta$
H	1	0	0	0
L	0	1	0	0
Me	0	0	1	0
HL	1	1	0	10.06
H_2L	2	1	0	19.35
H_3L	3	1	0	24.04
MeL	0	1	1	15.94
MeL_2	0	2	1	20.86
MeL_2H	1	2	1	29.58
$MeLH_{-1}$	−1	1	1	6.55

MeH_{-1} if the total concentrations are chosen appropriately. The system is a rather complicated one, but the equilibrium processes can be separated into two pH ranges. Below pH ~ 7, formation of MeL is the only important complex formation reaction, and thus only the presence of the associations H_3L, H_2L, HL and MeL need be considered.

To illustrate the application of (3.116), in Table 3.10 we present a description of the system with the various species chosen as component k_3, together with the concentration products featuring in the numerator of the first derivative.

From the signs of the concentration products in the lower half of Table 3.10 it is clear that [Me] and [H_3L] increase monotonously, while [L] and [MeL] decrease monotonously as the hydrogen ion concentration is elevated. An extremum (change in sign) can occur only in the concentration distribution curves for HL and H_2L.

To establish the possibility of a concentration minimum in accordance with the considerations discussed before, the second derivatives for the extrema of [HL] and [H_2] are given in Tables 3.11 and 3.12.

The left-hand columns of Tables 3.11 and 3.12 contain the first derivatives. The second derivatives are obtained by multiplying every element of the left-hand column by the numbers in the corresponding row and by the concentrations indicated in the headings of Table 3.12, the concentration products then being summed. Since the second derivatives are given at the zero points of the first derivative, an arbitrary number may be added to any column of Table 3.12. From the data and their signs in Table 3.11, it may be seen that the only term of the second derivative which has a positive coefficient is the concentration product [Me][MeL][MeL]. However, if −1 is added to the

Table 3.10 Composition matrices of species formed up to pH 7 in the copper(II)–diethylenetriamine–proton system, with the various species chosen as third component. The numerators of the first derivatives of the distribution curves are calculated on the basis of Eq. (3.116)

Species	Components																	
	k_1 H	k_2 L	k_3 Me	k_1 H	k_2 Me	k_3 L	k_1 H	k_2 Me	k_3 HL	k_1 H	k_2 Me	k_3 H_2L	k_1 H	k_2 Me	k_3 H_3L	k_1 H	k_2 Me	k_3 MeL
H	1	0	0	1	0	0	1	0	0	1	0	0	1	0	0	1	0	0
L	0	1	0	0	0	1	−1	0	1	−2	0	1	−3	0	1	0	−1	1
Me	0	0	1	0	1	0	0	1	0	0	1	0	0	1	0	0	1	0
HL	1	1	0	1	0	1	0	0	1	−1	0	1	−2	0	1	1	−1	1
H_2L	2	1	0	2	0	1	1	0	1	0	0	1	−1	0	1	2	−1	1
H_3L	3	1	0	3	0	1	2	0	1	1	0	1	0	0	1	3	−1	1
MeL	0	1	1	0	1	1	−1	1	1	−2	1	1	−3	1	1	0	0	1
Numerator	+[HL] [MeL] +2[H_2L] [MeL] +[H_3L] [MeL]			−[Me] [HL] −2[Me] [H_2L] −3[Me] [H_3L] −[HL] [MeL] −2[H_2L] [MeL] −3[H_3L] [MeL]			+[Me] [MeL] +[L] [Me] +[L] [MeL] −[Me] [H_2L] −[H_2L] [MeL] −2[Me] [H_3L] −2[H_3L] [MeL]			+2[Me] [MeL] +2[L] [Me] +2[L] [MeL] +[Me] [HL] +[HL] [MeL] −[Me] [H_3L] −[H_3L] [MeL]			+3[L] [Me] +3[L] [MeL] +2[Me] [HL] +[Me] [H_2L] +3[Me] [MeL] +2[HL] [MeL] +[H_2L] [MeL]			−[Me] [HL] −2[L] [H_2L] −3[Me] [H_3L]		

Table 3.11 Numerator of the $d^2\ln[HL]/d\ln[H]^2$ at the zero-points of the first derivative

A_j	[Me]	[MeL]
First derivative*	$((p_1+q_1)\alpha_{j2}^2-(p_2+q_2)\alpha_{j1}\alpha_{j2})[A_j])$**	
+[Me] [MeL]	−1	1
+[L] [Me]	−1	0
+[L] [MeL]	−2	−1
−[Me] [H_2L]	1	2
−[H_2L] [MeL]	0	1
−2[Me] [H_3L]	2	3
−2[H_3L] [MeL]	1	2

* $(p_1q_2-q_1p_2)(p_2q_3-q_2p_3)[A_p][A_q]$

** see Eq. (3.121)

Table 3.12 Numerator of the $d^2\ln[H_2L]/d\ln[H]^2$ at the zero points of the first derivative

A_j	[Me]	[MeL]
First derivative*	$((p_1+q_1)\alpha_{j2}^2-(p_2+q_2)\alpha_{j1}\alpha_{j2})[A_j])$**	
+2[Me] [MeL]	−2	2
+2[L] [Me]	−2	0
+2[L] [MeL]	−4	−2
+[Me] [HL]	−1	1
+[HL] [MeL]	−3	−1
−[Me] [H_3L]	1	3
−[H_3L] [MeL]	−1	1

* $(p_1q_2-q_1p_2)(p_2q_3-q_2p_3)[A_p][A_q]$

** see Eq. (3.121)

right-hand column of Table 3.11, then the signs of all of the concentration products will be negative. This means that there is only a single extremum in the concentration distribution curve of HL, and this is a maximum.

A similar analysis of the data in Table 3.12 demonstrates that the addition (or subtraction) of any number to the columns always leaves concentration products with both signs. Consequently, more than one extremum (i.e. a minimum too) may occur in the distribution curve of H_2L.

A special point of the distribution curve is that at which the values of both the first and second derivatives are zero, i.e. where there is a horizontal inflexion point in the curve. In the given system, this point can be described by

$$T_L=[L]+[HL]+[H_2L]+[H_3L]+[MeL] \tag{3.124}$$

$$T_{Me}=[Me]+[MeL]\,. \tag{3.125}$$

By rearrangement of the numerator of the first derivative

$$([H_3]-[HL]-2[L])([Me]+[MeL])=2[Me][MeL] \qquad (3.126)$$

and by rearrangement of the numerator of the second derivative

$$(4[L]+[HL]+[H_3L])([Me]+[MeL])^2=4[Me][MeL]([MeL]-[Me]). \qquad (3.127)$$

Equations (3.124)–(3.127) are overdefined for [H], [L] and [Me]; thus, in the interest of the solution of the equation system, one of the parameters (the value of T_L, T_{Me} or one of the formation constants) must be regarded as a parameter to be calculated. Obviously, in a real chemical system only the total concentrations can be chosen freely. For the sake of simplicity, however, in the following discussion not only [H], [L] and [Me], but also β_{MeL} will be regarded as unknown.

Equations (3.125) and (3.126) can be rearranged

$$[Me]=\frac{T_{Me}}{1+\beta_{MeL}[L]} \qquad (3.128)$$

$$\beta_{H_3L}[H]^3-\beta_{HL}[H]-2)\,(1+\beta_{MeL}[L])=2\beta_{MeL}[Me]. \qquad (3.129)$$

Substituting Eq. (3.129) into Eq. (3.128) and multiplying by [L]

$$[L]\,(\beta_{H_3L}[H]^3-\beta_{HL}[H]-2)\,(1+\beta_{MeL}[L]=2T_{Me}\frac{\beta_{MeL}[L]}{1+\beta_{MeL}[L]}. \qquad (3.130)$$

The use of (3.126) and (3.127) then leads to

$$\beta_{MeL}[L]=\frac{3\beta_{H_3L}[H]^3-\beta_{HL}[H]}{\beta_{H_3L}[H]^3-3\beta_{HL}[H]-8}. \qquad (3.131)$$

Substitution of this expression into Eq. (3.130) gives

$$[L]=2T_{Me}\frac{(3\beta_{H_3L}[H]^3-\beta_{HL}[H])\,(\beta_{H_3L}[H]^3-3\beta_{HL}[H]-8)}{(\beta_{H_3L}[H]^3-\beta_{HL}[H]-2)\,(4\beta_{H_3L}[H]^3-4\beta_{HL}[H]-8)^2}. \qquad (3.132)$$

Finally, substitution of Eq. (3.132) into Eq. (3.124) and rearranging yields

$$T_L/T_{Me}=\frac{3\beta_{H_3L}[H]^3-\beta_{HL}[H]}{4(\beta_{H_3L}[H]^3-\beta_{HL}[H]-2)}+$$

$$+\frac{(3\beta_{H_3L}[H^3-\beta_{HL}[H])(\beta_{H_3L}[H]^3-3\beta_{HL}[H]-8)(1+\beta_{HL}[H]+\beta_{H_2L}[H]^2+\beta_{H_3L}[H]^3)}{8(\beta_{H_3L}[H]^3-\beta_{HL}[H]-2)^3}. \qquad (3.133)$$

The surprising result from Eq. (3.133) is that T_L/T_{Me} is clearly defined by the pH of the horizontal inflexion point. If T_L/T_{Me} is calculated at various pH values, all of the unknowns ([L], [Me] and β_{MeL}) can be calculated by means of the above explicit formulae.

The mutual correlation between the $\log \beta_{MeL}$ values and the concentration ratio T_L/T_{Me} relating to the horizontal inflexion point is illustrated in Fig. 3.25. Figure 3.25 shows that a minimum can occur in the concentration distribution curve of H_2L only if the T_L/T_{Me} and $\log \beta_{MeL}$ data lie in the region defined by the "limiting lines". The region displays some characteristic features.

(1) If $\log \beta_{MeL} < 7.806$, or if $T_L/T_{Me} > 26.15$, there cannot be a minimum in the H_2L concentration.

(2) There is no upper limiting value of $\log \beta_{MeL}$ which eliminates the possibility of a minimum.

(3) At very large $\log \beta_{MeL}$, the curves asymptotically approach the limiting values $1 < T_L/T_{Me} < 9/8$.

(4) At the experimental value of $\log \beta_{MeL}$ (15.94), there can be a minimum in the H_2L concentration distribution curve only if the $1.0024 < T_L/T_{Me} < 1.164$ relation is fulfilled.

The correlations presented in Fig. 3.25 are also illustrated in Figs 3.26 and 3.27, where the H_2L concentration distribution curves are given at various T_L/T_{Me} and $\log \beta_{MeL}$ values.

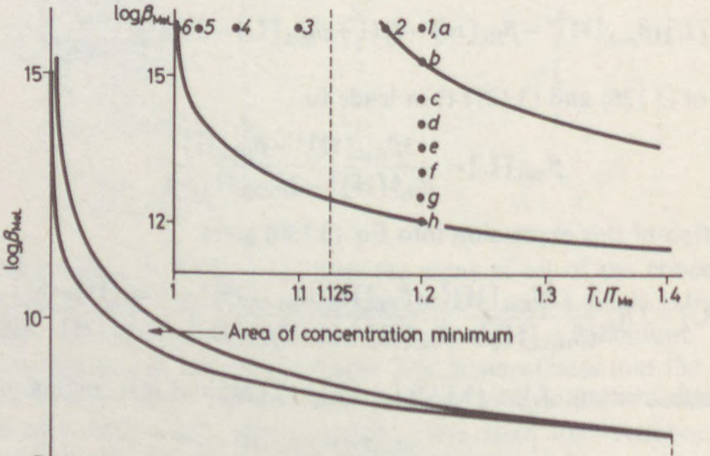


Fig. 3.25 Correlation of $\log \beta_{ML}$ and T_L/T_{Me} at the horizontal inflexion points of the distribution curve $[H_2L] = f(pH)$ in the Cu^{2+}–diethylenetriamine–proton equilibrium system. The insert shows the same function on an extended T_L/T_{Me} scale. The individual points correspond to the distribution curves of Fig. 3.26 *(1–6)* and Fig. 3.27 *(a–h)* [71] (Reproduced with permission from *Talanta*, **30**, 593 (1983))

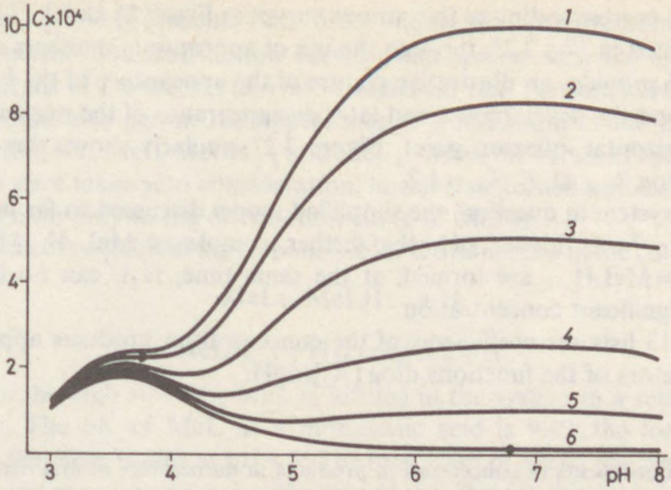


Fig. 3.26 Concentration distribution of the species H_2L in the Cu^{2+}–diethylenetriamine–proton equilibrium system, at various concentration ratios T_L/T_{Me}. $T_{Me} = 0.005\ M$, $T_L/T_{Me} =$ *1* — 1.2; *2* — 1.164; *3* — 1.1; *4* — 1.05; *5* — 1.02; *6* — 1.0024. The horizontal inflexion points are shown in Curves *2* and *6* [71]
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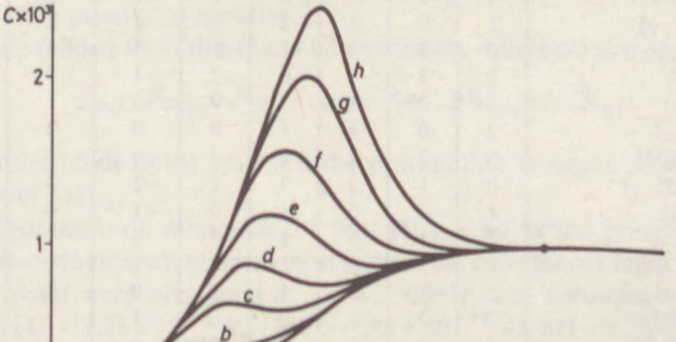

Fig. 3.27 Concentration distribution of the species H_2L in the Cu^{2+}–diethylenetriamine–proton equilibrium system, at various $\log \beta_{MeL}$ values. $T_{Me} = 0.005$, $T_L = 0.006$, $\log \beta_{MeL} = a$ — 15.94; *b* — 15.271; *c* — 14.5; *d* — 14.0; *e* — 13.5; *f* — 13.0; *g* — 12.5; *h* — 12.091. The horizontal inflexion points are shown in Curves *b* and *h* [71]
(Reproduced with permission from *Talanta*, **30**, 593 (1983))

The data corresponding to the various curves in Figs 3.26 and 3.27 have also been indicated in Fig. 3.25, through the use of appropriate numbers or letters. Figure 3.26 provides an illustrative picture of the appearance of the horizontal inflexion, and the development and later disappearance of the minimum via a second horizontal inflexion point. Figure 3.27 similarly shows the effects of change in log β_{MeL} at $T_L/T_{Me} = 1.2$.

For the system in question, the simplified model discussed so far holds only up to pH ~ 7. At higher pH, the further complexes MeL_2H, MeL_2 and $MeL(OH) = MeLH_{-1}$ are formed; at the same time, H_3L can no longer be found in significant concentration.

Table 3.13 lists the coefficients of the concentration products appearing in the numerators of the functions dlog $[A_j]$/dpH.

Table 3.13 Coefficients of concentration products in numerators of first derivatives of concentration distribution curves for species formed in the copper(II)–diethylenetriamine–proton equilibrium system

	Third component*							
	Me	L	HL	H_2L	MeL	MeL_2	MeL_2H	$MeLH_{-1}$
Concentration product	Coefficients							
[L] [Me]	0	0	1	2	0	0	1	−1
[L] [MeL]	0	0	1	2	0	0	1	−1
[L] $[MeL_2]$	0	0	1	2	0	0	1	−1
[L] $[MeL_2H]$	−1	0	1	2	−1	−1	0	−2
[L] $[MeLH_{-1}]$	1	0	1	2	1	1	2	0
[Me] [HL]	0	−1	0	1	−1	−2	−1	−2
[Me] $[H_2L]$	0	−2	−1	0	−2	−4	−3	−3
[Me] [MeL]	0	0	1	2	0	0	1	−1
[Me] $[MeL_2]$	0	0	4	8	0	0	4	−4
[Me] $[MeL_2H]$	0	−2	2	6	−2	−4	0	−6
[Me] $[MeLH_{-1}]$	0	1	2	3	1	−2	3	0
[HL] [MeL]	1	−1	0	1	0	−1	0	−1
[HL] $[MeL_2]$	2	−1	0	1	1	0	1	0
[HL] $[MeL_2H]$	1	−1	0	1	0	−1	0	−1
[HL] $[MeLH_{-1}]$	2	−1	0	1	1	0	1	0
$[H_2L]$ [MeL]	2	−2	−1	0	0	−2	−1	−1
$[H_2L]$ $[MeL_2]$	4	−2	−1	0	2	0	−1	1
$[H_2L]$ $[MeL_2H]$	3	−2	−1	0	1	−1	0	0
$[H_2L]$ $[MeLH_{-1}]$	3	−2	−1	0	1	−1	0	0
[MeL] $[MeL_2]$	0	0	1	2	0	0	1	−1
[MeL] $[MeL_2H]$	1	−1	0	1	0	−1	0	−1
$[MeL_2]$ $[MeLH_{-1}]$	2	−1	0	1	1	0	1	0
$[MeL_2H]$ $[MeLH_{-1}]$	3	−2	−1	0	1	−1	0	0

* The second component is L in the case of Me, while it is Me for the other species.

The signs of the coefficients lead to the finding that an extremum can occur in the concentration distribution curves of all species with the exception of H_2L. Analysis of the second derivative indicated that the *stoichiometry* of the system would also permit the appearance of a minimum in the distribution curves of Me, HL, MeL, $MeLH_{-1}$ and MeL_2. When the values of the formation constants were taken into consideration, however, it turned out that there can be a minimum only in the distribution curve of $MeLH_{-1}$.

The following equilibria are responsible for the minimum in the concentration of $MeLH_{-1}$

$$MeL \rightleftharpoons MeLH_{-1} + H$$

$$MeLH_{-1} + H_2L \rightleftharpoons MeL_2 + H$$

Because of the high stability, MeL is formed in the system in a relatively low pH range. The pK of MeL as a monobasic acid is 9.49; the formation of $MeLH_{-1}$ therefore begins at pH ~ 8. The formation of MeL_2 too begins in this pH range, but as a consequence of the second equilibrium, this process decreases the concentration of $MeLH_{-1}$ with increase of the pH. As the pH is further raised, the effect of the second equilibrium disappears, because of the decrease in the H_2L concentration, and thus the concentration of $MeLH_{-1}$ increases again.

In full accordance with these considerations, it can be seen in Table 3.13 that the only concentration product with a positive coefficient is $[MeL_2][H_2L]$.

At the same time, the change in the concentration product $[HL][MeL_2H]$ is strictly parallel to the change in $[MeL_2][H_2L]$, and the sign of this latter concentration product is negative.

It clearly follows from this that a concentration minimum can appear only if

$$\beta_{H_2L} \cdot \beta_{MeL_2} > \beta_{HL} \cdot \beta_{MeL_2H} \quad \text{i.e.} \quad pK^H_{HL} > pK^H_{MeL_2}$$

This relation holds in the system if the protonation constant of HL is larger than that of MeL_2.

As a concentration minimum for $MeLH_{-1}$ is an actual possibility in the copper(II)–diethylenetriamine–proton system, the coordinates of the horizontal inflexion point were calculated at $T_{Me} = 0.005$ M. The following results were obtained: $[L] = 1.38 \times 10^{-4}$ M, $[Me] = 2.47 \times 10^{-16}$ M, pH = 9.225. These data determine $T_L = 0.01167$.

Figure 3.28 depicts the concentration distribution of the mixed hydroxo complex $MeLH_{-1}$ at $T_{Me} = 0.005$ and various total ligand concentrations. Figure 3.28 reveals that a minimum does not develop at low T_L values. There is a horizontal inflexion at $T_L = 0.01167$ (Curve *c*), and a minimum at larger T_L values. It should be noted that, in contrast with the distribution curves in Fig. 3.26, a second inflexion point does not appear with the increase of T_L; the minimum does not disappear.

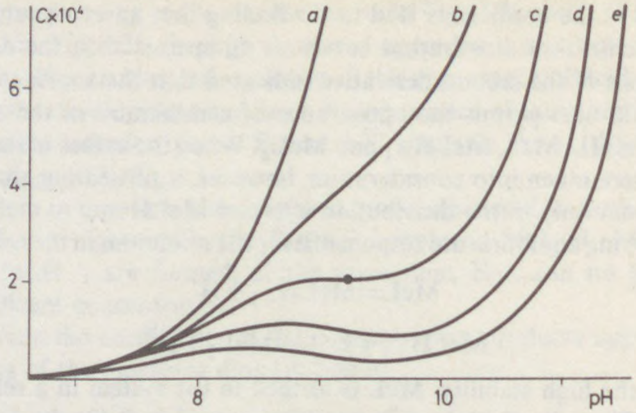

Fig. 3.28 Concentration distribution of the complexes $MeLH_{-1}$ in the Cu^{2+}–diethylenetriamine–proton equilibrium system. $T_{Me} = 0.005$, $T_L = a$ — 0.008; b — 0.010; c — 0.01167 (horizontal inflexion point); d — 0.015; e — 0.020 [71] (Reproduced with permission from *Talanta*, **30**, 593 (1983))

3.6.4.3.4 Thermodynamic asymmetry

It has already been mentioned in Section 3.6.4.1.3 that, in spite of the agreement of the maximum ligand numbers relating to the individual subsystems, the mixed complex equilibrium systems may be asymmetric if one of the intermediate complexes is missing or is formed only in very low concentration. The effects of this type of asymmetry on the concentration distribution curves are demonstrated on the example of the Hg^{2+}–Cl^-–OH^- system.

This system was investigated by Sjöberg [76], whose equilibrium data are given in Table 3.14.

Table 3.14 Formation constants of complexes present in the Hg^{2+}–Cl^-–OH^- equilibrium system at $T_{Cl^-}/T_{Hg^{2+}} < 2$ [76]

Species	$\log \beta$
HgCl	7.22
$HgCl_2$	14.00
HgOH	10.64
$Hg(OH)_2$	22.20
Hg(OH)Cl	18.35

* $pK_W = 14.22$

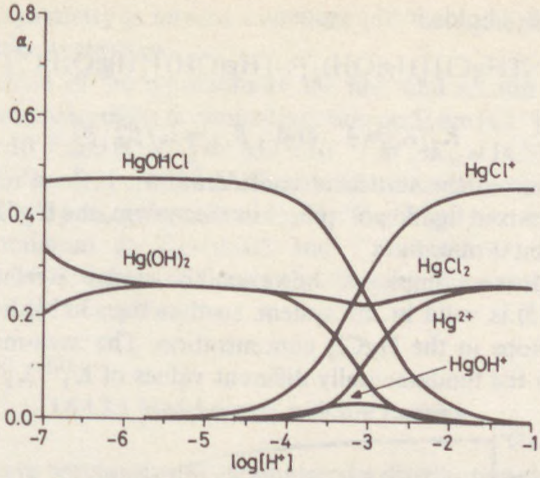

Fig. 3.29 Partial mole fractions of complexes formed in the Hg^{2+}–Cl^-OH^- system as a function of pH. $T_{Hg}=0.005$, $T_{Cl^-}=0.005$ *M* [76]
(Reproduced with permission from *Acta Chem. Scand.* **A31,** 705 (1977))

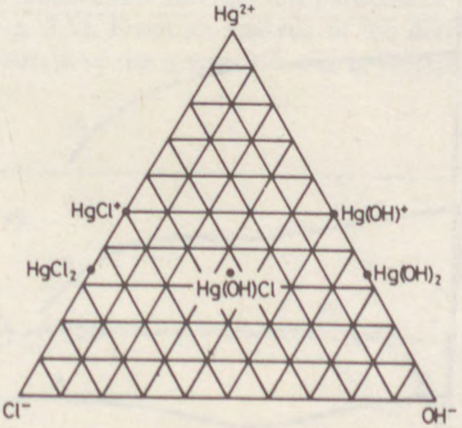

Fig. 3.30 Compositions of species formed in the Hg^{2+}–Cl^-–OH^- system [70]
(Reproduced with permission from *Coord. Chem. Rev.* **43,** 233 (1982))

His calculations showed that at constant T_{Cl}/T_{Hg} the $HgCl_2$ concentration displays a minimum as a function of pH, as shown in Fig. 3.29. The triangle diagram describing the system is given in Fig. 3.30.

It may be seen in Fig. 3.30 that the triangle diagram of the system is symmetric, but that there is nevertheless a concentration minimum in the curve. In order to interpret this phenomenon, the first and second derivatives were obtained. These demonstrated that the reason for the minimum is that the relation

$2K_1^{Cl}\cdot K_2^{OH} > \beta_{11}$ holds in the system

$$2[HgCl][Hg(OH)_2] > [Hg(OH)][Hg(OH)Cl]. \qquad (3.134)$$

The relations

$$K_1/K_2 = 4 \quad \text{and} \quad \beta_{11} = 2\sqrt{\beta_2^A \cdot \beta_2^B}$$

can be derived from the statistical considerations. If these relations hold for the parent and mixed ligand complexes in the system, the $HgCl_2$ concentration could not exhibit a minimum.

For the hydroxo complexes, however, the unusual relation $K_2^{OH} > K_1^{OH}$ ($K_1^{OH}/K_2^{OH} = 0.15$) is valid in the system, so that Eq. (3.133) holds true, and a minimum develops in the $HgCl_2$ concentration. The asymmetry in this case originates from the fundamentally different values of K_1^{OH}/K_2^{OH} and K_1^{Cl}/K_2^{Cl}.

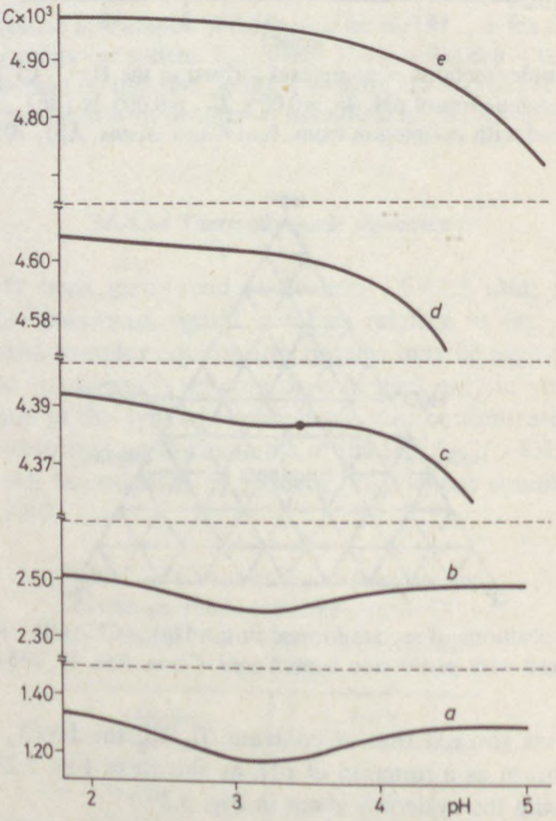

Fig. 3.31. Concentration distribution of $HgCl_2$ in the Hg^{2+}–Cl^-–OH^- equilibrium system. $T_{Hg} = 0.005$; $T_{Cl} = a$ — 0.005; b — 0.007; c — 0.00937 (horizontal inflexion point); d — 0.0096; e — 0.01 [70]
(Reproduced with permission from *Coord. Chem. Rev.* **43**, 233 (1982))

This type of asymmetry is termed asymmetry of the equilibrium constants, or thermodynamic asymmetry.

From the solution of the equations of the first and second derivatives, at $T_{Hg} = 0.005$ the coordinates of the horizontal inflexion point are $[Cl^-] = 3.963 \times 10^{-6}$, $[Hg^{2+}] = 2.792 \times 10^{-6}$ and $[OH^-] = 1.659 \times 10^{-11}$ M ($pK_w = 14.22$, i.e. pH = 3.44). From these data, $T_{Cl} = 9.37 \times 10^{-3}$ M. Figure 3.31 illustrates the concentration distribution of $HgCl_2$ as a function of pH. The Figure reveals the $HgCl_2$ concentration minimum at $T_{Cl} = 0.005$ and $T_{Cl} = 0.007$ M, the horizontal inflexion at $T_{Cl} = 0.00937$ M, and finally the disappearance of the inflexion at higher total chloride concentrations.

3.6.4.3.5 Model system with five extrema

Although we have previously not encountered a distribution curve with more than one minimum in the literature, the possibility of this can not be excluded. The simplest model system in which five extrema can appear is probably that in which the associations H_2L, HL, MeL_2 and $Me(OH)_4$ are formed.

The results of one model calculation on this particularly asymmetric system are to be seen in Fig. 3.32. From an analysis of the derivatives, the special concentration distribution of the species HL can be interpreted as follows. In

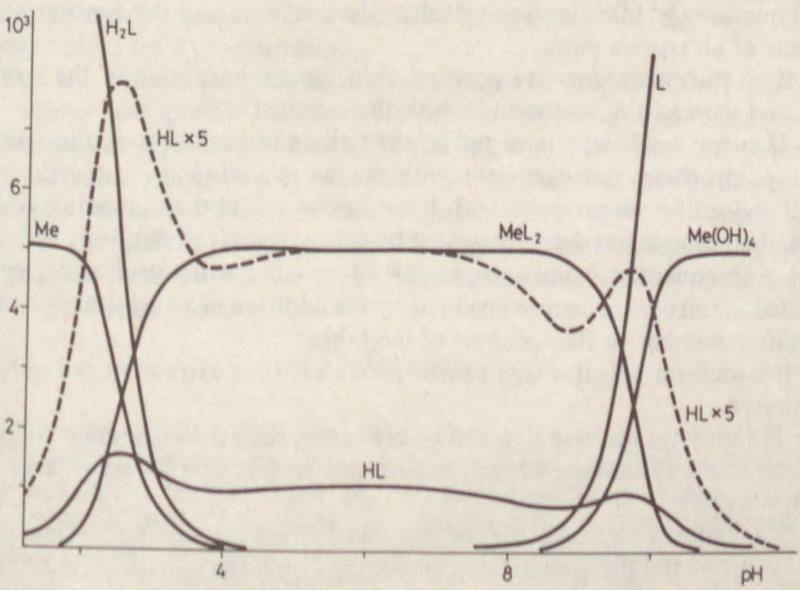

Fig. 3.32 Concentration distribution of HL in an L–H model system. $T_L = 0.011$; $T_{Me} = 0.005$; $\log \beta_{HL} = 9.00$; $\log \beta_{H_2L} = 12.00$; $\log \beta_{MeL_2} = 8.50$; $\log \beta_{MeH_{-4}} = -25.00$ [71]
(Reproduced with permission from *Talanta*, **30**, 593 (1983))

the absence of metal ion, the concentration of HL would increase with increase of the pH up to pH ~ $(pK_1 + pK_2)2$. Via the equilibrium $Me + 2HL \rightleftharpoons MeL_2 + 2H$, however, the formation of MeL_2 decreases the concentration of HL, and this decrease overcompensates the rise in [HL]. The formation of MeL_2 is completed at pH ~ 4, and thus [HL] again rises. In the absence of metal ion, HL would decrease in the range pH > 6. However, in this pH range the process $MeL_2 \rightarrow Me(OH)_4 + + 2HL + 2H$ takes place, which increases [HL] with the increase of the pH, and overcompensates the decrease of [HL]. Finally, this process too is completed, and as a consequence of the dissociation $HL \rightleftharpoons L + H$[HL] again decreases with increase of the pH.

3.6.4.4 Algorithm of the analysis of concentration distribution

On the basis of the mathematical considerations and the examples presented in the preceding sections, the following general procedure and algorithm can be formulated for analysis of the concentration distribution curves in three-component equilibrium systems.

(1) The composition matrix is transformed so that the species in question should be the third component.

(2) Equation (3.115) is used to calculate the coefficients of the concentration products of all species pairs.

(i) If all the coefficients are positive, then the concentration of the species concerned increases monotonously with the increase of $[k_1]$.

(ii) If every coefficient is negative, then the concentration of the species concerned decreases monotonously with the increase of $[k_1]$.

(3) If concentration products with both signs occur in the numerator of Eq. (3.116), then the second derivative must be calculated in tabular form with Eq. (3.121). Subsequently, it must be examined whether a uniform sign can be generated for all concentration products by the addition of an arbitrary positive or negative number to the columns of the table.

(i) If a uniform negative sign can be produced, then extremum can only be a maximum.

(ii) If a uniform positive sign can be produced, then the extremum can only be a minimum. (This type of distribution has so far been found in a model system only.)

(4) If a uniform sign can not be produced, then (depending on the total concentrations and the numerical values of the formation constants) more than one extremum can occur.

The following step is the establishment of the correlations between the concentration products with positive and negative signs. If there are concentration products which can be given with identical powers of the concentrations of the components, but with different formation constants, then the values of the corresponding formation constants govern whether or not more than one extremum can occur.

If the above analysis points to the possibility of more than one extremum, then one of the mass-balance equations, together with the equations with the first and second derivatives equal to zero, must be solved for the roots $0 < [k_i] < T_i$, in order to obtain the coordinates of the horizontal inflexion point.

3.6.4.5 Conclusions

The considerations to this point refer to three-component systems, but they can readily be extended to systems with more components. On the simple example of the copper(II)–diethylenetriamine–proton system, it was seen that with appropriate constant ratios the concentration minimum can develop in the distribution curve of almost any species. It is very probable, therefore, that in more complicated equilibrium systems the species with distribution curves without the possibility of minimum are to be regarded as exceptions.

By the appropriate choice of the equilibrium conditions and total concentrations, systems can be produced in which the concentration of the given species is nearly constant in a wide pH range (but not the same as the corresponding total concentration).

Thus, use of the rules outlined above may also be of help in the planning of the various ion-specific buffers. It is known moreover that a number of mechanisms are operative in biological systems, which keep the concentrations of the individual species at almost constant levels. Chemical equilibrium systems in which the concentrations of certain species barely vary as a result of the mutually competitive processes may also play a role in biological regulation. The study of these may lead to a deeper understanding of some of the features of biological regulation.

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Chapter 4

Experimental methods

Complex formation leads to changes in numerous physical chemical properties of solutions. In principle, the measurement of any parameter which varies in response to complex formation provides a possibility for calculation of the compositions and formation constants of the complexes. In practice, however, the following conditions must also be satisfied if quantitative conclusions are to be drawn from the changes.

(a) The correlation(s) between the extent of complex formation and the measured parameter(s) must be known exactly.

(b) Complex formation must cause the parameter in question to change to an extent much higher than the experimental error.

(c) Measurements must be made in the range of total concentrations of the components where complex formation is well measurable, but not complete.

Questions relating to conditions (a) and (b) will be considered below, during the detailed treatment of the individual methods.

The available stability constant tables [1, 2] reveal that most equilibrium data were obtained by means of potentiometry (pH-metry) and visible-ultraviolet spectrophotometry. Recently, these two methods have undergone significant advances, primarily as a consequence of the development and widespread application of ion-selective electrodes and recording spectrophotometers. Nevertheless, a survey of the most recently published data reveals that their use has been declining, because of the elaboration and introduction of other spectroscopic (NMR, ESR, Raman) and extraction methods and calorimetry. Particularly NMR spectroscopy and calorimetry have become important in the chemistry of complex equilibria. The NMR spectrum provides information at the molecular level on the examined system. It may therefore be applicable for determination of the microconstants (to be discussed in detail later) which shed light on the connection between the chemical equilibrium and the structure. In some cases calorimetry is also suitable for determination of the equilibrium constants. However, its main importance is that it permits resolution of the free enthalpy change accompanying complex formation into the enthalpy and entropy changes, whereby certain structural conclusions may be drawn.

In general, the following correlation holds between the value of some parameter, X, which can be measured directly or can be calculated simply from the experimental data, and the concentrations of the species present in the equilibrium system

$$\mathrm{X} = \sum_{i=1}^{n} x_i[\mathrm{A}_i] \tag{4.1}$$

where x_i is the corresponding intensive factor. This equation holds, for example, for the description of data from spectrophotometric measurements.

In certain cases of application of extraction and NMR, ESR and Raman spectroscopy to equilibrium chemistry, the experimental data comprise a linear function of the concentration of a single species, i.e.

$$\mathrm{X} = x_k[\mathrm{A}_k]\,. \tag{4.2}$$

When the colligative properties are measured, all the intensive factors have the same value, and (4.1) can therefore be written in the form

$$\mathrm{X} = x \sum_{i=1}^{n} [\mathrm{A}_i]\,. \tag{4.3}$$

If potentiometry is carried out, X is the equilibrium concentration that can be calculated directly from the measured EMF (pH). The value of x_k relating to the component in question is therefore one, while for the other species $x_i = 0$, i.e.

$$\mathrm{X} = [\mathrm{A}_k]\,. \tag{4.4}$$

4.1 Measurement of colligative properties

A decrease in the number of species in a solution is a necessary consequence of the complex formation processes. Accordingly, the measurement of colligative properties, which depend on the number of dissolved species, may be suitable for the experimental study of equilibrium processes. As early as the beginning of this century, the measurement of freezing point depression was used to determine some acid dissociation constants. The quantitative aspects of the method have been discussed in detail by Souchay [3], Kenttämaa [4], Rossotti and Rossotti [5] and Tobias [6]. Although the experimental accuracy was increased considerably by the application of thermistors, the method has the unavoidable drawback that the studies can be made only at a single temperature, and there is no possibility to ensure a constant ionic strength. Measurement of the freezing point depression in itself is rarely sufficient for the determination of equilibrium constants. The experimental data do indicate that association occurs between the components of the system under study, but the corresponding equilibrium constants can be calculated only in the simplest cases.

However, application of the method may be of value for the determination of auxiliary data required for the investigation of more complicated systems. As an example, Jensen [7] studied the Cd^{2+}–imidazole system polarographically in the ligand concentration interval 0.01–1.00 *M*. Such a large change in the ligand concentration made determination of the activity coefficients necessary. For this purpose, he used measurement of the freezing point depression and the vapour tension. Henry and Marks [8] carried out a spectrophotometric study of the $PdCl_2$–LiCl interaction in anhydrous acetic acid. For evaluation of the data, they needed to know the equilibrium constant of the association $2LiCl \rightleftharpoons Li_2Cl_2$, which can not be followed photometrically. The dimerization constant calculated from their vapour tensiometric measurements agreed well with the value found earlier by Kenttämaa [9] from freezing point depression measurements. The specific hydration of the perchlorate ion in nitrobenzene was studied by Tarui by means of freezing point depression [10] and vapour pressure [11] measurements. Measurement of the freezing point depression in the future may primarily be of importance in studies of specific solvation, though vapour tension measurement may be applied in this case too. Through measurement of the freezing point depression for benzene solutions of $ZnCl_2$, Schaarschmidt *et al.* [12] established the formation of polynuclear chloro complexes.

Measurement of the boiling point elevation may in principle likewise be used for the determination of equilibrium constants, but the measurement is more difficult to carry out, the experimental accuracy is lower, and the higher temperature may be a disadvantage.

As concerns the colligative properties, measurement of the vapour tension of the solvent is the most important. The method most frequently applied for this is vapour pressure osmometry. As seen above, vapour pressure measurement is used to supplement or check freezing point depression measurements. Otherwise, it is mainly employed for the study of ion association [13–16]. The significance of vapour pressure osmometry is increased by the fact that, together with the measurement of conductivity, it is the most important method of checking the considerations of Yokoyama and Yamatera [16, 17] to synthetize the Debye–Hückel theory and the theory of ion association. Eliezer and Algavish [18] applied vapour pressure osmometry to study the association of mercury halides in organic solvents.

As concerns equilibrium measurements based on the measurement of colligative properties, it can be stated in general that they are best used in combination with other methods or when the process under consideration can not be investigated by a simpler, more direct method.

4.2 Optical methods

The most striking phenomenon accompanying complex formation is the change in colour of a solution. The spectra of complexes in the visible or ultraviolet region permits valuable structural conclusions, particularly in the solution of transition metal and charge-transfer complexes. This field will not be dealt with in the present book. Reference may be made to relevant monographs [19–21].

The photometric methods are based on the mass balance equations and the Bouguert–Lambert–Beer law

$$T_1 = \sum_{j=1}^{n} \alpha_{j1}\beta_j[\mathrm{k}_1]^{\alpha_{j1}} \dots [\mathrm{k}_m]^{\alpha_{jm}}$$

$$\vdots$$

$$T_m = \sum_{j=1}^{n} \alpha_{jm}\beta_j[\mathrm{k}_1]^{\alpha_{j1}} \dots [\mathrm{k}_m]^{\alpha_{jm}} \tag{4.5}$$

$$A_p = \log\left(\frac{I_0}{I}\right)_p = d \sum_{j=1}^{n} \varepsilon_{jp}\beta_j[\mathrm{k}_1]^{\alpha_{j1}} \dots [\mathrm{k}_m]^{\alpha_{jm}}$$

where A_p is the absorbance of the solution, d is the cell length, and ε_{jp} is the molar absorption coefficient of the jth species at the wavelength denoted by index p. Photometric measurements are generally made at several wavelengths. In measurements involving different wavelengths, it is advantageous to select wavelengths in the vicinity of the maxima of the bands in the spectrum. The agreement of separately calculated formation constants at the different bands appreciably increases their reliability. If measurements at different wavelengths are evaluated jointly, the reliability of the constants is demonstrated by the results of appropriate statistical tests.

Spectrophotometric measurements may basically be divided into two groups, depending on whether exclusively the photometric data are utilized, or the calculations involve the use of data obtained from other measurements on the system (e.g. pH, pL, pMe). The majority of systems studied exclusively by spectrophotometric means are two-component ones, or systems which can be treated in practice as consisting of two components.

An account will be given below of the more important methods of investigation of two- and subsequently multicomponent systems, and also of photometric methods supplemented with other techniques.

4.2.1 Photometric study of two-component systems

In the following discussion the two components will be denoted by Me and L, with reference to metal ion–ligand systems. The ligand–proton interaction will be neglected, i.e. in the case of ligands that are conjugate bases to weak acids the considerations apply only in that pH range in which protonation of the ligand can be disregarded, or where the effect of protonation always appears in the same way in the course of the measurements. Me may denote a solvated metal ion, but it may also denote a stable or inert complex formed with a ligand L′, this complex not dissociating under the conditions of the study.

In two-component systems, the measurements are made with systematic variation of the total concentrations T_L and/or T_{Me}. The individual methods differ from one another in the manner in which the total concentrations are varied.

(a) $T_L + T_{Me}$ is kept constant, and the ratio T_L/T_{Me} is varied. This procedure is known as the method of continuous variation, or the *Job* method.

(b) T_{Me} is kept constant, and T_L is varied. This is known as the mole ratio method or, to distinguish it from method (c), the mole ratio L method.

(c) T_L is kept constant, and T_{Me} is varied. This is the mole ratio Me method.

(d) T_L/T_{Me} is kept constant, and T_L and T_{Me} are varied. This procedure is known as stoichiometric dilution.

(e) T_L and T_{Me} are varied so that the correlation $T_L = [L] + \bar{n}T_{Me}$ is satisfied at the same [L] and $\bar{n}$ values. The procedure was elaborated by Bjerrum [22], and is known as the method of corresponding solutions.

The above methods are illustrated in Figs. 4.1–4.3; these diagrams show the concentration plane defined by the T_L and T_{Me} axes (see Országh and Beck [61]).

It must be noted that the modern computational possibilities permit the calculation of equilibrium constants from spectrophotometric data situated irregularly in the T_L vs. T_{Me} plane. However, the *regular* variation of the concentrations remains important, for in this way characteristic plots can be obtained that give information of the greatest value on the composition and stability of the complexes formed; what is more, this information is available directly, or almost at a glance. The warning by Rossotti *et al.* [23] should be borne in mind: prior to a computer evaluation "a small dose of manual calculation is invaluable in giving him (the experimenter) a 'feel' for the functions he is using". The truth of this is obvious, but it must be stressed again and again: even nowadays, numerous equilibrium studies are reported containing diagrams that reveal at once to the experts that the result is based on an incorrect assumption and/or faulty considerations. We shall deal with this question in more detail in Chapter 5.

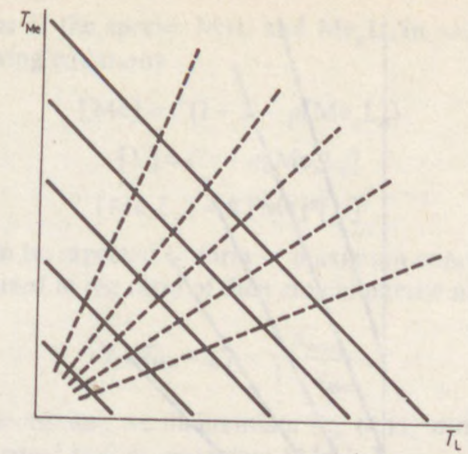


Fig. 4.1. Variation of total concentrations in the Job method (continuous lines) and for stoichiometric dilution (dashed lines) [61]
(Reproduced with permission from *Acta Chem. Scand.*, **A33**, 63 (1979))

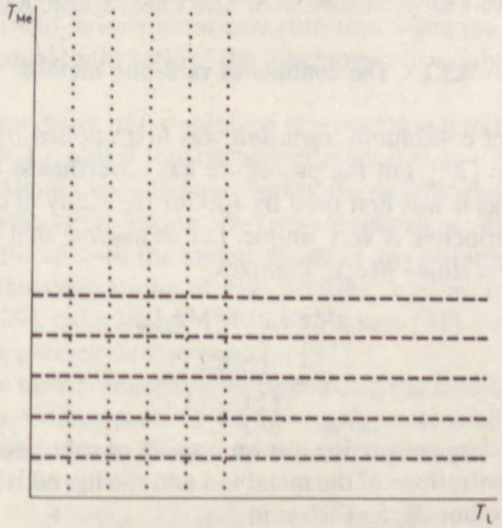


Fig. 4.2. Variation of total concentrations in the mole ratio L (dashed lines) and mole ratio Me (dotted lines) methods [61]
(Reproduced with permission from *Acta Chem. Scand.*, **A33**, 63 (1979))

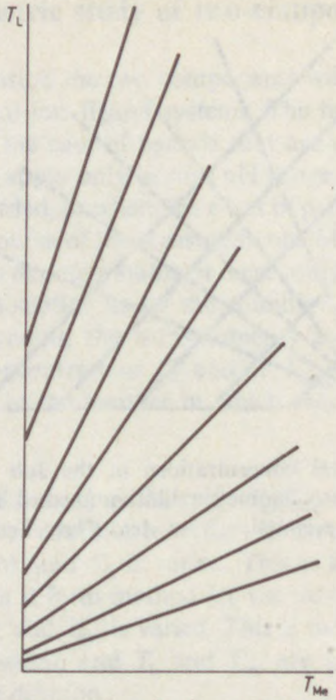


Fig. 4.3. Variation of total concentrations in the method of corresponding solutions [61] (Reproduced with permission from *Acta Chem. Scand.*, **A33**, 63 (1979))

4.2.1.1 The continuous variation method

The principle of continuous variation was first applied by Ostromisslensky [24] and Denison [25], but the procedure has nevertheless become known as the Job method, as it was first used by Job for the study of complex equilibria [26]. The basic principle is very simple. Let us assume that a metal ion and a ligand form only a single Me_pL_q complex

$$p\mathrm{Me} + q\mathrm{L} \rightleftharpoons \mathrm{Me}_p\mathrm{L}_q$$
$$K = \frac{[\mathrm{Me}_p\mathrm{L}_q]}{[\mathrm{Me}]^p[\mathrm{L}]^q}\,. \tag{4.6}$$

The measurements are carried out on a series of solutions in which the sum of the total concentrations of the metal ion and the ligand is constant, but their ratio varies continuously, as shown in Fig. 4.1

$$T_{\mathrm{Me}} + T_{\mathrm{L}} = C \tag{4.7}$$
$$x = T_{\mathrm{L}}/(T_{\mathrm{Me}} + T_{\mathrm{L}}) = T_{\mathrm{L}}/C\,. \tag{4.8}$$

The concentrations of the species MeL and Me_pL_q in solution can be given through the following equations

$$[\mathrm{Me}] = C(1-x) - p[\mathrm{Me}_p\mathrm{L}_q] \tag{4.9}$$

$$[\mathrm{L}] = Cx - q[\mathrm{Me}_p\mathrm{L}_q] \tag{4.10}$$

$$[\mathrm{Me}_p\mathrm{L}_q] = K[\mathrm{Me}]^p[\mathrm{L}]^q\,. \tag{4.11}$$

The complex can be expected to form in maximum concentration when the components are mixed in the ratio of their stoichiometric numbers p and q, i.e.

$$T_\mathrm{L}/T_\mathrm{Me} = q/p = \frac{x_\mathrm{max}}{1-x_\mathrm{max}}\,. \tag{4.12}$$

To confirm the assumption, we differentiate Eq. (4.11) with respect to x, and put the derivative equal to 0 at maximum $[Me_pL_q]$

$$\frac{d[\mathrm{Me}_p\mathrm{L}_q]}{dx} = Kp[\mathrm{Me}]^{p-1}[\mathrm{L}]^q\frac{d[\mathrm{Me}]}{dx} + Kq[\mathrm{Me}]^p[\mathrm{L}]^{q-1}\frac{d[\mathrm{L}]}{dx} = 0$$

$$\text{i.e.}\quad p[\mathrm{L}]\frac{d[\mathrm{Me}]}{dx} + q[\mathrm{Me}]\frac{d[\mathrm{L}]}{dx} = 0\,. \tag{4.13}$$

If Eqs (4.9) and (4.10), together with their differential quotients, are substituted into Eq. (4.13), we obtain Eq. (4.12), i.e. the assumption that $T_\mathrm{L}/T_\mathrm{Me} = q/p$ is correct. For multicomponent systems too, Ramanathan [27] demonstrated that any complex is formed in maximum concentration when the ratio of the total concentrations is equal to the ratio of the stoichiometric numbers of the complex in question.

Thus, if some parameter of the solution is proportional to the concentration of the complex Me_pL_q, and if this parameter is plotted as a function of x, the abscissa of the maximum gives the quotient of the stoichiometric numbers. The method is used most often during spectrophotometric studies, but the basic principle can be utilized with the measurement of any parameter proportional to the quantity (concentration) of the product, e.g. in the evaluation of conductivity [28, 29], calorimetric [30] and Raman [31] measurements, and even to establish a precipitate composition [32].

For photometric measurements, if the ligand and the metal ion absorb light, then the absorbance difference $A/d - \varepsilon_\mathrm{L}T_\mathrm{L} - \varepsilon_\mathrm{Me}T_\mathrm{Me} = A'$ must be plotted as a function of x. This absorbance difference is a linear function of the concentration of Me_pL_q

$$A' = (\varepsilon_{\mathrm{Me}_p\mathrm{L}_q} - p\varepsilon_\mathrm{Me} - q\varepsilon_\mathrm{L})[\mathrm{Me}_p\mathrm{L}_q]\,. \tag{4.14}$$

The data ε_Me and ε_L may be obtained from the results of measurements for the limiting cases $x=0$ and $x=1$.

If a single complex is formed, the method also provides additional information. It was demonstrated by Klausen and Langmyhr [33] that at $x_{\max}=0.5$, if $p=q>1$, the curve has inflexion points in the vicinity of $x=0$ and $x=1$. If these are not present, $p=q=1$, i.e. formation of the complex MeL is suggested. Klausen [34] developed a method for differentiating between the complexes MeL and Me_2L_2, and for the determination of their constants; this method is based on the data from measurements at various C and d values, with the condition $dC=\text{constant}$. His method is in essence an efficient combination of the Job method and the method of stoichiometric dilution.

If a very stable complex is formed, the continuous variation plot consists of two strictly straight lines, intersecting each other at $x=p/q$. In this case, of course, no inflexion point appears in the experimental plot even for $p=q>1$. When moderately stable complexes are formed, linearity is observed only in the immediate vicinity of $x=0$ and $x=1$; at intermediate values the plot is curved. The stability constant and the molar absorbance of the complex Me_pL_q can be calculated from the difference between the experimentally obtained plots and those found by extrapolation of the linear sections in the vicinity of $x=0$ and $x=1$.

The accuracy of the method clearly depends on the extent of the equilibrium conversion; besides the values of x and the stability constant, this is in turn a function of the sum of the total concentrations too. It was shown by Slovák and Borák [35] that, if a 1:1 complex is formed, a reliable stability constant can be obtained only if the condition $2<KC<15$ is met.

If formation of the complex MeL is assumed the following simple correlation can be derived between the product KC and the equilibrium conversion ($y=[\mathrm{MeL}]/T_\mathrm{L}=[\mathrm{MeL}]/T_\mathrm{Me}=2[\mathrm{MeL}]/C$) at $x=0.5$

$$KC=2y/(1-y)^2\,. \tag{4.15}$$

The function $y=f(\log(KC))$ is presented graphically in Fig. 4.4, the limits given by Slovák and Borák [35] being indicated on the abscissa.

Of the efforts made to refine the Job method, mention should be made of the considerations of Likussar [36, 37], who extended the 'normalized absorbance' concept of Momoki *et al.* [38] to the Job method.

Likussar set out from the principle of 'normalized absorbance' and proposed the introduction of a normalized scale in place of the plotting of absorbance differences. The normalizing factor used is the absorbance difference obtained at the value $T_\mathrm{Me}=(1-x_{\max})C$ with a large ligand excess ($T_\mathrm{Me}\approx p[\mathrm{Me}_p\mathrm{L}_q]$), $x_{\max}$ having been determined preliminarily. Accordingly, the straight lines starting from $x=0$ and $x=1$ intersect at $y=1$, and the Job curves relating to all systems in which complexes of the same composition are formed, and which are characterized by the same equilibrium conversion, coincide on the normalized scale. If the experimental possibilities permit an independent determination of

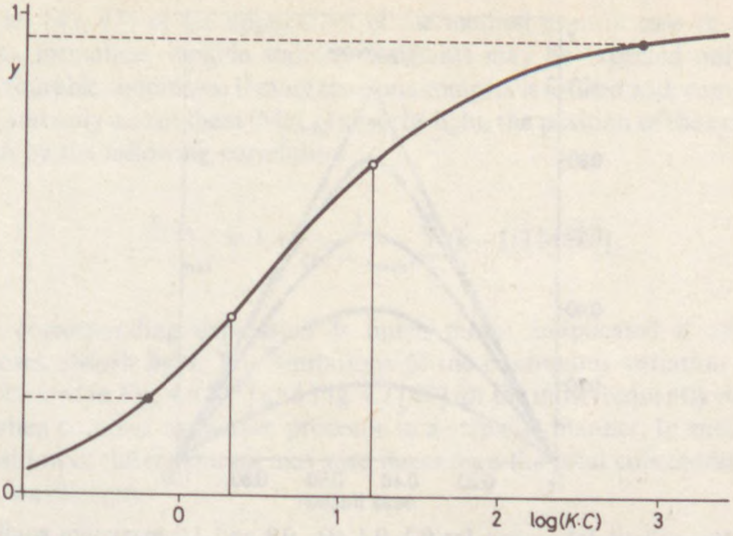


Fig. 4.4. Correlation between the product KC and the equilibrium conversion, assuming formation of the complex MeL at mole ratio $T_L/T_{Me} = 1$. The limits suitable for determination of the constants are indicated on the axes; those on the abscissa were reported by Slovák and Borák [35], and those on the ordinate by Likussar [37]

the normalizing factor, this method is definitely advantageous. Normalized Job curves for the formation of complexes MeL are depicted in Fig. 4.5.

It may readily be seen that the normalization means in fact the independent determination of the molar absorbance of the complex Me_pL_q. Thus, a single unknown must be calculated: the value of K. Likussar's considerations indicated that an accurate equilibrium constant can be calculated in the interval $0.2 < y_{max} < 0.95$. If a 1:1 complex is formed, y_{max} agrees with the previously defined equilibrium conversion. The ordinate of Fig. 4.4 shows the limits based on the Likussar considerations. It can be seen that in this way a possibility arises for determination of the constants in an essentially wider range. This is a natural consequence of the fact that, of the two constants to be calculated (ε_{MeL} and K), the value of ε_{MeL} is actually determined in an independent experiment.

At the beginning of Chapter 4, we outlined the effect of the equilibrium conversion on the accuracy of the equilibrium constant. Measurements must be made in that range of total concentrations of the components for which complex formation is already well measurable, but not yet stoichiometric.

The inequalities $0.2 < y_{max} < 0.95$ and $2 < KC < 15$, derived in different ways by Likussar [36, 37] and by Slovák and Borák [35], but reflecting the same chemical content, give a quantitative expression of this basic principle in the case of the Job method.

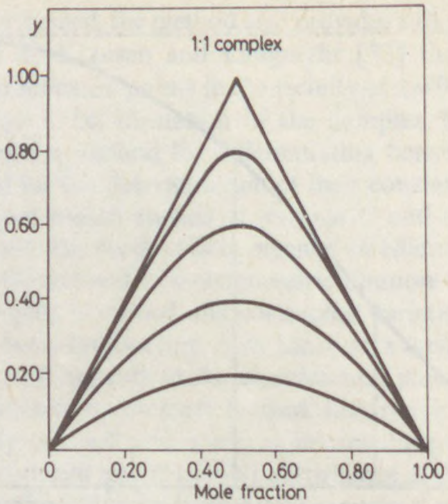


Fig. 4.5. Normalized Job curves for 0.2, 0.4, 0.6, 0.8 and 1.0 maximum equilibrium conversion, assuming formation of the complex MeL [36]
(Reproduced with permission from *Anal. Chem.*, **43**, 1265 (1971))

With regard to the findings of Klausen [34], Momoki *et al.* [38], Likussar [36, 37] and Slovák and Borák [35], but in particular to the drawbacks of the method outlined below, in our opinion there is no sense in refining the method further.

Before the Job method is applied for the study of unknown systems, the following limitations must be taken into consideration:

(1) The method is not suitable for the determination of q/p values larger than 3. At mole ratios of 4:1, 5:1 and 6:1, the values of x_{max} are 0.800, 0.833 and 0.857. An error of 1–3% in the measurements can therefore cause a difference of even a whole unit in the mole ratio.

(2) The measurements must be made at constant ionic strength [39, 40]. During the study of weak complexes, where a large value must of necessity be chosen for $T_L + T_{Me}$, this condition does not always hold, nor in every solvent. The constancy of ionic strength is particularly questionable when the concept of normalized absorbance is used and the normalizing factor is determined.

(3) If the ligand is the conjugate base of a weak acid, the extremum may be pH-dependent [39, 41]. This question will be dealt with in more detail in Section 4.2.2.2.

(4) The starting condition that only a single complex should be formed in the system in question is met only exceptionally. If more than one complex is formed, the method may give unrealistic results [41]. Although there are a few

examples [42, 43] of the application of the method even in case of stepwise complex formation, reliable stability constants may be expected only under very favourable conditions. If more than one complex is formed with composition MeL_i, and only one of them (MeL_k) absorbs light, the position of the extremum is given by the following correlation

$$\frac{x_{\max}}{1-x_{\max}} = k + \frac{1}{c(1-x_{\max})}\sum_{1}^{N}(k-1)i[\mathrm{MeL}_i]\,. \tag{4.16}$$

The corresponding expression is much more complicated if all of the complexes absorb light. The limitations of the continuous variation method are illustrated in Fig. 4.6 [45] and Fig. 4.7 [44] for the most frequently occurring case, when complex formation proceeds in a stepwise manner. In such a case, the position of the maximum may also depend on the total concentration and on the wavelength.

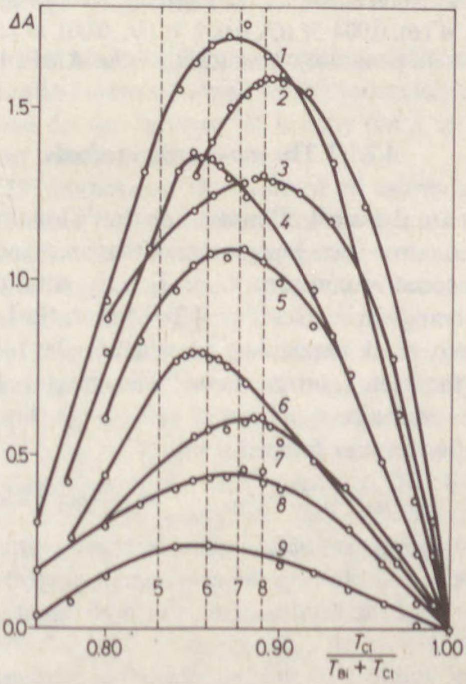


Fig. 4.6. Continuous variation curves obtained at various wavelengths in the Bi(III)–Cl^- system [45]
(Reproduced with permission from *J. Am. Chem. Soc.*, **79**, 4576 (1957))

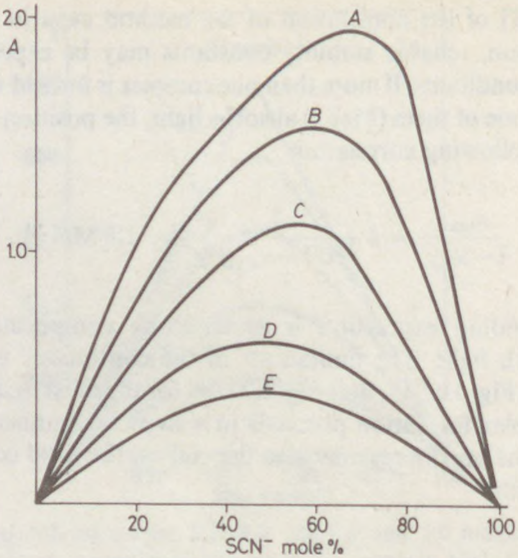


Fig. 4.7. Continuous variation curves for the Fe(III)–SCN$^-$ system. $T_{Fe}+T_{SCN}=0.1M$ (*A*), 0.01 *M* (*B*), 0.004 *M* (*C*), 0.002 *M* (*D*), 0.001 *M* (*E*) [44]
(Reproduced with permission from *Zh. Obshchei Khim.*, **16,** 1551 (1946))

4.2.1.2 The mole ratio methods

The mole ratios are the most often used methods for the photometric study of complex formation processes. The essence of these methods is that the solution absorbance is measured at constant T_L or T_{Me}, the total concentration of the other component being varied (see Fig. 4.2). Mole ratio L and mole ratio Me methods are distinguished, depending on whether the total concentration of the ligand or of the metal ion is varied. The measured absorbance value, decreased by the products $\varepsilon_{Me}T_{Me}$ and $\varepsilon_L T_L$, is a linear function of the concentration of the complex formed

$$A/d-\varepsilon_{Me}T_{Me}-\varepsilon_L T_L=(\varepsilon_{Me_pL_q}-p\varepsilon_{Me}-q\varepsilon_L)[Me_pL_q]\,. \tag{4.17}$$

The mole ratio diagrams are obtained by determining the molar absorbances ε_{Me} and ε_L separately, and plotting the absorbance corrected as in Eq. (4.17) as a function of T_L or T_{Me}, the total concentration of the other component being kept constant.

If a single, very stable complex is formed, the diagram consists of two intersecting straight lines. The ratio T_L/T_{Me} corresponding to the point of intersection gives the quotient of the stoichiometric coefficients. In this case, only the molar absorbance of the complex formed can be determined.

The diagram obtained when a moderately stable complex is formed does not display a sharp break: the initially linear section gradually approaches a limiting value and becomes horizontal. The q/p value is then given by the abscissa value corresponding to the point of intersection of the extrapolated linear sections. In a favourable case, the stability constant of the complex formed can also be calculated from the difference between the linear sections and the actual curve.

When a weak complex is formed, the horizontal section of the curve (the constancy of the corrected absorbance) can not be attained in realistic T_L or T_{Me} concentration ranges, particularly if it is considered that constancy of the activity coefficients must be ensured in these measurements too. In such cases, even the value of q/p can not be determined.

A number of authors have dealt with theoretical and practical aspects of the mole ratio method. It was demonstrated by Harvey and Manning [46], Bent and French [47] and Budesinsky and Svec [48] that, through analysis of the mole ratio curves, not only the quotient q/p, but also the numerical values of the stoichiometric coefficients can be determined. Kingery and Hume [49] found that more reliable results can be obtained from a combination of the Bent and French and the Job methods than from either of the individual methods.

The considerations by Marcus [50] draw attention to the fact that the linear sections of the mole ratio curves obtained when moderately and relatively weak complexes are formed do not intersect at exactly the true ratio q/p, and this may lead to incorrect conclusions.

Momoki *et al.* [38] elaborated the concept of normalized absorbance in connection with the mole ratio methods. The essence of this is that a large excess of the component with variable concentration must be attained during the experiments, at this large excess the component with constant concentration being present practically completely in the form of the complex in question, Me_pL_q. When the measured data are normalized to the resulting absorbance difference, the mole ratio curves always tend asymptotically to 1. Under such conditions, mole ratio curves with the same equilibrium conversion, i.e. with the same KC value ($C = T_{Me}$ or T_L) for formation of the complex MeL, coincide. As observed in the discussion of the Job method, the Momoki method has the advantage that only K remains unknown, and can thus be calculated more accurately. However, experiments designed for determination of the normalizing factor require very careful planning.

Normalized absorbance curves for formation of the complex MeL are shown in Fig. 4.8. Normalized curves obtained with various q and p values are to be found in the original publication [38].

It is evident from the normalized curves that the question of the applicability of the mole ratio methods is also connected with the equilibrium conversion. If total conversion can be attained within a realistic interval of the variable

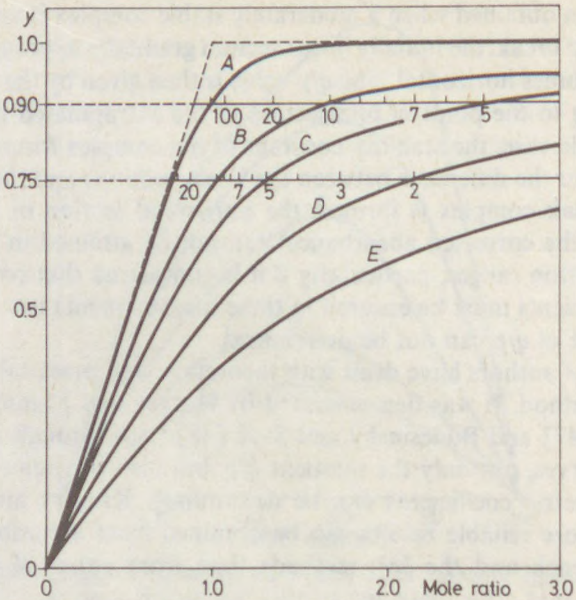


Fig. 4.8. Theoretical normalized mole ratio curves at various KC values for formation of the complex MeL [38]. $KC = 100$ (*A*), 10 (*B*), 5 (*C*), 2 (*D*), 1 (*E*) (Reproduced with permission from *Anal. Chem.*, **41**, 1286 (1969))

concentration, then normalization of the curve is possible and the desired constant can be calculated more accurately. In the opposite case, two unknowns ($\varepsilon_{\mathrm{MeL}}$ and K) must be calculated, which can only be done with a larger error than in the case of one unknown. The lower the conversion attained within the realistic concentration interval (assuming the same experimental error), the greater the error in the data obtained. For a maximum conversion less than about 10%, only the product $\varepsilon_{\mathrm{MeL}}K$ can be calculated, but not the value of K [51].

If the complex MeL is formed (at given KC), the total symmetry means that the mole ratio L and the mole ratio Me methods should lead to coincident curves. It was pointed out by Johansson [52] that this is not always the case. The cause of the difference is that, when the Me method is used, the excess Me is to be found practically in the form $\mathrm{Me(H_2O)}_xA_y$ (where x and y are constants, and A is the anion of the background electrolyte), while with the L method the ligand must replace the anion of the background electrolyte. Accordingly, it is possible that a smaller constant is obtained with the L method than with the Me method. In a fortunate case, the stability constant describing the interaction between the metal ion and the anion of the background electrolyte can also be calculated, from the difference between the constants found with the two methods. Further theoretical and experimental work is required in this field, in order to characterize weak interactions as completely as possible.

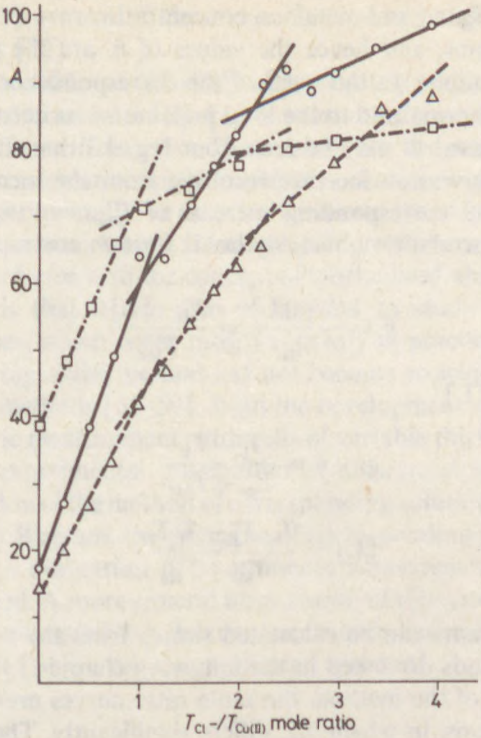


Fig. 4.9. Mole ratio curves for the copper(II)–chloride system in dimethylsulphoxide [53]. ○ — 1100 nm; △ — 1300 nm; □ — 1500 nm
(Reproduced with permission from *Inorg. Chim. Acta*, 7, 293 (1973))

In the event of stepwise complex formation, if all of the complexes are sufficiently stable and the equilibrium processes do not overlap one another, the mole ratio diagram consists of several linear sections (see Fig. 4.9 [53]). The slopes of the straight sections are governed by the molar absorption coefficients of the stepwise complexes. It is stated by Meyer and Ayres [54] that the mole ratios of these stepwise complexes can be determined if the following condition holds

$$K_i \geqq 600 K_{i+1}\,. \tag{4.18}$$

4.2.1.3 The method of corresponding solutions [22]

It was seen in Chapter 3 that, during the stepwise formation of mononuclear complexes, the free ligand concentration unambiguously determines the value of $\bar{n}$, and thus the concentration distribution of the complexes formed. Solutions in which the total ligand and metal ion concentrations are different but the free ligand concentrations, and hence the values of $\bar{n}$, are the same, are termed corresponding solutions. In the sense of the correspondence, the absorbances of these solutions, normalized to the total metal ion concentration, agree in the entire spectral interval. It may be seen from Fig. 4.3 that the correspondence means that the conversion increase resulting from the increase of T_L is just compensated by the 'corresponding' increase of T_{Me}.

The following correlation obviously holds for two corresponding solutions

$$\bar{n} = \frac{T_L - [L]}{T_{Me}} = \frac{T'_L - [L]}{T'_{Me}}. \tag{4.19}$$

Solving for $\bar{n}$ and [L]

$$\bar{n} = \frac{T_L - T'_L}{T_{Me} - T'_{Me}} \tag{4.20}$$

$$[L] = \frac{T_{Me}T'_L - T_L T'_{Me}}{T_{Me} - T'_{Me}}. \tag{4.21}$$

The stability constants can be calculated simply from the $\bar{n}$ and [L] pairs by means of the methods discussed in the following chapter.

For application of the method, the mole ratio curves must be recorded for at least two solutions, in which T_{Me} differs significantly. The compositions of the corresponding solutions are established by interpolation, and the $\bar{n}$ and [L] data pairs are calculated via Eqs (4.20) and (4.21). Figure 4.10 depicts formation curves for the copper(II)–ammonia system; these plots were obtained spectro-

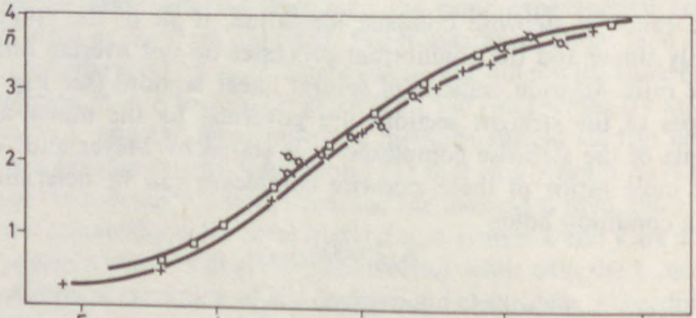


Fig. 4.10. Formation curves for the copper(II)–ammonia system [22]. ○ — data obtained with method of corresponding solutions; + — data obtained potentiometrically; □ — data obtained by measurement of vapour tension of ammonia (Reproduced with permission from *Kgl. Dansk Vid. Selskab Mat. Fys. Medd.*, **21.** No. 4. (1941))

photometrically, by means of the method of corresponding solutions, and potentiometrically [22].

The method is suitable for the study of moderately stable complexes, under concentration conditions where T_L–[L] is substantially smaller than T_L, but is still appreciably distant from zero. The method has the very great advantage that knowledge or calculation of the molar absorbances is not necessary: these are eliminated experimentally. In all other methods, the values of the constants and the molar absorbances must be calculated simultaneously, or determined separately in accordance with the concept of 'normalized absorbance'. Another great advantage is that it can also be applied to study stepwise complex formation processes, which occur most frequently in practice. In spite of these undoubted advantages, the method has not become so widespread as the Job or the mole ratio methods [55–59]. With the development of the techniques of spectrophotometric measurement, with cells of variable thickness, and with the extension of the experimental possibilities of differential spectrophotometry, the wider application of the method of corresponding solutions is to be expected. As pointed out by Bjerrum, the principle of corresponding solutions may also be suitable for the evaluation of photometric measurements made with the competition method. A more general formulation of the criterion of correspondence has been attempted by Belyevantseev and Peshevitskii [60] and by Országh and Beck [61] in more complicated systems.

4.2.1.4 The method of stoichiometric dilution [62]

When the Job and the mole ratio methods are used, at a given T_L/T_{Me} value the equilibrium conversion is determined by the products $K(T_{Me}+T_L)$, KT_{Me} or KT_L, and the value of the product is unchanged during the measurement. In the dilution method of Cilento and Sanioto, the quotient T_L/T_{Me} is held constant while the absolute values of the concentrations are varied; this is naturally accompanied by a change in the equilibrium conversion. The formation constant of the complex in question can be determined the more accurately, the higher the concentration interval spanned within the equilibrium conversion limits 0 and 1. The possibilities and limitations of the method have not yet been satisfactorily explored, and relatively few examples of its application are found [63–65]. Since the manner of varying the concentration in this method is very similar to that in the method of corresponding solutions (see Figs. 4.2 and 4.3), but the method itself is substantially simpler experimentally, it seems to be important to establish the basic principles and the possibilities and limitations of application.

4.2.1.5 Photometric study of ligand protonation

The large majority of complex equilibrium investigations relate to ligands that are conjugate bases of weak acids. Accordingly, the extent of complex formation depends on the pH, and the protonation constants of the ligands must be known if the stability constants of the metal complexes are to be determined.

Under favourable conditions, any of the methods discussed so far may be suitable for determination of the protonation constants; the role of L in the above considerations is simply taken over by the hydrogen ion, and that of Me by L. The separate treatment of this topic is justified by the fact that, in studies on protonation processes, the equilibrium concentration of one of the components can be determined through simple pH measurements. The experimental data are therefore obtained by the systematic variation not of T_L and T_H, but of T_L and $[H^+]$ (i.e. the pH). The value of T_H is generally not known, whereas the necessary pH can be adjusted by means of appropriately selected buffers. A knowledge of the equilibrium concentration of one of the components essentially simplifies the determination of the constants.

In the photometric study of a process $H + L \rightleftharpoons HL$, the spectra may be recorded as a function of pH. At sufficiently low ($pH < pK - 3$; $[HL] \approx T_L$) or high ($pH > pK + 3$; $[L] \approx T_L$) pH values, the molar absorption coefficients of the species L and HL can be determined directly. An apparent absorbance referred to T_L, measured in the intermediate pH range, is the sum of these two molar absorbances, weighted in proportion to the partial mole fractions

$$\bar{\varepsilon} = \frac{A}{dT_L} = \varepsilon_L \frac{[L]}{T_L} + \varepsilon_{HL} \frac{[HL]}{T_L} \tag{4.22}$$

i.e. $T_L = [L] + [HL]$

$$K_{HL} = \frac{[HL]}{[H][L]} = \frac{\bar{\varepsilon} - \varepsilon_L}{\varepsilon_{HL} - \bar{\varepsilon}} \cdot \frac{1}{[H]}. \tag{4.23}$$

In this case too, it is advisable to carry out the calculations in the interval of equilibrium conversion, i.e. the ratio $[L]/T_L$, between 0.1 and 0.9.

When multistep protonation processes are examined in which the steps occur separately, the above considerations can be applied to the individual protonation steps. As an example, Curve *I* of Fig. 4.11 presents the correlation between pH and the absorbance at 260 nm of a solution of 2,3-dihydroxybenzoic acid [66].

If overlapping equilibria are studied, only the molar absorbances of the species H_NL and L can be determined directly. In such a case, evaluation of the experimental data and the corresponding pK values also means calculation of the molar absorbances of the species H_iL ($N > i > 0$), which necessitates application of a more sophisticated calculation procedure (see Chapter 5).

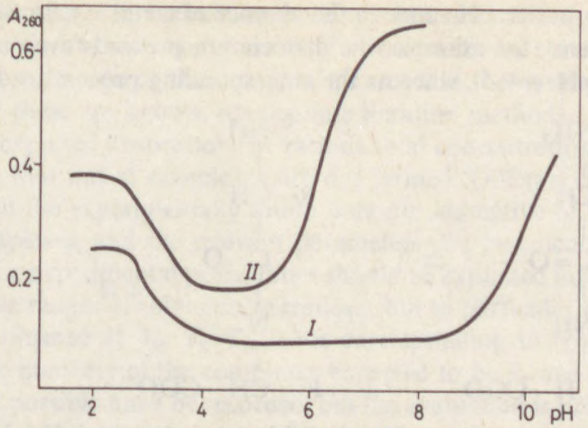
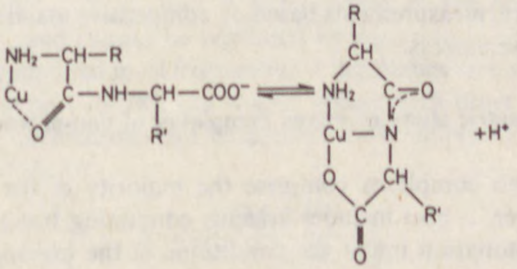


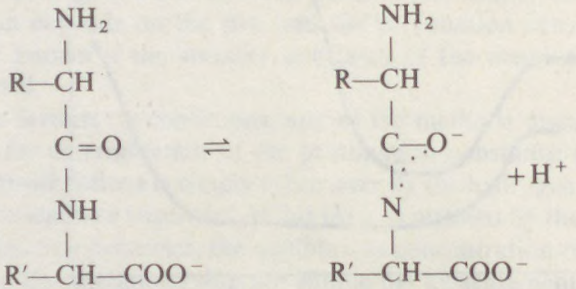
Fig. 4.11. pH-dependence of absorbance measured at 260 nm in (*I*) a 1.103×10^{-4} *M* solution of 2,3-dihydroxybenzoic acid, and (*II*) a 1 : 1 molar mixture of 1.103×10^{-4} *M* 2,3-dihydroxybenzoic acid and copper(II) [66]
(Reproduced with permission from *Bull. Chem. Soc. Japan*, **44**, 3459 (1971))

If the ligand undergoes protonation in the very acidic range, the spectrum must be recorded as a function of the Hammett acidity rather than the experimentally measured pH. However, use of the Hammett function poses special questions that must be considered carefully prior to the experiments. Thus, the value of the Hammett acidity function depends among others on the type of substance undergoing protonation, and different acidity functions must be utilized for ligands of different types [67–72]. We shall not deal in detail with this question, as the protonation of ligands in the very acidic range is generally not important as concerns the study of complex formation equilibria.

The quantitative characterization of protonation or dissociation in very basic solutions, however, may be essential from the aspect of determination of the stability constants of metal complexes. With ligands containing peptide bond, an amide and/or an alcoholic OH group, for instance, it frequently occurs that, in the pH interval of formation of metal complexes, certain protons in the ligand become capable of dissociation. These protons otherwise do not dissoci-



ate in the measurable pH range in the absence of metal ion. In the copper(II)–dipeptide systems, for example, the dissociation proceeds even in the weakly acidic range (pH ~4–5), whereas the corresponding process



$$\begin{array}{c} NH_2 \\ | \\ R\text{—}CH \\ | \\ C{=}O \\ | \\ NH \\ | \\ R'\text{—}CH\text{—}COO^- \end{array} \rightleftharpoons \begin{array}{c} NH_2 \\ | \\ R\text{—}CH \\ | \\ C\text{—}O^- \\ |\!\!: \\ N \\ | \\ R'\text{—}CH\text{—}COO^- \end{array} + H^+$$

takes place only in the range pH > 14. With the application of basicity functions, these processes too may be studied spectrophotometrically or with some similar method. Although attempts have been made to establish basicity functions [73–75], this area is by no means as thoroughly developed as that relating to processes in very acidic medium. A detailed investigation of basicity functions is expected to encounter the same theoretical and practical difficulties as those met during the use of the Hammett functions.

4.2.2 Photometric study of systems with three or more components

Photometry is most often applied for determination of the compositions and stability constants of complexes formed in systems with three or more components. Since the ligands are more often than not weak bases, photometric study of the M–L interaction is generally carried out in solutions containing the components H, L and Me. In this case, however, measurements are made in series of solutions of known pH (measured separately) or at fixed pH values. Nevertheless, the photometric measurements are used alone if mixed complex formation is studied in a solution containing one metal ion and two non-protonating ligands. Below, we shall deal first with these systems, and then survey photometric measurements based on competitive reactions, supplemented with pH measurements.

4.2.2.1 Photometric study of mixed complexes of non-protonating ligands

Mixed halogeno complexes comprise the majority of the systems in this category. However, it also includes systems containing basic ligands that do not undergo protonation under the conditions of the investigation. Study of three-component systems containing metal ion Me and halide ions X and Y is generally preceded by determination of the compositions, stability constants and molar absorbances of the complexes formed in the systems Me–X and Me–Y. When these are known, appropriate iteration methods can be used to calculate the expected absorptions at various total concentrations T_{Me}, T_X and T_Y, assuming that mixed complexes are not formed. Differences between the calculated and the experimentally found data are indicative of the formation of mixed complexes, and the relevant parameters can be calculated from the differences. The experimental possibilities should be exploited fully to cover the widest possible ranges of total concentrations, but in particular measurements should be performed at $T_M : T_X : T_Y$ ratios corresponding to the ratios of the stoichiometric numbers of the complexes expected to be formed. As complete a spectrum as possible must be recorded, but the evaluation is preferably based primarily on data relating to the wavelengths where mixed complex formation has the greatest effect. In the study of such complicated systems, use of a computer to evaluate the experimental data is virtually indispensable, and planning of the experimentation is similarly best based on computer analysis.

The photometric study of mixed halogeno complexes is most frequently performed to determine the equilibrium constants of the processes

$$i\,\mathrm{MeX}_n + j\,\mathrm{MeY}_n \rightleftharpoons n\,\mathrm{MeX}_i\mathrm{Y}_j \qquad (4.24)$$

$$i+j=n.$$

Two cases differing in principle are distinguished in investigations of equilibria of this type.

In the first case, the complexes MeX_n and MeY_n are stable and undergo little dissociation; the concentrations of the complexes MeX_{n-i} and MeY_{n-i} and of free halide ions are therefore negligibly low. Under such conditions, the system can be regarded in practice as a two-component system, the components being MeX_n and MeY_n. However, there is a fundamental difference between the two-component systems Me–L and MeX_n–MeY_n: all equilibrium constants corresponding to Eq. (4.24) are dimensionless numbers, whereas the formation constants of the complexes MeL_i have dimensions of [concentration]$^{-i}$. This has the obvious consequence that the equilibrium conversion is a function only of the quotient $T_{MeX_n} : T_{MeY_n}$, but is independent of the concentration sum $C = T_{MeX_n} + T_{MeY_n}$, and cannot be regulated by variation of the latter.

This case is encountered most frequently during studies on mercury(II)–halide–pseudohalide systems [76–78], but it also occurs with other complexes [79]. The quantitative correlations can be derived most simply for the equilibrium $MeX_2 + MeX_2 \rightleftharpoons 2MeXY$

$$K = \frac{[\mathrm{MeXY}]^2}{[\mathrm{MeX}_2][\mathrm{MeY}_2]} \qquad (4.25)$$

$$T_{\mathrm{MeX_2}} = [\mathrm{MeX_2}] + 0.5[\mathrm{MeXY}] \tag{4.26}$$

$$T_{\mathrm{MeY_2}} = [\mathrm{MeY_2}] + 0.5[\mathrm{MeXY}] \tag{4.27}$$

$$T_{\mathrm{Me}} = T_{\mathrm{MeX_2}} + T_{\mathrm{MeY_2}}; \qquad R = T_{\mathrm{MeX_2}}/T_{\mathrm{MeY_2}}. \tag{4.28}$$

The partial mole fraction of the mixed complex is

$$\alpha_{\mathrm{MeXY}} = \frac{[\mathrm{MeXY}]}{T_{\mathrm{Me}}}. \tag{4.29}$$

After appropriate algebraic transformation of Eqs (4.25–4.28), α_{MeXY} can be expressed as a function of K at a given R value, and vice versa

$$\alpha_{\mathrm{MeXY}} = \frac{1 \pm \sqrt{1 - \frac{4R}{(1+R)^2}(1 - 4K^{-1})}}{1 - 4K^{-1}} \tag{4.30}$$

$$K = \frac{4\alpha^2_{\mathrm{MeXY}}}{(1-\alpha_{\mathrm{MeXY}})^2 - \left(\frac{1-R}{1+R}\right)^2}. \tag{4.31}$$

In accordance with the earlier statements relating to the equilibrium conversion, it may be seen from Eqs (4.30) and (4.31) that α_{MeXY} is not influenced by the sum of the total concentrations, but only by their ratio R. The value of α_{MeXY} can be calculated from the spectrophotometric data. A precondition for this is that the spectrum should contain a wavelength interval in which the molar absorbance of the mixed complex differs significantly from the average of the molar absorbances of the two parent complexes. In the opposite case, there is not even a possibility to detect formation of the mixed complex.

The absorbance of the equilibrium system in a 1 cm cell is

$$A = \varepsilon_{\mathrm{MeX_2}}[\mathrm{MeX_2}] + \varepsilon_{\mathrm{MeY_2}}[\mathrm{MeY_2}] + \varepsilon_{\mathrm{MeXY}}[\mathrm{MeXY}]. \tag{4.32}$$

Let us introduce the notations

$$\Delta\varepsilon = \varepsilon_{\mathrm{MeXY}} - \frac{\varepsilon_{\mathrm{MeX_2}} + \varepsilon_{\mathrm{MeY_2}}}{2} \tag{4.33}$$

and

$$\Delta A = A - (\varepsilon_{\mathrm{MeX_2}} T_{\mathrm{MeX_2}} + \varepsilon_{\mathrm{MeY_2}} T_{\mathrm{MeY_2}}). \tag{4.34}$$

We then have

$$\alpha_{\mathrm{MeXY}} = \frac{\Delta A}{\Delta\varepsilon \cdot T_{\mathrm{Me}}}. \tag{4.35}$$

The molar absorbances $\varepsilon_{\mathrm{MeX_2}}$ and $\varepsilon_{\mathrm{MeY_2}}$ can be determined in independent experiments. If the value of R is varied in a satisfactorily wide range, α_{MeXY} and

K can be calculated from the above equations through graphical or numerical methods.

As an example to illustrate systems of this type, Figs 4.12 and 4.13 present spectra obtained by Spiro and Hume [80] in connection with the system Hg(II)–Br^-–I^-, and functions $\alpha_{MeXY} = f(K, R)$.

A procedure based on photometric measurements was developed by Gaizer and Beck [81] for determination of the formation constants of mixed complexes obtained in the reaction between the non-dissociating complexes MeX_3 and MeY_3. Their method was applied to study the system $BiCl_3$–BiI_3 dissolved in absolute dioxane. In this case, two mixed ligand complexes, BiI_2Cl and $BiICl_2$, may be formed

$$BiCl_3 + 2BiI_3 \rightleftharpoons 3BiI_2Cl \tag{4.36}$$

$$K_{21} = \frac{[BiI_2Cl]^3}{[BiCl_3]\,[BiI_3]^2}$$

$$2BiCl_3 + BiI_3 \rightleftharpoons 3BiICl^2 \tag{4.37}$$

$$K_{12} = \frac{[BiICl_2]^3}{[BiCl_3]^2\,[BiI_3]}.$$

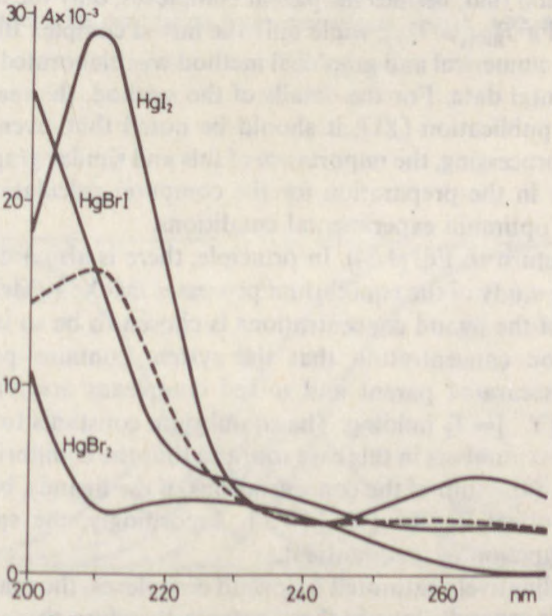


Fig. 4.12. Spectra of HgI_2, $HgBr_2$ and HgIBr in aqueous solution. The dashed line is the arithmetical mean of the absorbances of $HgBr_2$ and HgI_2 [80] (Reproduced with permission from *J. Am. Chem. Soc.*, 83, 4305 (1961))

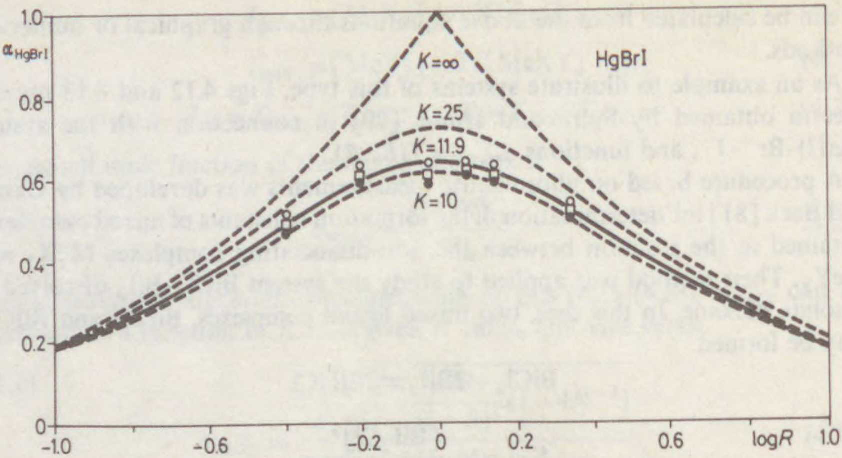


Fig. 4.13. Partial mole fractions (α_{MeXY}) of the mixed complex HgBrI as a function of log *R*. ● — 219 nm; □ — 220 nm; ○ — 221 nm. The dashed lines depict the function $\alpha_{MeXY} = f(\log R)$ calculated at various *K* values [80]
(Reproduced with permission from *J. Am. Chem. Soc.*, **83**, 4305 (1961))

On the assumption that, besides the parent complexes, only the mixed complex $BiICl_2$ is formed if $T_{BiCl_3} \gg T_{BiI_3}$, while only the mixed complex BiI_2Cl is formed if $T_{BiI_3} \gg T_{BiCl_3}$, a numerical and graphical method was elaborated for evaluation of the experimental data. For the details of the method, the reader is referred to the original publication [81]; it should be noted that, even in the age of computer data processing, the importance of this and similar graphical analyses remains, mainly in the preparation for the computer calculations and in the selection of the optimum experimental conditions.

Let us now return to Eq. (4.24). In principle, there is also a different case of the photometric study of the equilibrium processes $i\text{MeX}_n + j\text{MeY}_n \rightleftharpoons n\text{MeX}_i\text{Y}_j$, when the sum of the ligand concentrations is chosen to be so large compared to the metal ion concentration that the system contains practically only coordinatively saturated parent and mixed complexes ($n = N$), the relations $[X^-] = T_X$ and $[Y^-] = T_Y$ holding. The equilibrium constants to be determined are dimensionless numbers in this case too, and thus the equilibrium conversion is independent of the sum of the concentrations of the ligands, being a function only of the quotient $T_X/T_Y = [X^-]/[Y^-]$. Accordingly, the spectra are best recorded as a function of this quotient.

For the coordinatively saturated halogeno complexes, the maximum coordination number is generally four; in these systems, therefore, three different mixed ligand complexes may be formed. Here again, useful information may be obtained from qualitative and semiquantitative studies of the changes in the spectra when the quotient $[X^-]/[Y^-]$ is varied, and also from partial graphical analysis; a complete evaluation, however, demands the use of an appropriate computer program. As an example of investigations of this type, which have been carried out on complexes of gold [82, 83], nickel(II) [84] and palladium [85, 86], Figs 4.14 and 4.15 give results obtained by Elding and Gröning [83] for the system Au(III)–Cl^-–Br^-.

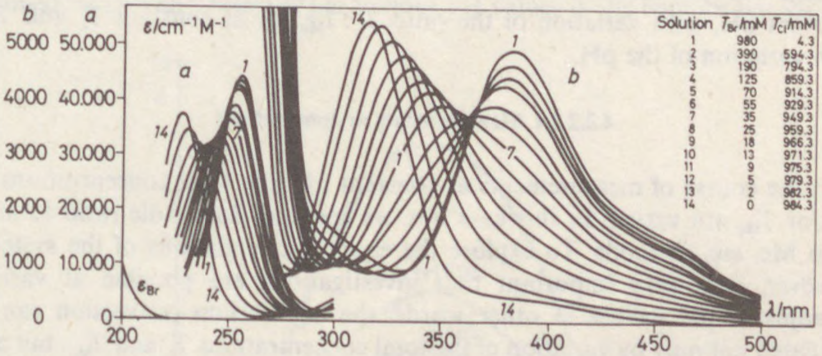


Fig. 4.14. Apparent molar absorbances ($\varepsilon = A/T_{Au}$) obtained in the Au(III)–Cl^-–Br^- system at various ratios T_{Br^-}/T_{Cl^-}. $T_{Au} = 1.71 \times 10^{-4}$ *M*. Curve *1* — 100% $AuBr_4^-$; Curve *14* — 100% $AuCl_4^-$ [83]
(Reproduced with permission from *Acta Chem. Scand.*, **A32**, 867 (1978))

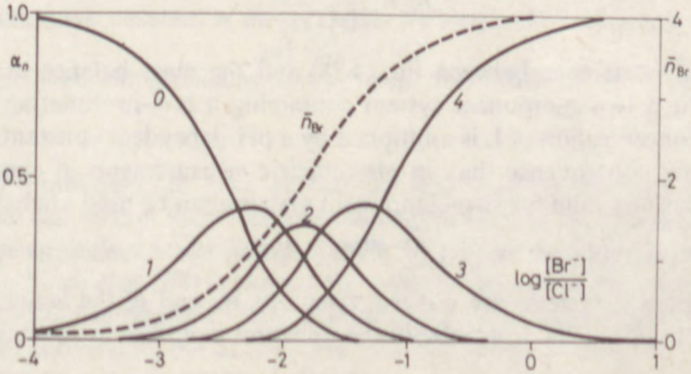


Fig. 4.15. Partial mole fraction distribution of the complexes $AuCl_{4-n}Br_n^-$ ($n = 0$, 1, 2, 3, 4) as a function of $\log[Br^-]/[Cl^-]$ [83]
(Reproduced with permission from *Acta Chem. Scand.*, **A32**, 867 (1978))

4.2.2.2 Study of the Me–L interaction in three-component equilibrium systems H–L–Me

The large majority of photometric studies belong in this category. In these systems, the extent of complex formation depends on the hydrogen ion concentration, and the photometric measurements must therefore be supplemented with pH measurements. Photometry is generally performed either at constant pH, with variation of the ratio $T_L : T_{Me}$, or at constant T_L and T_{Me}, with variation of the pH.

4.2.2.2.1 Measurements at constant pH

In the course of measurements at constant pH, the total concentrations T_L and/or T_{Me} are varied. In this case too, we speak of Job, mole ratio L, mole ratio Me, etc. methods. To explore the equilibrium relations of the systems, however, it is very important that investigations are possible at various preadjusted pH values; in other words, the equilibrium conversion can be regulated not only by variation of the total concentrations T_L and T_{Me}, but also by variation of the pH.

If only a single complex Me_xL_y is formed, and the ligand participates only in a stepwise protonation equilibrium, the total concentrations can be given as follows

$$T_L = [L] \sum_{i=0}^{N} \beta_i^H [H]^i + y[Me_xL_y] \tag{4.38}$$

$$T_{Me} = [Me] + x[Me_xL_y] \tag{4.39}$$

where

$$\beta_i^H = \frac{[H_iL]}{[L][H]^i}.$$

The only difference between Eq. (4.38) and the mass balance that can be written for a two-component system containing a non-protonating ligand is that the concentration of L is multiplied by a pH-dependent constant. This has the obvious consequence that, in photometric measurements at constant pH, the correlations valid for two-component systems can be used unchanged, [L] merely being replaced by $[L] \sum_{i=0}^{N} \beta_i^H [H]^i$. When the correlations relating to two-component systems are utilized, therefore, instead of the actual constant $K = [Me_yL_y]/[Me]^x[L]^y$ we obtain the apparent equilibrium constant

$$K' = \frac{[Me_xL_y]}{[Me]^x \left\{ [L] \sum_{i=0}^{N} \beta_i^H [H]^i \right\}^y}. \tag{4.40}$$

Accordingly, the considerations on the equilibrium conversion and the determination of the constant(s), discussed in Section 4.2.1, remain true without change. There is a fundamental difference, however: within the product $K'C$ regulating the equilibrium conversion, not only the value of C, but also that of K', can be varied through appropriate regulation of the pH. Thus, there are much wider experimental possibilities for selection of the optimum conditions for photometric measurements. Figure 4.16 depicts Job curves obtained by Das and Nair [87] at various pH values in the equilibrium system

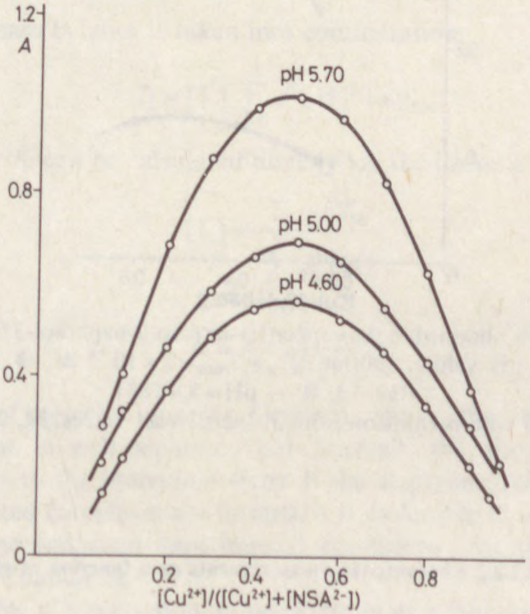


Fig. 4.16. Job curves obtained in the copper(II)–5-nitrosalicylic acid system at various pH values [87]
(Reproduced with permission from *J. Inorg. Nucl. Chem.*, **34**, 1271 (1972))

copper(II)–5-nitrosalicylic acid. It can be seen that, as the pH rises, the equilibrium conversion increases, but the composition of the complex formed does not vary (within the pH range illustrated). Figure 4.17 shows Job curves obtained by Singh *et al.* [88] at various pH values in the system copper(II)–nitroso-2-naphthol-3,6-disulphonate. This Figure clearly shows the increase in the equilibrium conversion, but at the same time the change in the composition of the dominating metal complex.

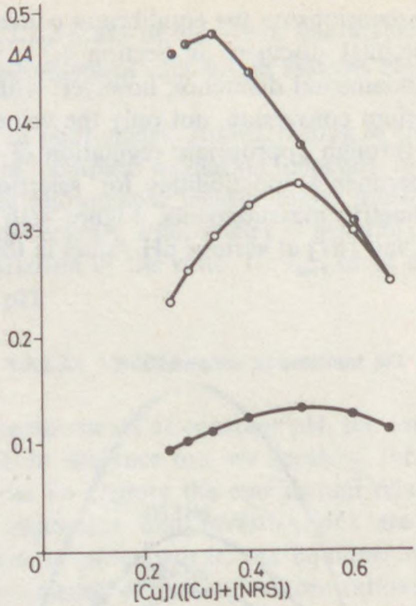


Fig. 4.17. Job curves obtained in the copper(II)–nitroso-2-naphthol-3,6-disulphonic acid system at various pH values. 490 nm; $T_{Cu}+T_{NRS}=2\times10^{-4}$ *M*. ◑ — pH = 2; ○ — pH = 4.3; ● — pH = 8.4 [88]

(Reproduced with permission from *J. Inorg. Nucl. Chem.*, **34**, 2551 (1972))

4.2.2.2.2 Photometric measurements as a function of pH

One of the most frequent methods of carrying out photometric measurements is to record the spectra as a function of pH at constant T_L and T_{Me}. The shape of the absorbance vs. pH function provides illustrative information on the system in question.

If the complex MeL is formed, the absorbance vs. pH curve exhibits a single step. At sufficiently low pH, the complex MeL is not yet formed, and the absorbance does not vary as the pH is increased, assuming that the ligand and its protonated forms do not absorb light at the given wavelength. In the pH range corresponding to formation of the complex MeL, the absorbance varies monotonously; finally, after MeL has formed, the absorbance again becomes constant.

From the resulting data, the stability constant can be calculated from point to point in the range of change of [MeL]. The molar absorbance referred to the total metal ion concentration is the weighted sum of the molar absorbances

$\varepsilon_{\mathrm{Me}}$ and $\varepsilon_{\mathrm{MeL}}$ (these are weighted in proportion to the partial mole fractions)

$$\bar{\varepsilon}=\frac{A}{dT_{\mathrm{Me}}}=\varepsilon_{\mathrm{Me}}\cdot\frac{[\mathrm{Me}]}{[\mathrm{Me}]+[\mathrm{MeL}]}+\varepsilon_{\mathrm{MeL}}\cdot\frac{[\mathrm{MeL}]}{[\mathrm{Me}]+[\mathrm{MeL}]}\,. \tag{4.41}$$

Through the rearrangement of Eq. (4.41), the average ligand number can be calculated directly

$$\bar{n}=\frac{[\mathrm{MeL}]}{[\mathrm{Me}]+[\mathrm{MeL}]}=\frac{\bar{\varepsilon}-\varepsilon_{\mathrm{Me}}}{\varepsilon_{\mathrm{MeL}}-\varepsilon_{\mathrm{Me}}}\,. \tag{4.42}$$

If the ligand mass balance is taken into consideration

$$T_{\mathrm{L}}=[\mathrm{L}]\sum_{i=0}^{N}\beta_i^{\mathrm{H}}[\mathrm{H}]^i+\bar{n}T_{\mathrm{Me}} \tag{4.43}$$

[L] and hence K can be calculated directly via the formula

$$[\mathrm{L}]=\frac{T_{\mathrm{L}}-\bar{n}T_{\mathrm{Me}}}{\sum\limits_{i=0}^{N}\beta_i^{\mathrm{H}}[\mathrm{H}]^i} \tag{4.44}$$

$$K=\frac{\bar{n}}{(1-\bar{n})\,[\mathrm{L}]}\,. \tag{4.45}$$

In the event of stepwise complex formation, when the complex formation processes occur in well separated pH intervals, the above considerations naturally apply to the individual steps. If the stepwise equilibria overlap, or more complicated complexes are formed, it is preferable to carry out both the planning of the optimum experimental conditions and the evaluation by computer (see Chapter 5).

As an example of a spectrophotometric study as a function of pH, Fig. 4.18 depicts absorbance vs. pH curves obtained by Karadakov and Venkova [89] at various wavelengths and at various metal ion–ligand concentration ratios in the system Bi(III)–nitrilotriacetate.

Figure 4.18 clearly reveals that, in the vicinity of pH = 0, the complex BiL is formed at a pH value that decreases in parallel with the increasing ligand excess. It can also be seen that the effect of formation of the complex BiL is considerable at 243 nm, but barely discernible at 271 nm. The appreciable change at pH ~ 5 in the absorbance vs. pH curves obtained at a metal ion–ligand concentration ratio of 1 : 1 (Curves *1* and *4*) can be interpreted in terms of hydrolysis of the complex.

With a ligand excess, a similar type of change is observed at lower pH values, which unambiguously confirms that this effect is caused not by hydrolysis, but by formation of complexes $\mathrm{MeL_2}$. At higher pH values (pH ~ 7–8), however, the complex $\mathrm{MeL_2}$ also undergoes hydrolysis.

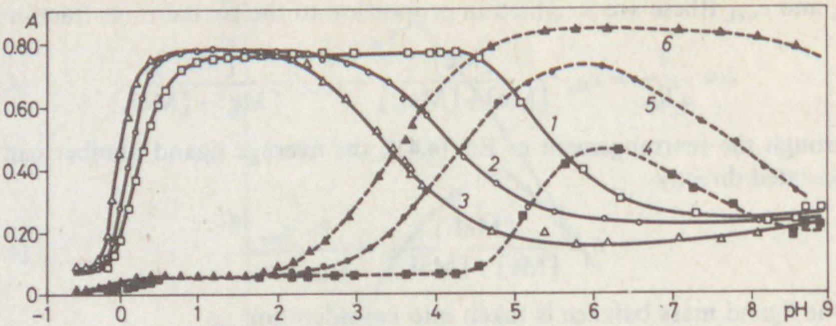


Fig. 4.18. Absorption vs. pH in the Bi^{3+}–NTA system. *1–3* — 243 nm; *4–6* — 271 nm. $T_{Bi} = 10^{-4}$ *M*. T_{NTA} — *1* and *4* — 10^4 *M*; *2* and *5* — 2×10^4 *M*; *3* and *6* — 5×10^{-4} *M* [89]

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4.2.2.3 Competition methods

Photometric studies combined with pH measurements in the systems H–L–Me can, in a broader sense, be classified as competition methods. In these systems, the hydrogen ions and the metal ions compete for the ligand, and the position of the competition equilibrium is influenced through variation of the pH. The pH-dependence of the equilibrium state is followed photometrically, information thereby being obtained on the processes occurring between the components Me and L.

We also speak of competition studies if the position of equilibrium in the system Me–L is influenced by means of a third component Me′ or L′. In photometric studies, this means that, when a component Me (or L) is added to an equilibrium system Me′–L (or L′–Me) with known composition, stability and molar absorbance, there is a shift in the equilibrium Me′–L (or L′–Me) via the competition chain Me′–L–Me (or L′–Me–L), and information can be derived from this shift with regard to the interaction Me–L, which itself can not be investigated photometrically.

These two different types of competition method will each be illustrated with one example. We shall present the method based on competition of the type Me′–L–Me and the principle of corresponding solutions. As an example, the experimental results of Irving and Sharpe [90] on the system Cu^{2+}–EDTA–Cd^{2+} are to be seen in Fig. 4.19.

The complex $CuEDTA^2$ has a well-defined absorption band at 720 nm. The absorbance obtained at pH 5 at constant T_{Cu} and increasing T_{EDTA} is described by the straight lines *mpq*. The complex $CdEDTA^{2-}$ does not absorb light at 720 nm. Thus, the reason why Curves *2–5*, recorded at increasing values of T_{Cd},

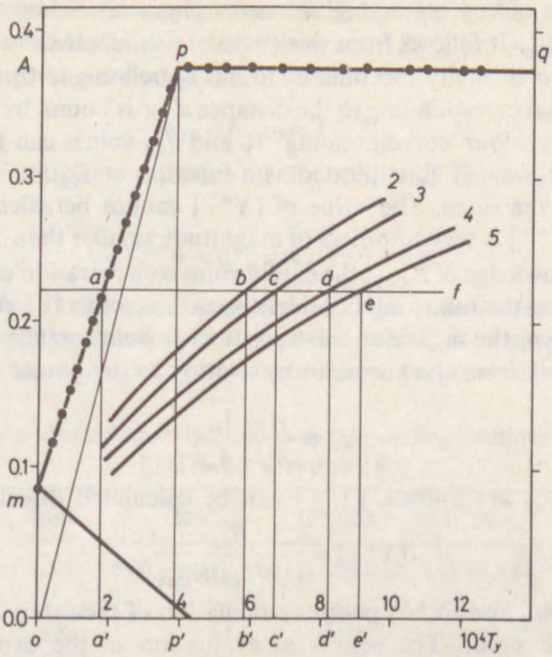

Fig. 4.19. Application of the method of corresponding solutions for determination of the stability constant of $CdEDTA^{2-}$. The plot *mpq* shows the absorbance as a function of T_{EDTA} at $pH = 5$ and $T_{Cu} = 4.064 \times 10^{-4}$ *M*. Curves *2–5* were obtained under the same conditions, but in the presence of 2.667×10^{-2}, 3.333×10^{-2}, 4.000×10^{-2} and 4.667×10^{-2} *M* T_{Cd}, respectively [90]

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differ from *mpq* is the equilibrium

$$CuY^{2-} + Cd^{2+} \rightleftharpoons CdY^{2-} + Cu^{2+} \tag{4.46}$$

where Y^{4-} = ethylenediaminetetraacetate. Expressing the absorbance of the solution in terms of the stability constant K_{CuY}

$$A/d = \varepsilon_{Cu}[Cu^{2+}] + \varepsilon_{CuY}[CuY]$$

$$T_{Cu} = [Cu^{2+}] + [CuY^{2-}] = [Cu^{2+}](1 + K[Y^{4-}])$$

$$K_{CuY} = [CuY^{2-}]/[Cu^{2+}][Y^{4-}]$$

$$A/d = \frac{T_{Cu}(\varepsilon_{Cu} + \varepsilon_{CuY}K_{CuY}[Y^{4-}])}{1 + K_{CuY}[Y^{4-}]}. \tag{4.47}$$

It can be seen from Eq. (4.47) that, apart from the constants, the value of A/d depends only on $[Y^{4-}]$. That is, any horizontal line in the diagram passes through a series of 'corresponding' solutions, characterized by the same values of $[Y^{4-}]$ and $\bar{n}_{Cd}$. It follows from this that the ligand excess corresponding to the distance b'–a' is totally coordinated to the T_{Cd} relating to Curve *2*. Similarly, the ligand excess corresponding to the distance d'–a' is bound by the T_{Cd} relating to Curve *4*. Thus, four 'corresponding' T_Y and T_{Cd} values can be given on the basis of the diagram. If T_Y is plotted as a function of T_{Cd} (see Fig. 4.3), $\bar{n}_{Cd}$ is obtained from the slope. The value of $[Y^{4-}]$ cannot be calculated from the intercept, as $[Y^{4-}]$ is several orders of magnitude smaller than T_Y at pH 5 (Fig. 4.20). In the knowledge of K_{CuY}, the equilibrium concentration of the ligand can be calculated via the following considerations. Since the 1 : 1 stoichiometry of CuY^{2-} is known, the $\bar{n}_{Cu}$ value relating to each point on the line *mp* can be calculated simply from the absorbances relating to the points *m* and *p*

$$\bar{n}_{Cu} = \frac{A - A_m}{A_p - A_m}. \tag{4.48}$$

As $\bar{n}_{Cu}$ and K_{CuY} are known, $[Y^{4-}]$ can be calculated directly through the formula

$$[Y^{4-}] = \frac{\bar{n}_{Cu}}{(1 - \bar{n}_{Cu})K_{CuY}}. \tag{4.49}$$

Knowledge of $\bar{n}_{Cd}$ and $[Y^{4-}]$ permits calculation of the formation constant of CdY^{2-} at each point. The results of evaluation of the experimental data presented in the Figures are listed in Table 4.1.

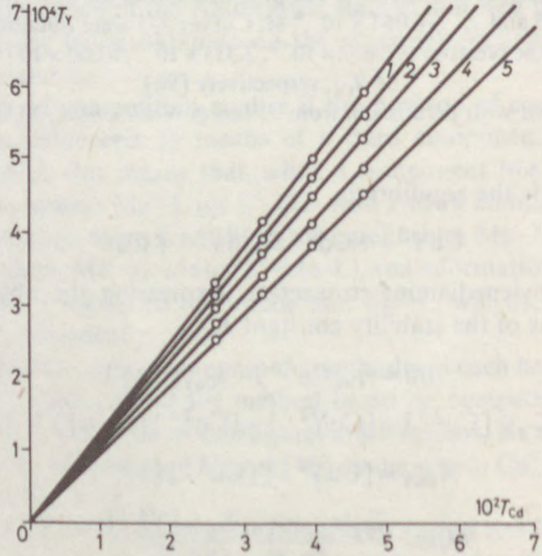

Fig. 4.20. T_Y vs. T_{Cd} plots based on Fig. 4.19. Plots *1*–*5* refer to data read off at $A = 0.200$, 0.195, 0.190, 0.185 and 0.160, respectively [90]
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The key question in the application of the method is the exact knowledge of K_{CuY}. Any error in this will naturally show up in K_{CdY} too. A further condition for application of the method is that

$$K_{\mathrm{CuY}}/K_{\mathrm{CdY}} \approx T_{\mathrm{Cd}}/T_{\mathrm{Cu}}$$

should hold, i.e. through variation of T_{Cd} it should be possible to shift the equilibrium

$$\mathrm{CuY}^{2-} + \mathrm{Cd}^{2+} \rightleftharpoons \mathrm{CdY}^{2-} + \mathrm{Cu}^{2+}$$

sufficiently in the direction of formation of CdY^{2-}. In the example we have given, these conditions are naturally satisfied. Use of a similar method to investigate unknown systems, however, demands great circumspection in planning the experimentation. The essence is the choice of an 'indicator metal ion' such that, when the expected stability of the complex MeL is taken into account, the condition $T_{\mathrm{Me'}}/T_{\mathrm{Me}} \approx K_{\mathrm{MeX}}/K_{\mathrm{Me'Y}}$ should be ensured at constant ionic strength and at the $T_{\mathrm{Me'}}$ necessary for accurate absorbance measurements.

Table 4.1 Results of calculations relating to 'corresponding solutions' in the Cu^{2+}–EDTA–Cd^{2+} system [90]

	$10^4 C_Y$	$10^2 C_{\mathrm{Cd}}$	10^4[CdY]	10^2[Cd]	$\log K_{\mathrm{CdY}}$
$A = 0.180$; [CuY] $= 1.9303 \times 10^{-4}$; [Cu] $= 2.1205 \times 10^{-4}$; [Y] $= 1.4427 \times 10^{-19}$					
2	3.938	2.6667	2.008	2.6466	16.72
3	4.562	3.3333	2.632	3.3070	16.74
4	5.182	4.0000	3.252	3.9675	16.75
5	6.010	4.6667	4.080	4.6259	16.79
$A = 0.190$; [CuY] $= 2.0375 \times 10^{-4}$; [Cu] $= 2.0096 \times 10^{-4}$; [Y] $= 1.6067 \times 10^{-19}$					
2	4.275	2.6667	2.238	2.6443	16.72
3	5.108	3.3333	3.071	3.3026	16.76
4	5.900	4.0000	3.862	3.9614	16.78
5	6.715	4.6667	4.678	4.6199	16.79

To illustrate the method based on the competition L′–Me–L, we shall present results obtained by Norby [91], who studied the interaction Mg^{2+}–ATP via the competition chain 8-hydroxyquinoline–Mg^{2+}–ATP. In a solution containing 8-hydroxyquinoline and Mg^{2+} ions, the following equilibria and mass balances must be considered

$$K_1^{\mathrm{H}} = \frac{[\mathrm{HOx}]}{[\mathrm{H}^+][\mathrm{Ox}^-]} \tag{4.50}$$

$$K_2^{\mathrm{H}} = \frac{[\mathrm{H_2Ox}^+]}{[\mathrm{H}^+][\mathrm{HOx}]} \tag{4.51}$$

$$K=\frac{[\mathrm{MgOx}^+]}{[\mathrm{Mg}^{2+}][\mathrm{Ox}^-]} \tag{4.52}$$

$$T_{\mathrm{Ox}}=[\mathrm{H_2Ox}^+]+[\mathrm{HOx}]+[\mathrm{Ox}^-]+[\mathrm{MgOx}^+] \tag{4.53}$$

$$T_{\mathrm{Mg}}=[\mathrm{Mg}^{2+}]+[\mathrm{MgOx}^+]. \tag{4.54}$$

In the interval $\mathrm{pH}>\log K_2^{\mathrm{H}}+2$, $[\mathrm{H_2Ox}^+]$ can be neglected, and thus

$$T_{\mathrm{Ox}}=[\mathrm{HOx}]\frac{1+K_1^{\mathrm{H}}[\mathrm{H}^+]}{K_1^{\mathrm{H}}[\mathrm{H}^+]}+[\mathrm{MgOx}^+] \tag{4.55}$$

$$[\mathrm{HOx}]=(T_{\mathrm{Ox}}-[\mathrm{MgOx}^+])\frac{K_1^{\mathrm{H}}[\mathrm{H}^+]}{1+K_1^{\mathrm{H}}[\mathrm{H}^+]}. \tag{4.56}$$

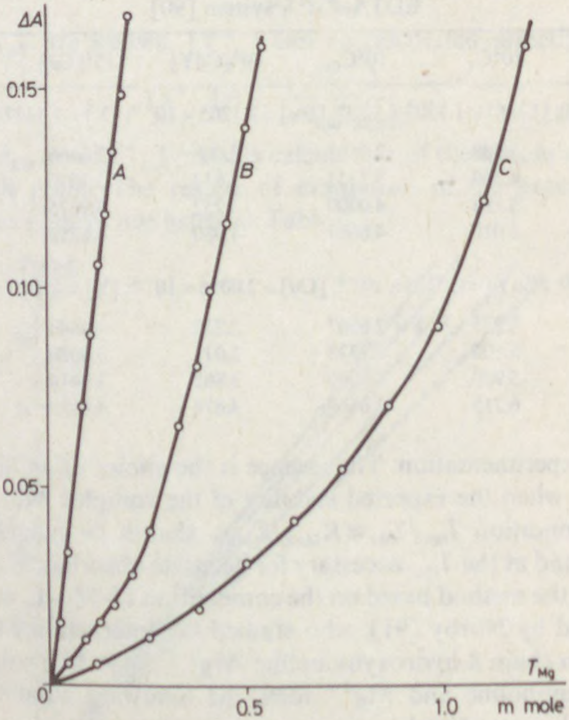

Fig. 4.21. Increase in absorbance of solutions with various 8-hydroxyquinoline and ATP contents as a function of T_{Mg} [91].

A — 3.3×10^{-4} *M* 8-hydroxyquinoline, pH = 8.37; *B* — 3.3×10^{-4} *M* 8-hydroxyquinoline, 4.0×10^{-4} *M* ATP, pH = 8.34; *C* — 3.3×10^{-4} *M* 8-hydroxyquinoline, 1.2×10^{-4} *M* ATP, pH = 8.32

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Using Eqs (4.50) and (4.52)

$$\frac{[\mathrm{MgOx}^+][\mathrm{H}^+]}{[\mathrm{Mg}^{2+}][\mathrm{HOx}]} = K/K_1^{\mathrm{H}} = K'. \tag{4.57}$$

Substituting Eqs (4.56) and (4.54) into Eq. (4.57)

$$K' = \frac{[\mathrm{MgOx}^+](1 + K_1^{\mathrm{H}}[\mathrm{H}^+])}{K_1^{\mathrm{H}}(T_{\mathrm{Mg}} - [\mathrm{MgOx}^+])(T_{\mathrm{Ox}} - [\mathrm{MgOx}^+])}. \tag{4.58}$$

For the calculation of K', only a knowledge of the pH and the concentration of MgOx^+ is required. The latter can simply be determined photometrically.

If the solution contains not only 8-hydroxyquinoline but also another ligand (in the present case ATP), the expression for T_{Mg} changes accordingly and, if the concentration of MgOx^+ is measured, the concentrations of Mg^{2+}, ATP and the complex MgATP can readily be calculated in the knowledge of the pH. As an example, Fig. 4.21 depicts the absorbance change accompanying increase of T_{Mg} in the presence and in the absence of ATP [91].

The progressive deviation of curves B and C from Curve *A* demonstrates the effect of formation of the complex MgATP. It also reveals the basis of the determination of the stability constant of the complex MgATP, which can not be studied directly by photometric means.

4.3 NMR and ESR methods

Both methods are primarily used for the study of chemical structure; their application to equilibrium chemistry has come into the foreground of attention during the past decades. The part they play within equilibrium chemistry is currently increasing rapidly.

The application of ESR to equilibrium work is restricted to the study of complexes of paramagnetic metal ions and of free radicals, whereas NMR can be used effectively to solve almost all equilibrium chemistry problems. The NMR method has the very great advantage that it not only provides the numerical values of the equilibrium constants, but also yields information on the structures of the associations under study and on the binding sites and binding modes of the ligands.

A series of excellent monographs deal with the fundamental principles of the methods and with the possibilities of their application [92–97]. These features will not be considered in the present discussion; we merely survey the methods from the aspect of the determination of equilibrium constants. We shall first examine the possibilities of application when the primary aim is the determination of numerical values of equilibrium constants, and then review the various possibilities of studying the equilibrium and the structure simultaneously.

The experimentally measurable parameters of NMR and ESR spectra (chemical shifts, relaxation times, band widths, coupling constants and g-factors) depend on the chemical environments containing the NMR or ESR-active nuclei in question, and on the rates of the exchange reactions taking place between them. In the case of slow exchange, the signals of the resonating nuclei in the various chemical environments may appear separately in both the NMR and the ESR spectra, whereas an 'averaged' signal is obtained in general if the exchange is fast. The experimentally found spectra may be suitable for determination of the equilibrium constants in both limiting cases; in the intermediate range (in a fortunate case), the equilibrium constants and the rate constants of the exchange reactions may be determined simultaneously.

4.3.1 Equilibrium measurements relating to slow exchange

The condition of 'slow exchange' generally holds only in solutions of complexes of non-labile metal ions. It then frequently happens that the signals of the different complexes appear well separated from one another in the NMR spectrum. The ratios of the integrated intensities of the bands coincide with the concentration ratios, and calculation of the equilibrium constants thus becomes a simple arithmetical operation, even in cases involving complicated equilibria. This possibility is primarily made use of to determine the constants of equilibrium processes of the following type [98–103]

$$i\mathrm{MeX}_n + j\mathrm{MeY}_n \rightleftharpoons n\mathrm{MeX}_i\mathrm{Y}_j.$$

As an example, Fig. 4.22 presents the NMR spectrum of ^{27}Al in the system $AlCl_4$–$AlBr_4$, as reported by Jones [98].

The equilibrium method based on the ratios of the integrated intensities can naturally be used to study the complexes formed by non-labile metal ions in stepwise equilibria. The FT ^{13}C NMR method was effectively applied by Fuentes *et al.* [104], for instance, to investigate the equilibrium system Ni(II)–acetate (Fig. 4.23).

The tremendous advantages of the method are obvious. The spectrum directly reveals the number of complexes formed in the equilibrium system, and even their concentration ratios. Thus, the equilibrium constants may be calculated not by solving the parameter equations obtained via the various function connections, but through a direct formula, even in the case of simultaneous equilibria. Equilibrium information of comparable value can be obtained from the IR and Raman spectra only in a few fortunate cases. In the latter two methods, it frequently occurs that the bands overlap, which necessitates their

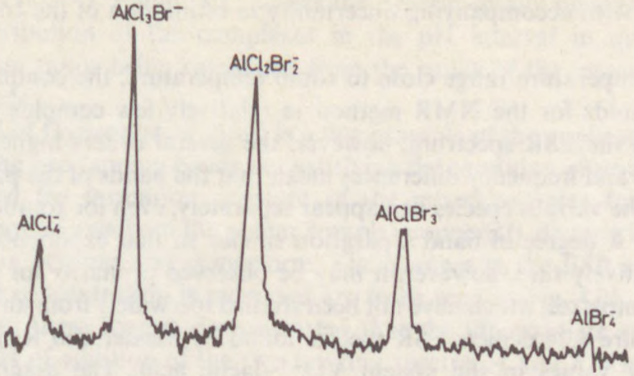

Fig. 4.22. ^{27}Al NMR spectrum of sample with average composition $AlBr_{1.55}Cl_{2.45}^-$ dissolved in acetonitrile (23.45 MHz) [98]
(Reproduced with permission from *J. Chem. Soc. Dalton*, 567 (1972))

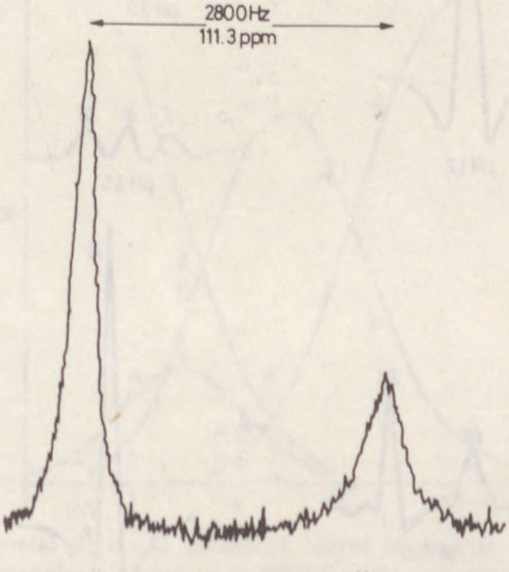

Fig. 4.23. ^{13}C NMR spectrum of a sample containing 0.701 M $Ni(ClO_4)_2$ and 0.552 M $CH_3\,^{13}COOH$ in D_2O at 0 °C at 25.2 MHz. The NMR band of free acetate appears at lower field strength, and that of the monoacetato complex at higher field strength [104]
(Reproduced with permission from *Inorg. Chem.*, **14**, 1837 (1975))

resolution, with accompanying uncertainty in estimation of the concentration ratios.

In the temperature range close to room temperature, the condition of slow exchange holds for the NMR method in relatively few complex equilibrium systems. In the ESR spectrum, however, the several orders higher resonance frequencies and frequency differences mean that the bands of the paramagnetic centres of the various species can appear separately, even for solutions of labile metal ions. A degree of band separation similar to that experienced in NMR is comparatively rare, however; it may be observed primarily for solutions of vanadyl complexes, which have not been studied too widely from an equilibrium aspect. Figure 4.24 depicts ESR spectra found by Reeder and Rieger [105] at various pH values in the system VO^{2+}–lactic acid. The diagrams clearly illustrate that the vanadyl ion exists in four different chemical environments in

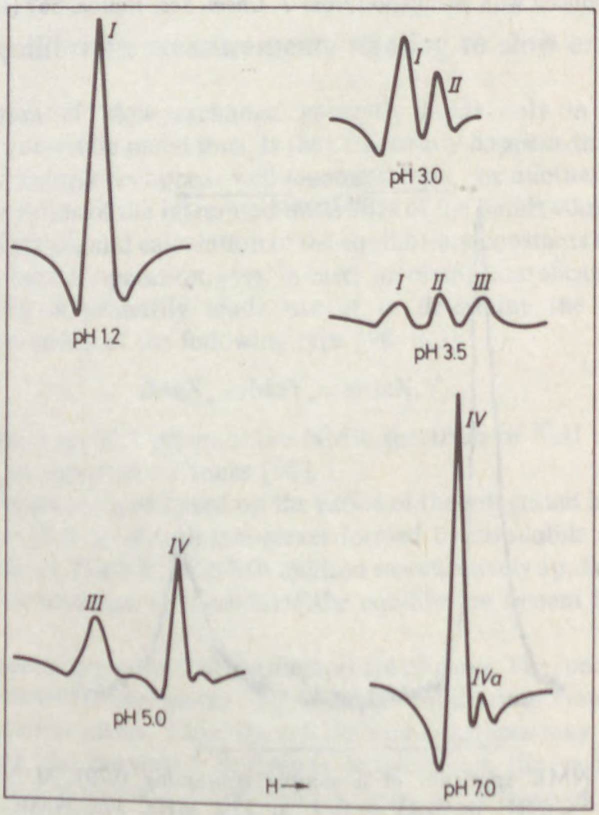

Fig. 4.24. Second derived ESR spectrum in the VO^{2+}–lactic acid system; $M_I = -7/2$ components as a function of pH at 25 °C, at $T_L/T_{Me} = 4$ [105]. (For symbols see Fig. 4.25) (Reproduced with permission from *Inorg. Chem.*, **10**, 1258 (1971))

the pH interval 1–7. Figure 4.25 shows the experimentally measured concentration distribution of the complexes in the pH interval in question, the concentration ratios being calculated from the ratios of the intensities of the various bands.

The work of Dyrssen *et al.* [106] is a fine example of the application of ESR spectra giving overlapping bands but satisfying the condition of slow exchange. They studied the formation constant of the mixed complex formed when pyridine is bound axially to the planar complex copper(II)–dimethylglyoximate in solution in benzene and chloroform. The changes in the ESR spectrum as the pyridine concentration is increased are to be seen in Fig. 4.26.

Analysis of these spectra demonstrated that the intermediate spectra *B–E* are resultants of addition of the two limiting spectra, *A* and *F*. This confirms that the condition of slow exchange between the coordinated and the free pyridine holds in all solutions; with regard to the difference in frequency of the bands, this means that the frequency of exchange between the bound and the free pyridine is less than 10^8 Hz. An essentially similar application of ESR to

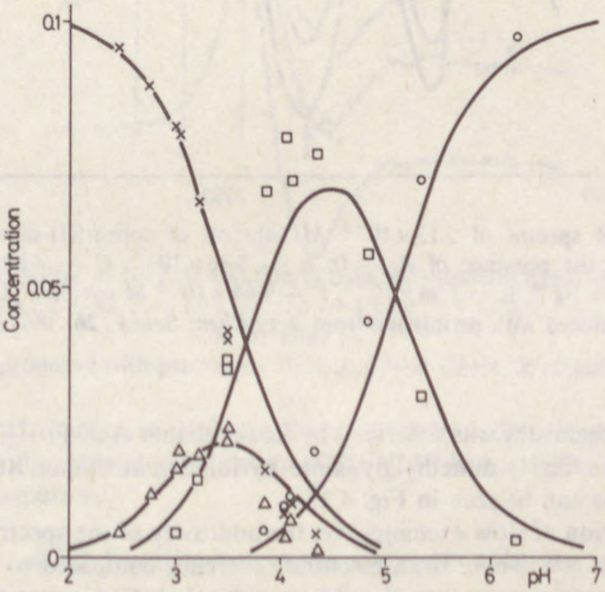

Fig. 4.25. Experimental data and calculated curves relating to the concentration distribution of the complexes formed in the VO^{2+}–lactic acid system as a function of pH at $T_1/T_{Me} = 4$ [105]

Symbols (also for Fig. 4.24): ×, *I* — free vanadyl ion + VO(HA) complex; △, *II* — VO(HA)$_2$ complex; □, *III* — VOA + VO(HA)A complex; ○, *IV* — VOA$_2$ complex

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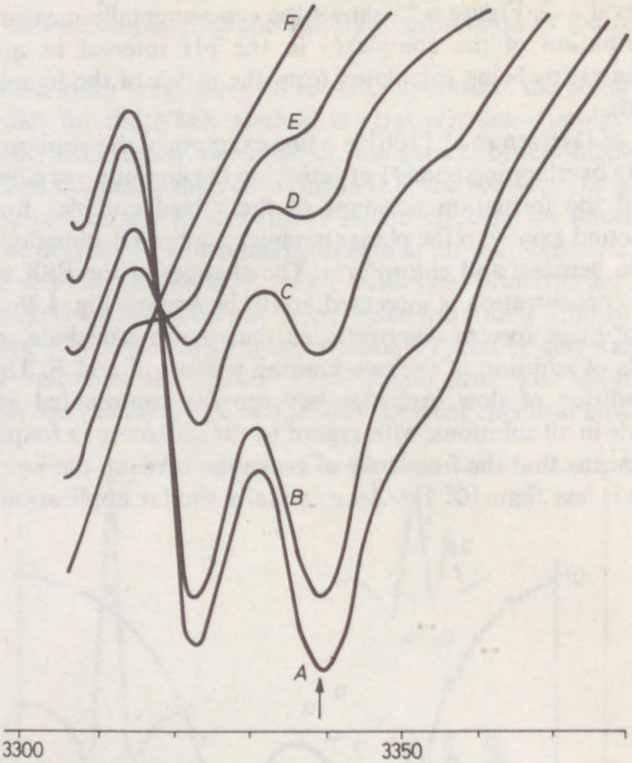


Fig. 4.26. ESR spectra of 5.13×10^{-5} M solution of copper(II)–dimethylglyoxime in benzene in the presence of A — 0; B — 3.46×10^{-5}; C — 4.80×10^{-4}; D — 9.64×10^{-4}; E — 1.96×10^{-3}; F — 9.64×10^{-3} M pyridine [106]
(Reproduced with permission from *Acta Chem. Scand.*, **26**, 3865 (1972))

equilibrium chemistry was described by Rockenbauer *et al.* [107], who studied the interaction Co(II)–dimethylglyoxime–pyridine in methanol. Results of their measurements can be seen in Fig. 4.27.

The condition of slow exchange, i.e. the additivity of the spectrum, was met in this system too. There is an essential difference compared to the previous system: two pyridines are bound axially to the cobalt(II)-bis-dimethylglyoxime, and neither the spectrum of the monopyridine complex, nor that of the bis-pyridine complex, can be measured directly.

Accordingly, evaluation of the measurements is a substantially more difficult task than in the previous case.

These two examples clearly illustrate that, even if the condition of slow exchange is satisfied, the greater degree of overlap of the ESR bands means

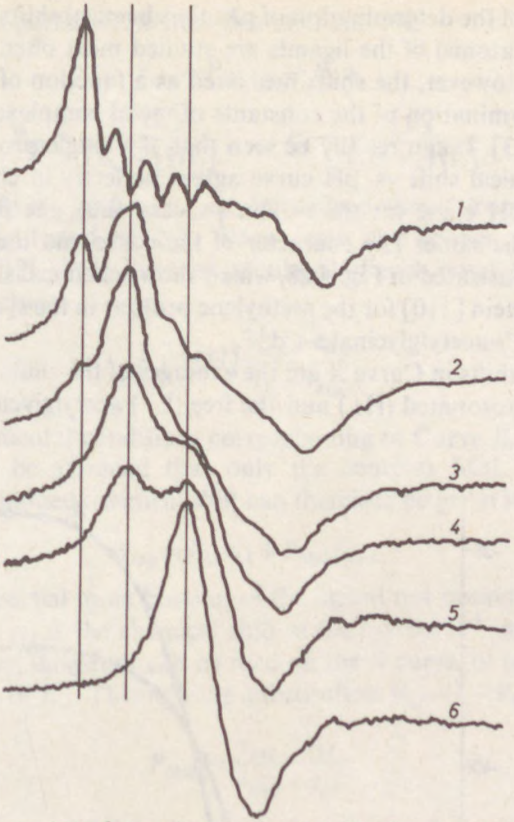


Fig. 4.27. ESR spectra of 10^{-2} *M* solution of cobalt(II)–dimethylglyoxime in methanol in the presence of *1* — 0; *2* — 1.4×10^{-2}; *3* — 4×10^{-2}; *4* — 0.2; *5* — 0.29; *6* — 2.32 *M* pyridine [107]
(Reproduced with permission from *J. Coord. Chem.*, **2**, 53 (1972))

that it is much harder to evaluate the experimental data here than in the calculation of the integrated intensities of the NMR bands, which are generally much better separated.

4.3.2 Equilibrium measurements relating to fast exchange

When fast exchange processes take place, the NMR spectrum shows a single signal, averaged in the proportions of the partial mole fractions of the active nuclei to be found in the various chemical environments. The averaging also shows up strikingly in the chemical shifts and in the reciprocal relaxation times (relaxation rates).

With the aim of the determination of p*K*, the chemical shifts of the non-labile protons (or ^{13}C atoms) of the ligands are studied most often as a function of pH [108–120]. However, the shifts measured as a function of pH may also be suitable for determination of the constants of metal complexes [110, 112, 113, 115–117, 121–123]. It can readily be seen that, if a single protonation process occurs, the chemical shift vs. pH curve agrees perfectly in character with the absorbance vs. pH curve for the similar process; thus, the principles of their evaluation are the same. The character of the curve and the principle of the evaluation are illustrated in Fig. 4.28, which shows chemical shift vs. pH curves found by Rabenstein [110] for the methylene protons in the systems H^+–acetylglycinate and H^+–acetylglycinate–Cd^{2+}.

The chemical shifts in Curve *A* are the averages of the shifts of the methylene protons of the protonated (HL) and the free (L^-) acetylglycinate, weighted in

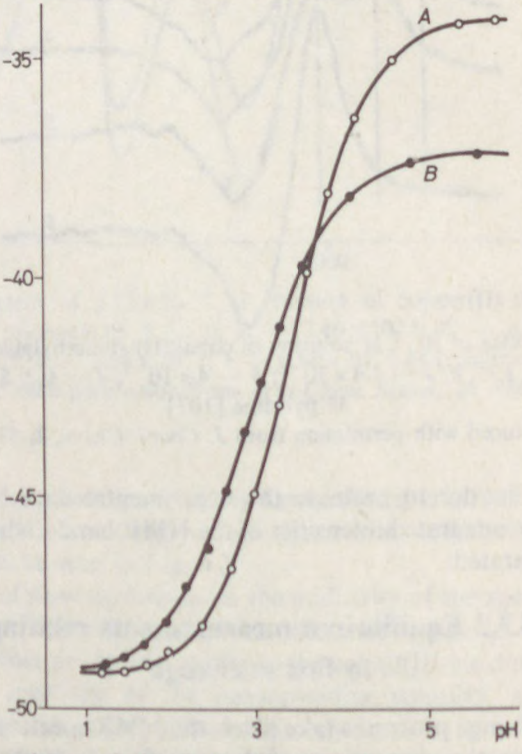


Fig. 4.28. pH-dependence of chemical shift of methylene protons in acetylglycine [110].
A — 0.2 *M* acetylglycine + 0.6 *M* KNO_3; *B* — 0.2 *M* acetylglycine + 0.2 *M* $Cd(NO_3)_2$
(Reproduced with permission from *Can. J. Chem.*, **50**, 1036 (1972))

proportion to the partial mole fractions of L and HL

$$\nu_{exp} = P_{HL}\nu_{HL} + P_L\nu_L \tag{4.59}$$

$$P_{HL} = \frac{[HL]}{[L]+[HL]}; \qquad P_L = \frac{[L]}{[L]+[HL]}. \tag{4.59a}$$

The chemical shifts ν_{HL} and ν_L can be determined simply from the diagram in the intervals $pH \lesssim 1$ and $pH \gtrsim 5$. When these are known, the dissociation constant $K_d = [H][L]/[HL]$ can be calculated at each point, from the data of the different pH ranges

$$K_d = [H]\frac{\nu_{exp} - \nu_{HL}}{\nu_L - \nu_{exp}}. \tag{4.60}$$

Under the experimental conditions corresponding to Curve *B*, at $T_L/T_{Me} = 1:1$, it can justifiably be assumed that only the complex MeL is formed. The experimentally obtained chemical shift can therefore be given by the expression

$$\nu_{exp} = P_{Lf}\nu_{Lf} + P_{MeL}\nu_{MeL} \tag{4.61}$$

where P_{Lf} is the partial mole fraction of the ligand not bound in the complex, i.e. L + HL, while ν_{Lf} is the chemical shift of the system H^+–acetylglycinate at the pH in question; this latter can be read off the *A* curve, or can be calculated in the knowledge of K_d. Through the substitution $P_{Lf} = 1 - P_{MeL}$

$$P_{MeL} = \frac{\nu_{exp} - \nu_{Lf}}{\nu_{MeL} - \nu_{Lf}}. \tag{4.62}$$

When P_{MeL} is known, [MeL] can readily be calculated

$$[MeL] = P_{MeL}T_L \tag{4.63}$$

where T_L is the total concentration of acetylglycine. For the calculation of P_{MeL} via Eq. (4.62), the value of ν_{MeL} must be known. It can be seen from Eq. (4.61) that $\nu_{MeL} = \nu_{exp}$ if $\nu_{MeL} = \nu_{Lf}$. ν_{MeL} is therefore obtained from the chemical shift value at the point where the chemical shift vs. pH curves for the systems H^+–acetylglycine and H^+–acetylglycine–Cd^{2+} intersect. Once ν_{MeL} is known, the value of the formation constant K_{MeL} can be calculated separately at each point of Curve *B*.

The correlations relating to the various concrete systems may naturally be much more complicated, but, similarly as above, the basic principle of the evaluation is always the same as that for photometric measurements. In this case, the shift measurements on the various protons or other NMR-active nuclei of the ligand correspond to photometric measurements at different wavelengths. As an example, Fig. 4.29 gives ^{13}C chemical shift vs. pH curves for the five different carbon atoms of L-glutamic acid [118].

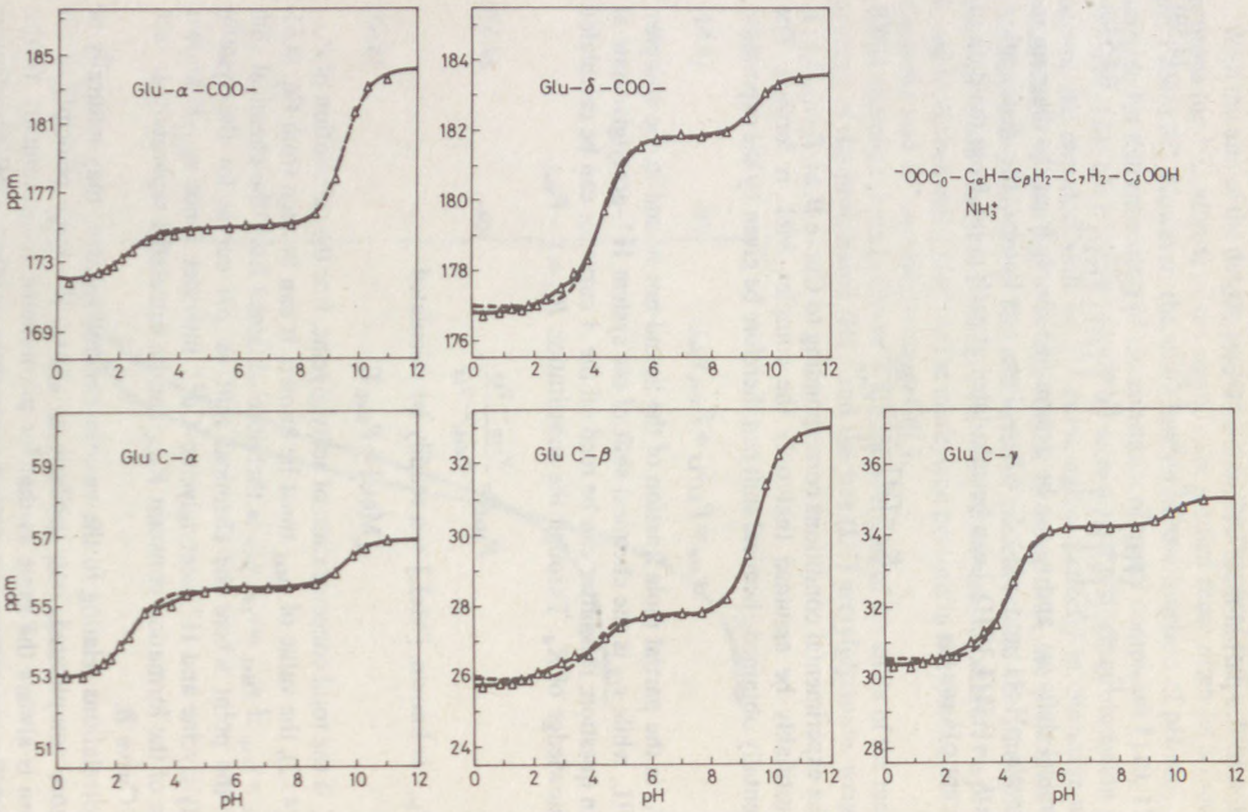


Fig. 4.29. pH-dependence of chemical shifts of the five different carbon atoms in glutamic acid [118]
(Reproduced with permission from *J. Am. Chem. Soc.*, **96,** 570 (1974))

The diagrams clearly demonstrate that the changes caused by protonation in the chemical shifts of the NMR-active nuclei depend on the distance from the protonating donor group. With ligands containing several protonating groups, this finding permits determination of the microscopic protonation constants. This question will be dealt with in more detail in Chapter 5.

Measurement of chemical shifts is not only suitable for equilibrium studies on protonation processes and on complexes of ligands that can be protonated, but, similarly to visible and UV spectrophotometry, can also be used if none of the equilibrium concentrations of the reacting components is known. In such cases, the photometric methods for two-component systems (mole ratio method, Job method, etc.) can naturally be applied. Figure 4.30 depicts chemical shift vs. mole ratio curves found by Hawland and Flurry [124] for the L-histidine–Pr(III) system.

Questions concerning the practical application and evaluation of chemical shift vs. mole ratio curves, and of the curves of other types discussed in Section

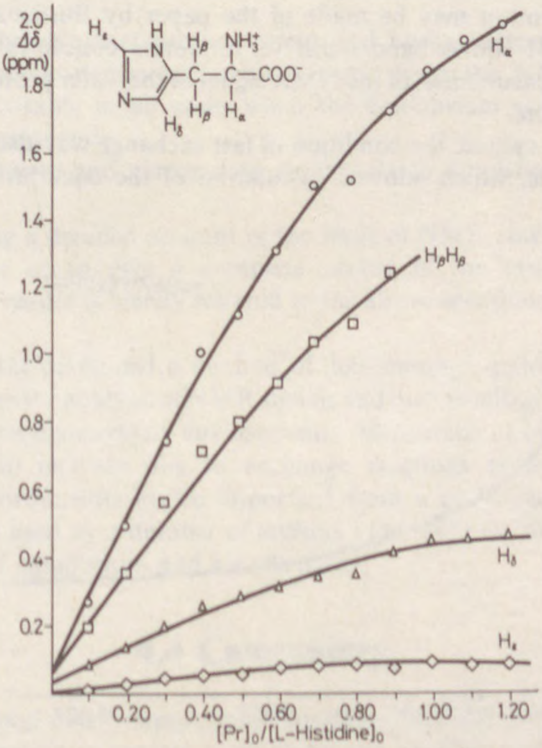


Fig. 4.30. Chemical shifts of various protons in histidine as a function of the ratio [Pr]/[L-histidine] [124]
(Reproduced with permission from *J. Inorg. Nucl. Chem.*, **38**, 1568 (1976))

4.2, based on chemical shift differences, coincide with the previous detailed treatment.

Besides the chemical shift, other important 'averaged' experimental data are the reciprocal of the relaxation time T_2, and the NMR (ESR) band-width, which is proportional to this. For NMR spectra, measurement of the band-width can be utilized for equilibrium purposes if a fast exchange process involves the participation of paramagnetic species. The measured data may then be an additive function of the concentrations of the paramagnetic species, and hence the equilibrium constant too can be calculated from the band-width measured as a function of the concentration ratios.

Detailed reviews of the application of band-width (relaxation time) measurement to equilibrium chemistry are to be found in the books by Popel [129, 130]. When the method is used, it must first be established that T_2^{-1} is really an additive function of the concentrations of the paramagnetic species, i.e. the rates of the exchange processes no longer appear in the band-width. As an example of the numerous equilibrium studies based on measurement of band-widths [125–134], mention may be made of the paper by Burlamacchi and Tiezzi [125]; Fig. 4.31 shows band-width vs. dithionite concentration curves they obtained by measurement of the NMR signal of the water protons in the system Mn^{2+}–dithionite.

In the given system, the condition of fast exchange was also satisfied on the ESR time scale, which allowed calculation of the equilibrium constant via

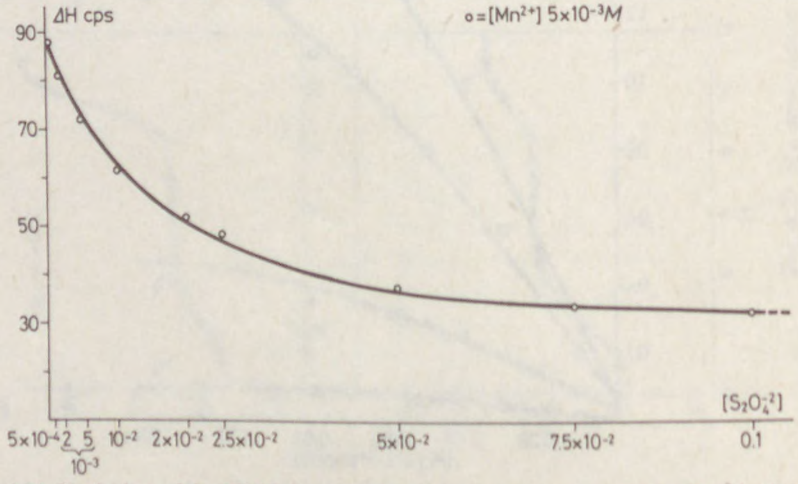


Fig. 4.31. Variation of the NMR band-width of the water protons in the Mn^{2+}–dithionite system as a function of the dithionite concentration [125]
(Reproduced with permission from *J. Inorg. Nucl. Chem.*, **31**, 2159 (1969))

measurement of the ESR band-width too [135]. Stevenson *et al.* [136–141] reported on a series of equilibrium studies based on measurement of the parameters of ESR spectra.

4.3.3 Simultaneous determination of equilibrium and kinetic constants

The previous two sections dealt with the possibilities and methods of carrying out NMR studies on equilibrium systems satisfying the condition of slow exchange or fast exchange. However, these conditions are each met only in a narrow group of equilibrium systems and only in limited concentration ranges. Most of the equilibrium systems investigated by NMR involve exchange at moderate rates. We may then distinguish two fundamentally different methods of evaluating the experimental results, i.e. of determining the equilibrium and kinetic constants.

(1) The equilibrium constants are determined by an independent method, and only the kinetic parameters are calculated from the NMR data. This procedure is advisable in all cases when the equilibrium constants can be determined independently.
(2) The equilibrium and kinetic data are calculated simultaneously.

Without giving a detailed account of the basis of NMR kinetic studies, it is not possible for us to give a complete survey of the possible methods; accordingly, the reader is merely referred to the above-mentioned monographs [92–97].

Dahlquist [142] developed a method of determining equilibrium and rate constants through the analysis of NMR signals and lines resulting from exchange processes between diamagnetic environments. Measurement of the relaxation rate (band-width) increase due to exchange reactions between para- and diamagnetic environments (more important from a coordination chemistry aspect) has been used by a number of authors [143–145] for the simultaneous determination of equilibrium and kinetic data.

4.4 Calorimetry

The experimental and computational conditions for the calorimetric study of complex formation processes in stepwise and parallel reactions in dilute solutions emerged during the past 20–30 years. Starting from the end of the 1950's, numerous calorimeters were developed in parallel with the progress relating to electric temperature sensors and electronics; nowadays, not only are 'home-built' solution calorimeters used, but reliable solution calorimeters too are commercially available.

The goal of calorimetric equilibrium measurements is the simultaneous determination of the reaction heat and the constants, or the determination of the reaction heat in the knowledge of the equilibrium constants. Below, we survey the various technical possibilities for the application of calorimetry to equilibrium chemistry; we shall not deal with calorimetry as a generally applicable method in analytical chemistry.

In principle, calorimetry is one of the most general methods, for practically all chemical reactions are accompanied by a definite change in heat. However, only calorimetry has the feature that the measurement must be made actually while the reaction is taking place; in the other methods, properties of the systems are measured that do not vary with time. This difference also shows up in the basic equations describing calorimetric measurements: the measured heat quantity corrected by the dilution heat ($Q_{\text{measd.}}-Q_{\text{dil.}}$) can be given as the sum of the formation enthalpies, weighted with the mole differences calculated from the concentration distributions characterizing the initial and final states, besides the mass balances expressed with the law of mass action. In a description of the equilibrium behaviour of the system, the solvent may be neglected as a component. In the case of solvents capable of autoprotolysis, however, the formation of solvent molecules must always be taken into consideration in calorimetry. Thus, the basic equation for the evaluation of calorimetric measurements is

$$Q_{\text{measd.}}-Q_{\text{dil.}}=\sum_{j=1}^{n}\{[A_j]_0V_0-[A_j](V_0+v)\}\Delta H_j+\Delta m_s\Delta H_s \qquad (4.64)$$

where V_0 is the volume of starting solution, v is the volume of the reagent, Δm_s is the change in the quantity of solvent in moles, ΔH_s is the formation heat of the solvent in the equilibrium process in question: in aqueous solutions the reaction heat of the process $H^+ + OH^- \rightleftharpoons H_2O$ under the experimental conditions, and ΔH_j is the formation heat of the jth association.

It is clear from Eq. (4.64) that calorimetric study of an equilibrium system necessitates measurements of heat quantities for numerous composition changes. Calorimetric measurements can be classified in three groups as concerns their technical performance

(1) Calorimetry involving portionwise addition of the reaction partners.
(2) The method of continuous titration.
(3) Calorimetry in a flow cell.

Many calorimeter types have been developed on the basis of portionwise addition of the reaction partners [146–151]. Of these, the solution calorimeter

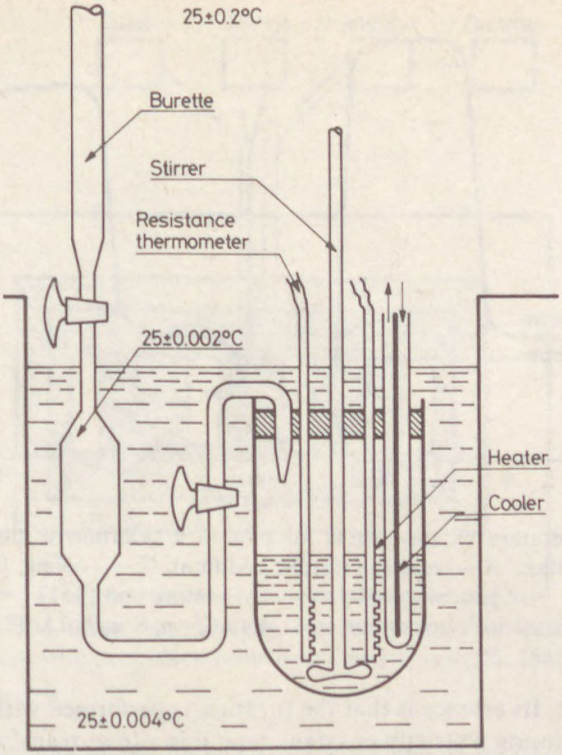


Fig. 4.32. The Schlyter–Sillén calorimeter [151]
(Reproduced with permission from *Acta Chem. Scand.*, **13**, 385 (1959))

devised by Schlyter and Sillén is particularly suitable for complex equilibrium studies; this type was later modified by Johansson [152] and by Arnek and Kakolowicz [153]. A schematic outline of the calorimeter may be seen in Fig. 4.32.

The reaction partners are at exactly the same temperature. The heating and cooling units permit restoration of the initial temperature after the addition of each portion of the titrant solution; hence, the temperature change during the titration is not significant. The individual steps of the titration, and the variation of temperature in the course of them, are illustrated in Fig. 4.33.

Calorimetry involving portionwise addition of the reaction partners is a very time-consuming and laborious process, especially when complicated equilibrium systems are investigated. Two methods are known whereby the time and labour requirements can be reduced; both of them are suitable for the study of "instantaneous" reactions. Gergely and Sóvágó [154] elaborated a method based on evaluation of calorimetric curves recorded during continuous titration

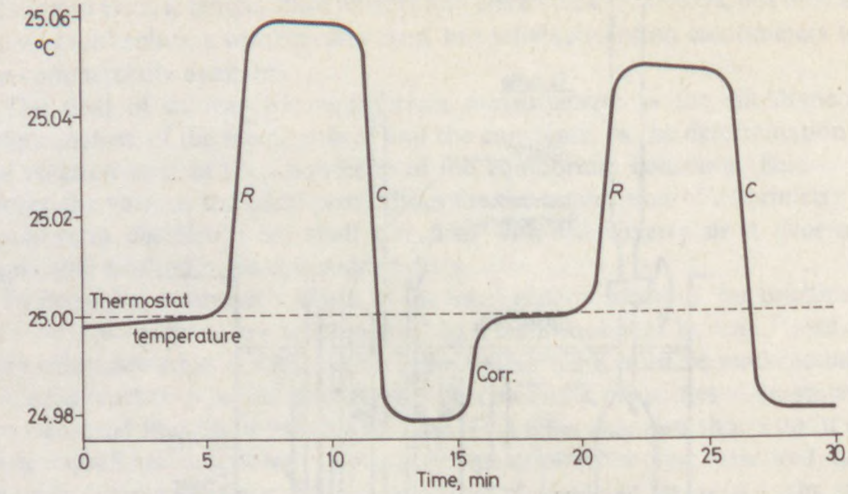


Fig. 4.33. Temperature vs. time curve for part of a calorimetric titration involving portionwise addition. *R* — reaction (titrant addition); *C* — cooling; Corr. restoration of temperature by means of heating unit [151]
(Reproduced with permission from *Acta Chem. Scand.*, **13**, 385 (1959))

at constant rate. Its essence is that the titration is performed with an automatic burette guaranteeing a strictly constant rate; this allows transformation of the resistance vs. time curve to a resistance vs. volume curve, the delay time of the thermistor also being taken into account. Evaluation is carried out by means of the Regnault–Pfaundler method, similarly proposed by Wadsö [155]. Account was taken of the heat exchange between the reaction vessel and the environment, the temperature difference between the titrant and titrated solutions, and the heat capacity change caused by the volume increase. The results obtained through portionwise and continuous titration agreed well.

The flow microcalorimetry method earlier applied in biochemistry [156, 157] was utilized by Bianchini *et al.* [158] for the study of stepwise complex equilibria. The design of the microcalorimeter is outlined in Fig. 4.34.

A metal block (*a*) contains a heat exchanger (*b*) and two twin-calorimeter units (*c*), (*d*) represents a 20 mm layer of polystyrene foam, (*e*) a cylindrical stainless steel jacket; (*f*) a water bath. The flow cells of the calorimeters are surrounded by surface-contact thermocouples, the other poles of which are connected to the metal block. The entire block is immersed in a thermostated water-bath. The solutions containing the reaction partners are pumped through the heat exchanger into one of the reaction cells, from where it exits from the calorimeter after the reaction has taken place. The potential obtained is the difference of the potentials from the two thermocouples, and thus the disturbing

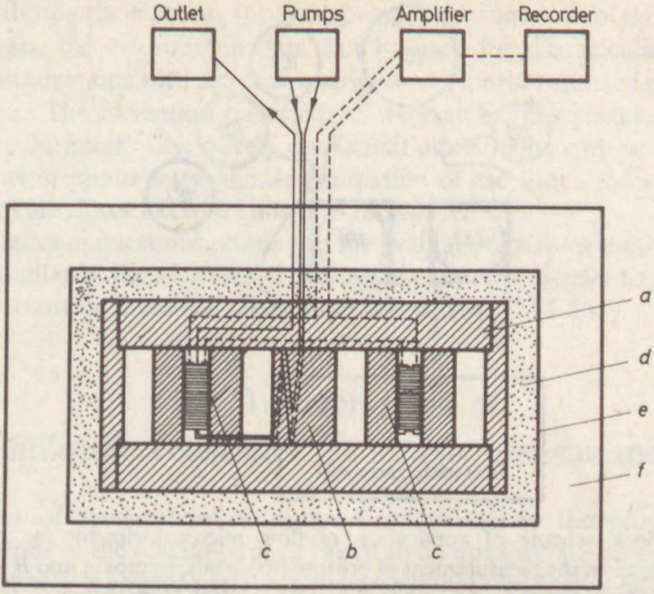


Fig. 4.34. Block scheme of the flow microcalorimeter [156]
(Reproduced with permission from *Acta Chem. Scand.*, **22**, 1842 (1968))

effects are largely eliminated. In one experiment, the liquid flows only through one cell, and the heat resulting from the friction of the liquid is taken into account with an appropriate correction. The reaction takes place in the mixing compartment of the flow cell. If the flow of the solutions of the reaction partners is continued for sufficient time, the temperature difference becomes constant, as does the resulting potential, which will therefore be proportional to the quantity of heat developing during unit time.

Bianchini *et al.* [158] used the flow calorimeter in the set-up outlined in Fig. 4.35.

For the calculation of formation heats, it was necessary for them to know the molar flow rates of the various species both before and after the reaction. Using the notations introduced in Chapter 3

$$\frac{V_i}{R} = \sum_{j=1}^{n} \beta_j \left(\frac{v_i}{R}\right)^{\alpha_{j1}} \cdots \left(\frac{v_k}{R}\right)^{\alpha_{jk}}$$

$$\frac{V_k}{R} = \sum_{j=1}^{n} \beta_j \left(\frac{v_1}{R}\right)^{\alpha_{j1}} \cdots \left(\frac{v_k}{R}\right)^{\alpha_{jk}} \tag{4.65}$$

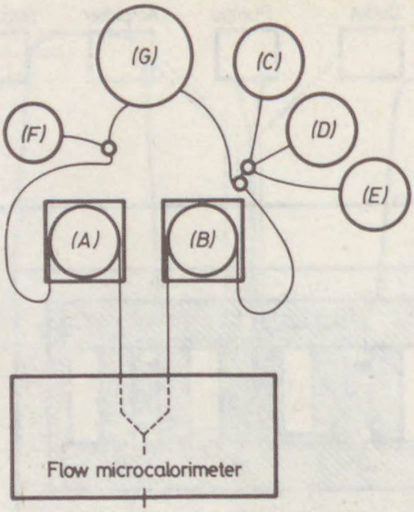


Fig. 4.35. Block scheme of application of flow microcalorimeter for equilibrium chemical studies. In the measurement of protonation heats, pumps A and B force amine hydrochloride from vessel F and standard NaOH solution from vessels C, D and E into the microcalorimeter. In calorimetric studies on metal complexes, vessel F contains metal ion at appropriate concentration too. Vessel G contains 0.5 M $NaClO_4$ [158]
(Reproduced with permission from *J. Chem. Soc. Dalton Trans.*, 1036 (1975))

where V_i is the total flow rate of the ith component, R is the sum of the rates of the two pumps, and v_i is the molar flow rate expressed with the equilibrium concentrations of the components.

If the non-linear equation system Eq. (4.65) is solved for v_i/R, the molar flow rate of any ionic species A_j can be calculated

$$\frac{v_{A_j}}{R} = \beta_j \left(\frac{v_1}{R}\right)^{\alpha_{j1}} \ldots \left(\frac{v_k}{R}\right)^{\alpha_{jk}}. \tag{4.66}$$

A knowledge of the v_{A_j} values before and after mixing permits the measured heat quantity flows to be broken down into the terms originating from the formation of the various species, i.e. the molar formation enthalpies can be calculated. This is a very fast method compared to the portionwise addition; nevertheless, it has not yet become widespread, even though the appropriate calorimeter is commercially available.

The aim of the calorimetric measurements may be to determine the equilibrium constant(s) and enthalpy change(s), or to determine the enthalpy change(s) in the knowledge of the constant(s). Since the calorimetrically measured heat quantity is always strictly proportional to the mole changes occurring during the reaction, the latter being linear functions of the concentration changes, the calorimetric data can be used for the calculation of the equilibrium constants with the same restrictions as for the results of photometric experiments. The formation constants of very stable complexes can not be measured calorimetrically; merely the formation enthalpy can be determined. Similarly as in photometry, the determination of the formation constants of very weak complexes likewise runs into difficulties.

Computational questions relating to the evaluation of calorimetric measurement are similar to the photometric ones. Here, we simply refer to some of the more important publications concerning this subject [158–166].

4.5 Determination of equilibrium constants via kinetic measurements

The rates of chemical reactions are proportional to the product of the concentrations of the reactants, each raised to an appropriate power. A formal kinetic treatment of equilibrium reactions reveals that the kinetic and equilibrium data are mutually supplementary; the equilibrium constants can be calculated from the results of kinetic measurements, while equilibrium data obtained through an independent method may be of considerable help in the elucidation of the reaction mechanism. Clearly, a certain period of time is required for any chemical reaction to take place. The expression 'instantaneous', applied to describe some reactions, simply means that the reaction takes place in a very short time, and can be followed only with a special method. Nowadays, even the fastest chemical reactions can be followed by means of modern reaction kinetic methods [167, 168], and primarily by the relaxation procedures developed by Eigen *et al.* With these methods, it is even possible to distinguish between inner sphere and outer sphere complexes [169].

Numerous chemical reactions are catalysed by ligands, metal ions or the complexes formed. Accordingly, equilibrium information may possibly be acquired from a study of catalytic effects [170].

If the reaction is of the first order with respect to some complex with an unknown formation constant, then the expression for the concentration-dependence of the overall reaction rate is analogous to the equation corresponding to the limiting case $\varepsilon_{Me} = \varepsilon_L = 0$ of Eq. (4.17). The kinetic data can then be evaluated with the same methods as for the results of photometric measurements. However, some important differences too must be borne in mind. The rate constants vary much more sensitively with temperature in general than do the molar absorbances; during the measurements, therefore, the temperature must be kept strictly constant. The photometric measurements may be made at various wavelengths; from a reaction kinetic aspect, however, a reaction can be characterized only by a single intensive factor. This may have a very large value, particularly in the case of catalytic reactions, and thus even complexes which are not very stable in a thermodynamic sense may have an appreciable effect on the reaction rate. The measurable range of reaction rate constants covers 10–13 orders of magnitude, while the range in which the molar absorbance can conveniently be measured spans only 4–5 orders of magnitude. The results of kinetic measurements may be changed fundamentally by even traces of contamination; the danger of this is generally lower in spectrophotometry.

When the possibilities of experimental error in the kinetic measurements are also taken into account, it is clear that reliable kinetic and equilibrium data can be obtained only for relatively simple systems. Equilibrium constants determined through independent methods are absolutely necessary for the reliable evaluation of experimental data on systems that are more complex from equilibrium and kinetic aspects.

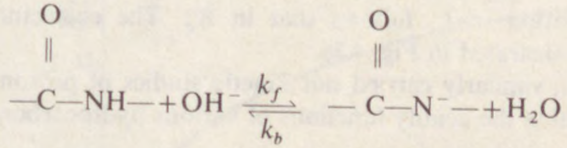
The evaluation of experiments designed to solve exclusively reaction kinetic questions frequently leads to the determination of the formation constant of an intermediate formed in a pre-equilibrium. We shall not deal with this possibility further; we shall discuss only those numerous kinetic methods in which the primary aim is the determination of complex formation constants.

4.5.1 Stoichiometric (uncatalysed) reactions

The formation constant of a species formed in some equilibrium reaction is the quotient of the rate constants of the decomposition and formation reactions. The values of the stability constants may therefore be determined through study of the formation and decomposition kinetics. This principle has been applied by many authors, for the determination of the formation constants of, among others, $CrSCN^{2+}$ [171], $Fe(phenanthroline)_3^{2+}$ [172, 173] and $Fe(bipyridyl)_3^{2+}$ [174]. Determination of the formation constants of ion pairs requires the use of relaxation methods, because of the high rates of formation and decomposition [175–179].

The decrease caused in the rate of a reaction by a metal ion or ligand can likewise be utilized for the calculation of equilibrium constants. For example, the rate of the redox reaction between $S_2O_3^{2-}$ and Fe^{3+} ions is decreased by Cd^{2+}, as a consequence of formation of the complex CdS_2O_3, and study of this redox reaction led to determination of the formation constant of CdS_2O_3 [180]. The reaction between BrCN and I^- is inhibited by Cl^- and Br^-; this permitted determination of the formation constants of the various interhalogen complexes [181]. The rate of the reaction between Fe^{3+} and I^- is influenced by the concentration of SO_4^{2-} and NO_3^-, due to the formation of the kinetically less active complexes $FeNO_3^{2+}$ and $FeSO_4^+$ [182]. Kodama made use of a similar principle to determine the equilibrium constants of a number of mixed ligand complexes of nickel(II) [183].

As concerns equilibrium measurements based on the study of decomposition and formation reactions, very important work was carried out by Scheinblatt [184], who applied an NMR method to determine the dissociation constant of the proton coupled with the nitrogen of the peptide bond, which does not undergo dissociation in the pH range that can be studied experimentally. He calculated the rate constant k_f of the base-catalysed proton-exchange of the CONH group



$$-\overset{\overset{\displaystyle O}{\|}}{C}-NH- + OH^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} -\overset{\overset{\displaystyle O}{\|}}{C}-N^- - + H_2O$$

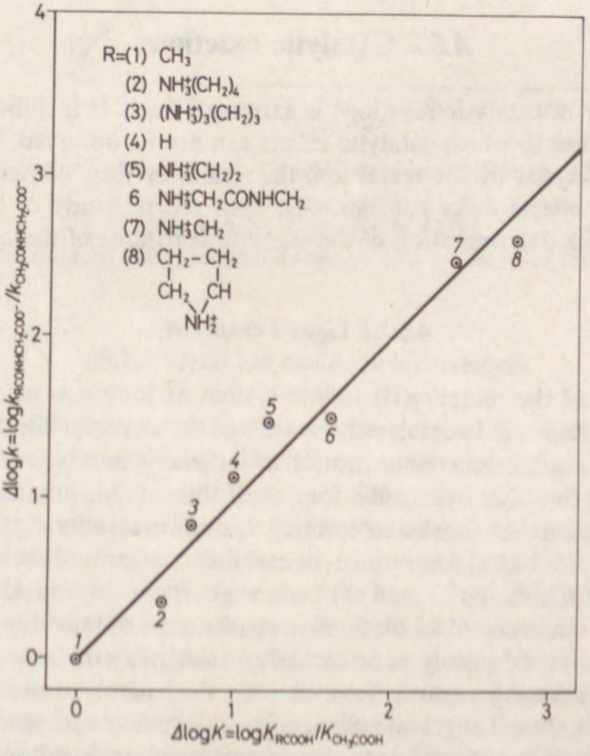


Fig. 4.36. Acidity (referred to acetylglycine) of hydrogen of peptide bond as a function of the acidity (referred to acetic acid) of carboxylic acids containing the same groups R [184]

(Reproduced with permission from *J. Am. Chem. Soc.*, **92**, 2505 (1970)) through analysis of the line shape given by the neighbouring CH_2 group. The dissociation constant of the peptide group is

$$K_d = \frac{k_f \cdot K_W}{k_b \cdot [H_2O]}$$

where k_f is the experimentally measurable rate constant. Although the value of k_b cannot be determined in an independent experiment, on the basis of the investigations on reactions of similar type it can justifiably be assumed that the back-reaction takes place with a diffusion-controlled rate, so that the value of k_b is the same for all peptides examined. Within a given series of peptides, therefore, the variation in k_f follows that in K_d. The correctness of the assumption is demonstrated in Fig. 4.36.

Streitwieser *et al.* similarly carried out kinetic studies of proton-exchange reactions to determine the acidity functions of various hydrocarbons [185].

4.5.2 Catalytic reactions

The number of catalytic reactions is extremely high. It is difficult to find a chemical reaction in which catalytic effects can not be observed. If a chemical reaction is catalysed by the metal ion, the ligand or their complex(es), and if their catalytic effects differ substantially, then kinetic study of the catalysed reaction permits determination of the stability constants of the complexes.

4.5.2.1 Ligand catalysis

In a study of the mercury(II)–iodide system as long ago as 1903, Sherrill [186] utilized the iodide-catalysed reaction of the decomposition of H_2O_2 to determine the equilibrium concentration of the iodide ion. Numerous reactions are catalysed by the hydroxide ion, and the equilibrium hydroxide ion concentration can therefore be determined through measurement of the reaction rate. Bell *et al.* [187, 188] determined the stability constants of the monohydroxo complexes of Ca^{2+}, Ba^{2+} and Tl^+ through study of the OH^--catalysed hydrolysis of diacetone-alcohol. Similar results were obtained from a study of the OH^--catalysed hydrolysis of carbethoxymethyltriethylammonium iodide [188]. It is interesting to note, however, that the hydrolysis of ethyl acetate is catalysed with almost the same efficiencies by the free hydroxide ion and by the hydroxo complexes, and accordingly this reaction is not suitable for the determination of the stability constants of the hydroxo complexes.

In OH^--catalysed hydrolysis, a metal ion may act not only as a retarding agent, but also as a promotor. This strongly suggests an interaction between the hydrolysing reactant and the metal ion, assuming that the rate of hydrolysis of the complex formed is higher than that of the free reactant. An example taken from the work of Hay and Clark [189] is presented in Fig. 4.37, which depicts the rate constant for the hydrolysis of 8-acetoquinoline-2-carboxylic acid as a function of the concentration of Zn^{2+}.

The decomposition of nitramide is catalysed by many anions (acetate, mandelate, salicylate, malate, fumarate). In the presence of metal ions (Ca^{2+}, Ba^{2+}, Zn^{2+}), the catalytic activity decreases [190]; this led to determination of the formation constants of the corresponding complexes.

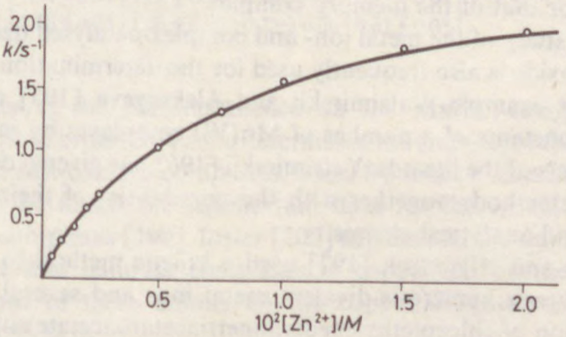


Fig. 4.37. Effect of zinc(II) concentration on OH^--catalysed hydrolysis of 8-acetoquinoline-2-carboxylic acid
pH = 6.18; 25 °C; $I = 0.1$ *M* [189]
(Reproduced with permission from *J. Chem. Soc.*, 1993 (1977))

4.5.2.2 Metal ion and complex catalysis

The transition metal ions are well known to exert catalytic effects in organic and inorganic redox reactions. The effects of various salts on the rates of catalysed reactions have similarly been studied in detail. The explanation of the primary salt effect is that the dissolved electrolytes change the activity coefficients of the reactants. The secondary or specific salt effect, however, is indicative of complex formation between the ions in question and the catalyst. Complex formation may either decrease or increase the catalytic activity, while in the case of stepwise complex formation it may even occur that the reaction rate displays several extrema as a function of the ligand concentration.

Particularly detailed investigations have been made of the effects of the ligands on isotope- and electron-exchange reactions. Hudis and Wahl [191], for instance, determined the constants of the complexes formed in the Fe^{3+}–F^- system from the dependence of the rate of the Fe^{3+}–Fe^{2+} electron exchange on the concentration of F^-. In a study of the Ce^{3+}–Ce^{4+} electron exchange in solutions of various acidities, Duke and Parcher [192] determined the formation constants of the species $Ce(OH)_2^{2+}$, $Ce(OH)_3^+$ and $CeOCe(OH)^{5+}$. Brubaker and Michel [193] calculated the formation constants of the complexes TlOH, $TlSO_4^+$, $TlSO_4^-$ and $Tl(OH)_2^+$ from the dependence of the Tl^{3+}–Tl^+ electron exchange on the pH and on the sulphate concentration. Cohen *et al.* [194] established the formation constants of the complexes NpO_2Cl^+ and NpO_2Cl_2 by examining the dependence of the Np(IV)–Np(V) exchange reaction on the chloride concentration. This reaction has an interesting feature: the catalytic activity of the monochloro complex is higher than that of the free neptunyl ion or that of the dichloro complex.

The kinetic study of the metal ion- and complex-catalysed decomposition of hydrogen peroxide is also frequently used for the determination of equilibrium constants. For example, Yatsimirskii and Alekseyeva [195] determined the equilibrium constants of a number of Mo(VI) complexes by investigating the inhibitory effects of the ligands. Yatsimirskii [196] has given a detailed account of the kinetic methods, together with the possibilities of their application in equilibrium and analytical chemistry.

Hutchinson and Higginson [197] used a kinetic method to study ion-pair formation between numerous divalent metal ions and several simple anions. The dissociation of chloro(ethylenediaminetriacetatoacetate)cobalt(III).

$$[Co(edta)Cl]^{2-} \rightleftharpoons [Co(edta)]^- + Cl^-$$

which is catalysed by metal ions in general, and which can conveniently be followed spectrophotometrically, was used as indicator reaction. The reaction is catalysed about 300 times more effectively by ions with a charge of +3, and about 10 times more effectively by ions with a charge of +2, than by ions with a charge of +1.

If the charge change accompanying ion-pair formation is taken into consideration, it is understandable that the catalytic activity varies very sensitively with increase of the anion concentration. The equilibrium constants found with this kinetic method are listed in Table 4.2.

Equilibrium constants may also be determined through study of the reactions of molecular hydrogen. By investigating the reaction between silver(I) and hydrogen in the presence of F^-, Beck and Gimesi [198] determined the formation constant of the complex AgF. Peters and Halpern [198a] observed that the reaction between Cr(VI) and molecular hydrogen is catalysed by the copper(II)–glycine complex in a pH-dependent manner. From the pH-dependence of the catalytic effect, they concluded that the effective catalyst is the doubly protonated bis-glycinato copper(II) complex. It is more probable, however, and this is not contradicted by the experimental data, that the active species is the monoglycinato complex, for the concentration of this exhibits a maximum at the pH in question.

Table 4.2 Formation constants log K_1 obtained for various ion-pairs with a kinetic method at 25 °C and an ionic strength $I = 0.1$ *M* [197] (Ac^- = acetate ion)

	Ac^-	Br^-	Cl^-	ClO_3^-	NO_3^-	NCS^-	[Co(EDTA)Cl]
Mn^{2+}	0.69 ± 0.05	0.13 ± 0.06	1.67 ± 0.08	1.73 ± 0.13	1.85 ± 0.06	0.65 ± 0.05	0.83 ± 0.09
Co^{2+}	0.81 ± 0.05	1.80 ± 0.08	0.07 ± 0.06	0.21 ± 0.08	1.85 ± 0.08	0.95 ± 0.04	0.94 ± 0.06
Ni^{2+}	0.83 ± 0.05	1.95 ± 0.05	0.07 ± 0.08	1.65 ± 0.08	0.08 ± 0.08	1.13 ± 0.05	0.97 ± 0.06
Cu^{2+}	1.72 ± 0.05	1.76 ± 0.25	0.15 ± 0.09	1.66 ± 0.08	1.87 ± 0.07	1.76 ± 0.07	1.31 ± 0.02
Zn^{2+}	0.63 ± 0.04	1.68 ± 0.05	1.94 ± 0.04	1.88 ± 0.05	1.88 ± 0.05	0.41 ± 0.05	0.60 ± 0.02
Cd^{2+}	1.26 ± 0.04	1.58 ± 0.04	1.34 ± 0.04	1.86 ± 0.09	0.07 ± 0.07	1.34 ± 0.04	1.08 ± 0.02
Pb^{2+}	2.21 ± 0.04	1.16 ± 0.05	1.08 ± 0.05	0.23 ± 0.06	0.62 ± 0.05		1.65 ± 0.02

From a study of the pH-dependence on the Mn(III)-catalysed reaction between oxalate and bromine, Taube determined the stepwise stability constants of the first three Mn-oxalato complexes, while from the effects of Cl^- and F^- on the reaction he found the equilibrium data for the Mn(III)–chloro and Mn(III)–fluoro complexes [199]. Lister [200] determined the stability constants of the periodate and tellurate complexes of copper(III) on the basis of the inhibitory actions of these anions on the copper(III)-catalysed reaction of hypochlorite with them.

4.5.2.3 Central atom exchange reactions

If a metal ion forms a catalytically active complex with some A ligand, but its complex with the B ligand is catalytically inactive, then the equilibrium constant of the reaction

$$MeA + B \rightleftharpoons MeB + A$$

can be determined from the kinetic data. If the formation constant of the complex MeB is regarded as known, the formation constant of MeA can be calculated. It can readily be seen that this method is the kinetic equivalent of the competition procedure employed in photometry and other examination methods, when conclusions relating to the parameters of the equilibrium system under study can be drawn from the effect on an auxiliary equilibrium system with a known constant. This principle was applied, for instance, to determine the formation constants of the Fe(III)–triethylenetetramine complex [201] and some metal ion–enzyme complexes [202, 203].

4.6 Extraction methods

We have already referred to the fact that the various experimental methods may be applied for the investigation of competition equilibria, i.e. conclusions on the parameters of the equilibrium system under study can be drawn by following the shift in the equilibrium state of an auxiliary equilibrium system with a known formation constant (constant series). Liquid–liquid extraction is essentially a competition method too, for the 'auxiliary equilibrium' relating to the distribution of the solute between immiscible liquids is connected with the equilibrium system under study, and the equilibrium constant(s) in question is (are) calculated from the concentration-dependence of the partition equilibrium.

In principle, any analytical chemistry method is suitable for following the partition equilibrium. In practice, however, the most generally used procedures are spectrophotometry, radioactive labelling and (more recently) atomic absorption analysis. Radioactive labelling has the very great advantage that it can be applied even when the metal ion concentration is very low; thus, it is possible to study mononuclear complexes even if the system displays a very high tendency to form polynuclear complexes. We shall not deal further with analytical methods employed to follow partition equilibria; we shall merely survey the main types of extraction methods.

The techniques in extraction experiments are very simple. It is important that the solvents used should be saturated with each other prior to the extraction. With a view to the calculation of the equilibrium constants, the distribution quotient must be determined as a function of the concentration in aqueous solution of some component influencing the position of the equilibrium. If simple laboratory techniques are employed, the recording of every point of this function necessitates a separate experiment. Nowadays, however, the apparatus developed by Reinhardt and Rydberg is commercially available under the name AKUFVE; this apparatus can be used to measure the distribution quotient even when the concentration conditions are varying [204].

For the quantitative characterization of extraction experiments, we define the distribution constant (*D*) and the distribution quotient (*q*). The distribution constant is the ratio of the concentrations in the two phases of a species participating in the partition equilibrium

$$D_A = \frac{[A]_{org}}{[A]_{aq}}. \tag{4.67}$$

The distribution quotient is defined as the quotient of the equilibrium concentration of the species in question in the organic phase and its total concentration in the aqueous phase

$$q_A = \frac{[A]_{org}}{T_{A\,aq}}. \tag{4.68}$$

The two quantities have the same value if $[A] = T_A$, i.e. the species taking part in the partition equilibrium is to be found in the aqueous phase exclusively in a form that can be extracted, and it does not participate in other equilibrium processes. The basis of the extraction methods is that, as a consequence of the equilibrium processes in the aqueous phase, $[A] \neq T_A$, i.e. $q \neq D$, and the measure of the difference is characteristic of the position of the equilibrium within the aqueous phase. In general, only neutral molecules take part in the partition equilibrium between the aqueous and organic phases, while the charged complexes remain in the aqueous phase.

An extremely high number of equilibrium constants have been determined with the extraction method, and numerous reviews are available [205–214]. Accordingly, in this brief survey we shall discuss merely the basic correlations, the classification of extraction methods, and certain difficulties that arise during the practical application of extraction.

4.6.1 Partition of the ligand

In principle, two different cases of partition of the ligand between two phases are possible. The neutral ligands may be extracted directly. The distribution quotient can then be given by the following formula

$$q_L = \frac{[L]_{org}}{[L]_{aq} + \sum_{i=1}^{N} i[MeL_i]_{aq}}. \tag{4.69}$$

A considerable proportion of negatively charged ligands are conjugated bases of weak acids. The protonated, neutral form can then be extracted into the organic phase, and we have

$$q_L = \frac{[H_nL]_{org}}{\sum_0^Z [H_jL]_{aq} + \sum_1^N i[MeL_i]_{aq}}. \tag{4.70}$$

This basic principle can be employed, for example, to determine the dissociation constants of organic acids [215, 216] or the equilibrium constants of their dimerization in organic solvents [217]. Dawson and McCrae [218] made use of this method as long ago as 1900, to study the copper(II)–ammonia system. Similar principles have been applied to study certain metal complexes of hydrazine [219], pyridine [220], aniline [221] and unsaturated hydrocarbons [222]. With the emergence of the competition extraction methods, there has recently been a relative decline in the number of extraction studies based on the partition of the ligands.

4.6.2 Partition of the metal complexes

In the course of stepwise complex formation between metal complexes and anionic ligands, neutral metal complexes soluble in apolar organic solvents may be formed. In this case, the distribution quotient for the metal ion is

$$q_{\mathrm{Me}}=\frac{\sum\limits_{0}^{N}[\mathrm{MeL}_i]_{\mathrm{org}}}{\sum\limits_{0}^{N}[\mathrm{MeL}_i]_{\mathrm{aq}}}. \tag{4.71}$$

In general, only a single complex is soluble in the organic phase, and Eq. (4.71) can therefore be written in the following form

$$q_{\mathrm{Me}}=\frac{[\mathrm{MeL}_\nu]_{\mathrm{org}}}{\sum\limits_{0}^{N}[\mathrm{MeL}_i]_{\mathrm{aq}}}. \tag{4.72}$$

After introduction of the distribution constant $D_{\mathrm{MeL}_\nu}=[\mathrm{MeL}_\nu]_{\mathrm{org}}/[\mathrm{MeL}_\nu]_{\mathrm{aq}}$ and simplifications arising from the mass balances, we have

$$q_{\mathrm{Me}}=\frac{D_{\mathrm{MeL}_\nu}}{\sum\limits_{0}^{N}\beta_i[\mathrm{L}]^{i-\nu}}. \tag{4.73}$$

The neutral complex dissolving in the organic phase may be the last member of the series ($\nu=N$), and the distribution quotient then varies in accordance

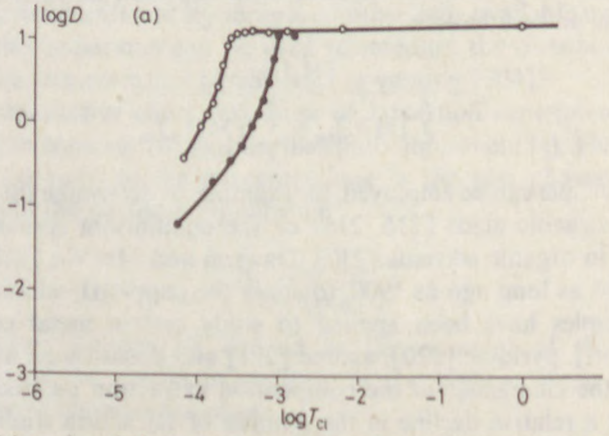


Fig. 4.38. Partition of methylmercury between *o*-xylene and an aqueous phase with ionic strength 1 *M* (Na, H) (ClO_4, Cl) at $-\log[\mathrm{H}]=1.699$. (a) Initial T_{Cl} of aqueous phase; (b) calculated equilibrium $[\mathrm{Cl}^-]$ of aqueous phase [223]
(Reproduced with permission from *Acta Chem. Scand.*, **27**, 1277 (1973))

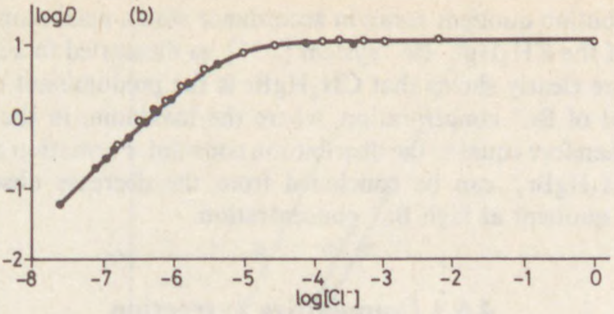


Fig. 4.38 (b)

with a saturation curve. In general, however, MeL_v is an intermediate member of the series, and the distribution quotient too then exhibits a maximum as a function of the free ligand concentration. As an example of the first case, Fig. 4.38, based on the studies by Budevsky *et al.* [223], depicts the dependence of the distribution quotient on the total and free ligand concentrations for the CH_3Hg^+–Cl^- system.

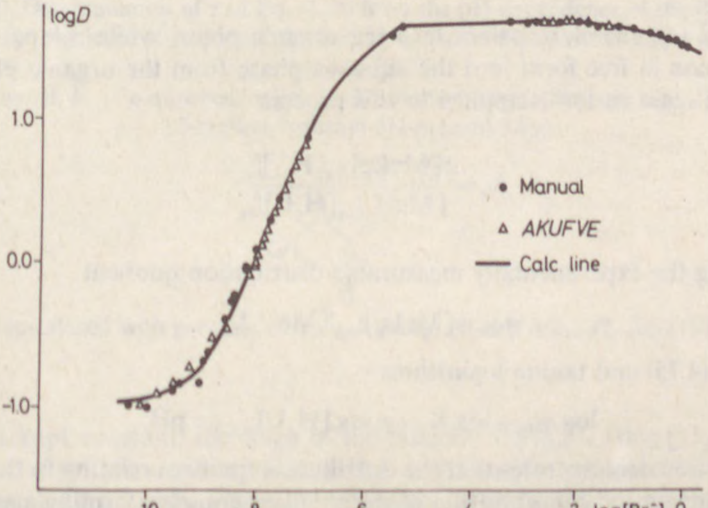


Fig. 4.39. Partition of methylmercury between *o*-xylene and an aqueous phase with ionic strength 1 *M* (Na, H) (ClO_4, Cl) as a function of the equilibrium bromide concentration of the aqueous phase, measured with different methods, at various total methylmercury concentrations [224]

(Reproduced with permission from *Acta Chem. Scand.*, **A32**, 7 (1978))

The distribution quotient varies in accordance with a maximum curve in the extraction of the CH_3Hg^+–Br^- system [224], as illustrated in Fig. 4.39.

This Figure clearly shows that CH_3HgBr is the predominant complex in a wide interval of Br^- concentration, where the maximum in the distribution quotient is therefore equal to the distribution constant. Formation of the anionic complex $CH_3HgBr_2^-$ can be concluded from the decrease observed in the distribution quotient at high Br^- concentration.

4.6.3 Competitive extraction

A large majority of the extraction equilibrium studies carried out in recent decades can be classified in this category. It was mentioned at the beginning of this chapter that extraction may be regarded as a competition method, for it is based on the competition of the partition and complex formation equilibria. The special nomenclature of the competitive extraction method is justified by the fact that in this method a ligand that is the conjugate base of a weak acid, and that is well soluble in the organic solvent, is introduced into the equilibrium system. The ligand forms an extractable complex with the metal ion

$$\mathrm{Me}^{z+}_{\mathrm{aq}} + p\mathrm{H}_q\mathrm{L}_{\mathrm{org}} \rightleftharpoons \mathrm{MeL}_{p\,\mathrm{org}} + z\mathrm{H}^+_{\mathrm{aq}}. \tag{4.74}$$

The metal ion therefore passes into the organic phase, while $z(=pq)$ bound protons pass in free form into the aqueous phase from the organic phase. If the law of mass action is applied to this process

$$K_e = \frac{[\mathrm{MeL}_p]_{\mathrm{org}}[\mathrm{H}^+]^z_{\mathrm{aq}}}{[\mathrm{Me}^{z+}]_{\mathrm{aq}}[\mathrm{H}_q\mathrm{L}]^p_{\mathrm{org}}}. \tag{4.75}$$

Expressing the experimentally measurable distribution quotient

$$q_{\mathrm{Me}} = [\mathrm{MeL}_p]_{\mathrm{org}}/[\mathrm{Me}^{z+}]_{\mathrm{aq}}$$

from Eq. (4.75) and taking logarithms

$$\log q_{\mathrm{Me}} = \log K_e + p\log[\mathrm{H}_q\mathrm{L}]_{\mathrm{org}} + z\,\mathrm{pH}. \tag{4.76}$$

This equation demonstrates that the distribution quotient relating to the metal ion depends on the concentration of the auxiliary complex forming agent H_qL in the organic phase, and on the pH of the aqueous phase. The concentration of H_qL in the organic phase in the course of the extraction is selected to be so high that the concentration decrease due to formation of the metal complex will be negligible: the equilibrium concentration of H_qL will effectively be the same as the initial value. Under these conditions, if the pH of the aqueous

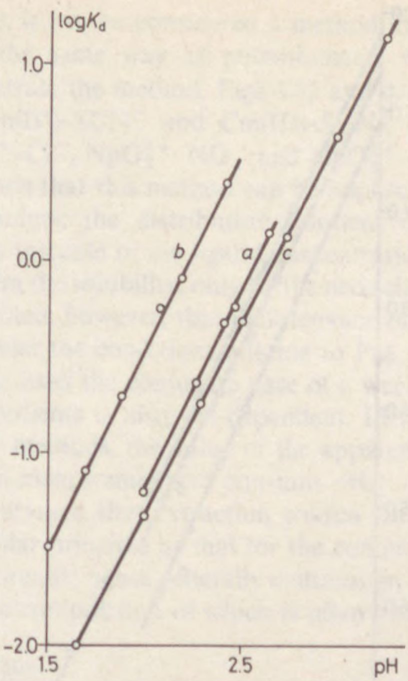
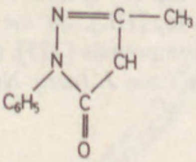


Fig. 4.40. Determination of z in Eq. (4.75) from the pH-dependence of the distribution quotient on the basis of uranium(VI) extraction studies with various dioxo compounds ($z=2$) [225]

a — Benzoyl; *b* — *p*-nitrobenzoyl; *c* — 3,5-dinitrobenzoyl derivative of 2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one



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phase is kept constant, the slope of the function $\log q_{Me} = f(\log [H_qL])$ gives the value of p; if the concentration of H_qL is constant, the slope of the function $\log q_{Me} = f(\text{pH})$ gives the value of z. Figures 4.40 and 4.41 illustrate the results of experiments aimed at the determination of p and z [225].

In competitive extraction equilibrium studies, this process can in effect be regarded as an 'auxiliary equilibrium', coupled with complex formation in the aqueous phase between the metal ion and the ligand under investigation. In the presence of a ligand A that forms a non-extractable complex in the aqueous

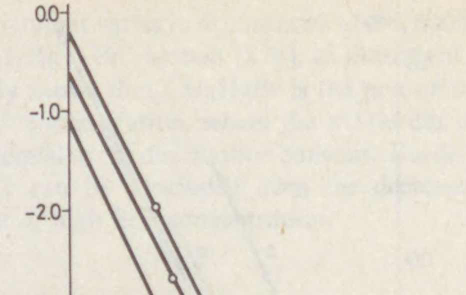

Fig. 4.41. Determination of p in Eq. (4.75) from the dependence of the logarithm of the distribution quotient on $-\log[\mathrm{HL}]$, on the basis of uranium(VI) extraction studies with various dioxo compounds [225]. (For symbols see Fig. 4.40) (Reproduced with permission from *J. Inorg. Nucl. Chem.*, **39**, 2057 (1977))

phase, the value of q_{Me} is modified

$$q'_{\mathrm{Me}} = \frac{[\mathrm{MeL}_p]_{\mathrm{org}}}{[\mathrm{Me}^{z+}]_{\mathrm{aq}} \sum_{0}^{N} \beta_i [\mathrm{A}]^i} \tag{4.77}$$

i.e. the quotient $q_{\mathrm{Me}}/q'_{\mathrm{Me}}$ gives the value of $\sum_{0}^{N} \beta_i [\mathrm{A}]^i$. If the value of the function $q_{\mathrm{Me}}/q'_{\mathrm{Me}} = f([\mathrm{A}])$ is measured at a sufficient number of points, the values of the stability constants β_i can be calculated.

On the above basis, it is clear that in this method the extraction serves in fact for measurement of the equilibrium metal ion concentration [226–240]; in principle, therefore, it can be considered a method for equilibrium chemistry investigations in the same way as potentiometry with metal ion-selective electrodes. To illustrate the method, Figs 4.42 and 4.43 present results on the Pu(III)–SCN$^-$, Am(III)–SCN$^-$ and Cm(III)–SCN$^-$ systems [226], and the Np^{4+}–NO_3^-, Np^{4+}–Cl^-, NpO_2^{2+}–NO_3^- and NpO_2^{2+}–Cl^- systems [230].

Figure 4.43 reveals that this method can be applied to determine even very low stability constants; the distribution quotient can be measured fairly accurately, and the increase of the ligand concentration in the aqueous phase is limited, apart from the solubility, only by the necessity to ensure the standard state. It must be noted, however, that maintenance of the standard state may be questionable under the conditions relating to Fig. 4.43.

If the ligand A is itself the conjugate base of a weak acid, then the ratio of the distribution quotients is also pH-dependent. In this case, similarly as in other experimental methods, the value of the apparent stability constant can be determined from measurements at constant pH.

It should be mentioned that extraction studies with liquid ion-exchangers are based on a similar principle as that for the competitive methods, with the difference that the organic phase generally contains an extractant with a higher molecular mass, the composition of which is often not known exactly.

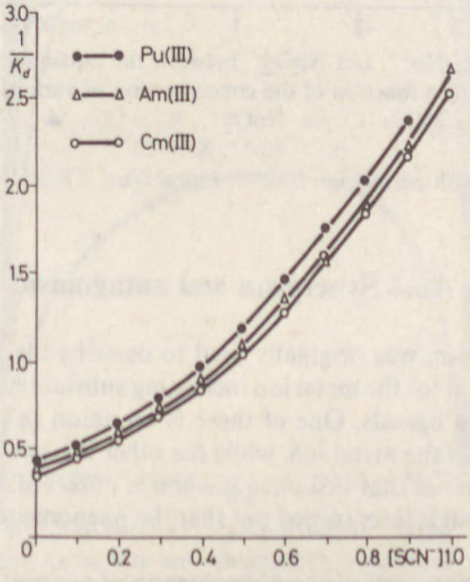

Fig. 4.42. Partition of Pu(III), Am(III), and Cm(III) between aqueous thiocyanate and n-heptane containing 0.01 *M* NH_4DNNS, as a function of the thiocyanate concentration at (30 ± 0.1) °C; I = 1 *M* (NH_4ClO_4–NH_4SCN); HDNNS = dinonylnaphthalenesulphonic acid [226]

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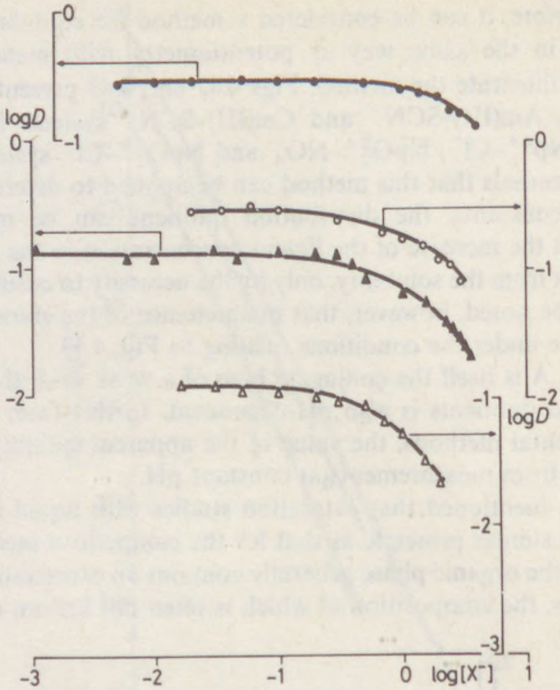

Fig. 4.43. Partition of Np^{4+} and NpO_2^{2+} between the aqueous phase and thionyltrifluoroacetone as a function of the concentration of various anions [230].
● — NpO_2^{2+}, $X^- = NO_3^-$; ○ — NpO_2^{2+}, $X^- = Cl^-$; ▲ — Np^{4+}, $X^- = NO_3^-$; △ — Np^{4+}, $X^- = Cl^-$
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4.6.4 Synergism and antagonism

The term synergism was originally used to describe the phenomenon of the distribution quotient for the metal ion increasing substantially when the organic phase contains two ligands. One of these is an anion in its ligand form and therefore neutralizes the metal ion, while the other is a neutral molecule [241]. It was initially believed that this phenomenon is observed for only a few metal ions and ligands, but it later turned out that the phenomenon is a quite general one [241].

A simplified explanation of the phenomenon of synergism is that the metal ion is not coordinately saturated by the number of extractant species (acting as anionic ligand) required to neutralize the charge; thus, the metal ion is able to bind further ligands. The affinity of the residual coordination sites for further, neutral ligand species becomes particularly marked in an organic solvent, for in aqueous medium this role may be filled by water molecules. The solubility of the coordinately saturated neutral mixed complex containing more apolar ligand than the parent complexes can clearly be substantially higher in the organic phase than that of the coordinately unsaturated, electrically neutral parent complex.

A characteristic example of synergism is shown in Fig. 4.44, for systems of Co(II)–thionyltrifluoroacetone with pyridine or a pyridine derivative. It may

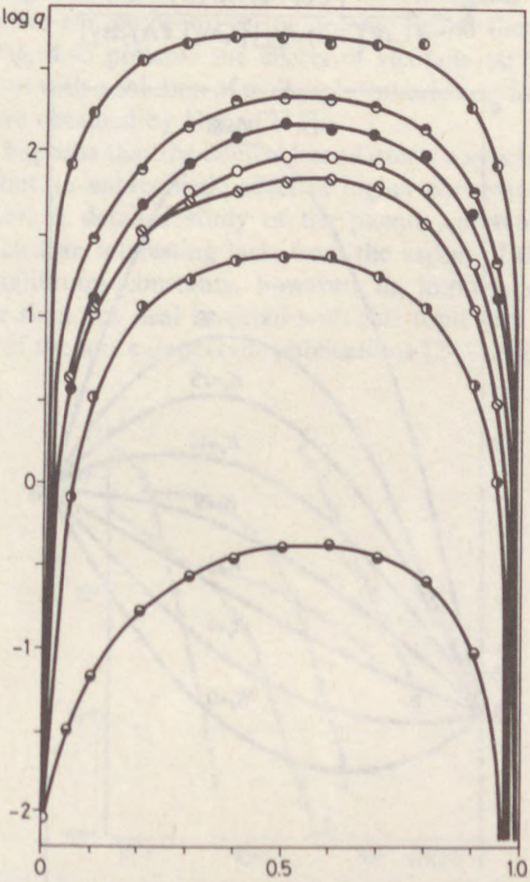

Fig. 4.44. Partition of ^{60}Co between aqueous acetate buffer of pH 4.93 and a mixture of heterocyclic bases (Q) and thionyltrifluoroacetone (TTA) dissolved in cyclohexane: $T_{TTA} + T_Q = 0.02\ M$ [205]
◐ — Isoquinoline; ◓ — 3-methylpyridine; ● — 4-methylpyridine; ○ — pyridine; ⊖ — 3-chloropyridine; ◑ — quinoline; ◒ — 2-methylpyridine
(Reproduced with permission from Dyrssen, D., Liljenzin, J. O. and Rydberg, J. (Eds), *Solvent Extraction Chemistry*, North-Holland, Amsterdam, 1967)

occur that when the residual coordination sites are occupied by two different neutral ligands, the resulting extractability is better than when these ligands are identical. An example of this was found by Irving [242]. For an interpretation of the phenomenon (in the case of the system presented in Fig. 4.44), it is necessary to take into account the following equilibrium process and equilibrium constant

$$Co(TTA)_2A_2 + Co(TTA)_2B_2 \rightleftharpoons 2Co(TTA)_2AB$$

$$K = \frac{[Co(TTA)_2AB]^2}{[Co(TTA)_2A_2]\,[Co(TTA)_2B_2]}\,. \tag{4.78}$$

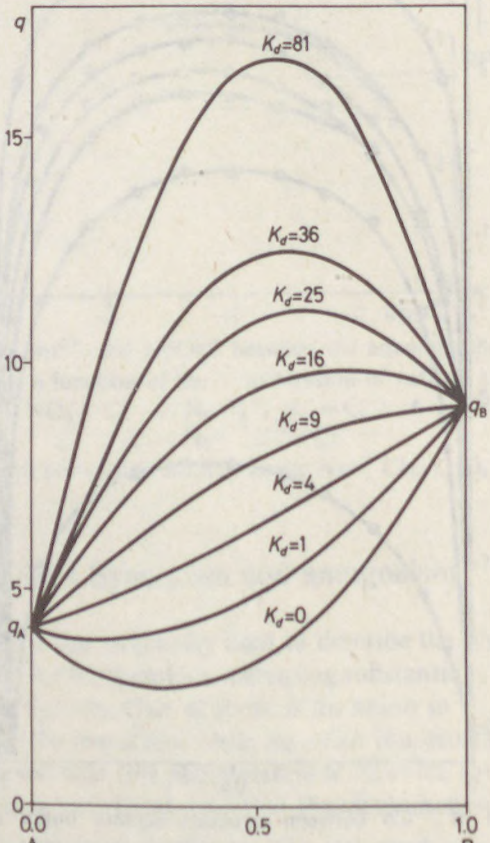

Fig. 4.45. Calculated partition curve of MeL_2 for a synergic combination of two bases (A and B). q_A and q_B are the distribution quotients of MeL_2A_2 and MeL_2B_2; K_d is the disproportionation constant as in Eq. (4.77) [205]

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Figure 4.45 depicts the distribution quotients calculated at various K values as a function of the ratio of the two neutral ligands. The diagram clearly reveals that this type of synergism too is connected with favoured mixed complex formation.

The opposite of synergism, i.e. antagonism, is likewise frequently observed during extraction studies. Antagonism shows up as a decrease in extractability in the presence of the neutral ligand; it indicates that association (generally hydrogen-bonding) takes place between the neutral ligand and the charged ligand, the effective concentration of the anionic ligand thereby diminishing. As examples, Fig. 4.46 presents the effects of alcohols on the extraction of various metal ions with a solution of dialkylphosphoric acid in petroleum ether; these results were obtained by Upor [243].

It sometimes happens that the neutral ligand exerts a synergetic effect at low concentration, but an antagonistic effect at higher concentration, as may be seen in Fig. 4.47. A detailed study of the phenomenon of synergism and antagonism is itself an interesting task; from the aspect of the determination of complex equilibrium constants, however, its importance is secondary. Accordingly, we shall not deal in detail with this topic, but merely refer the reader to some of the more important publications [244–255].

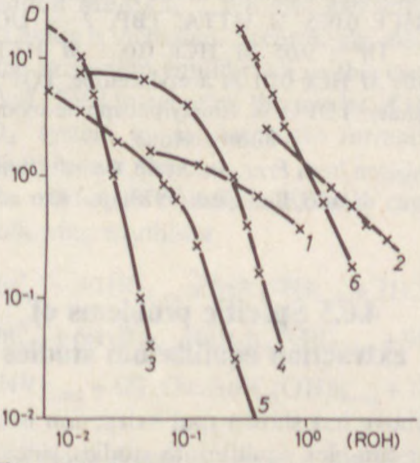

Fig. 4.46. Antagonistic effect of alcohols on extraction with dialkylphosphoric acid [243]. *1* — Ti^{4+}; 6.0 *M* HCl; 0.05 *m* HDBP; butanol; *2* — UO_2^{2+}; 0.1 *M* HCl; 0.005 *m* HDBP; butanol; *3* — Th^{4+}; 4.0 *M* HCl; 0.01 *M* HDBP; butanol; *4* — Eu^{3+}; 0.25 *M* HCl; 0.05 *M* HDBP; butanol; *5* — Eu^{3+}; 0.25 *M* HCl; 0.05 *M* HDBP; 2-ethylhexanol; *6* — Zr^{4+}; 6.0 *M* HCl; 0.005 *M* HDBP; butanol; HDBP = dibutylphosphoric acid

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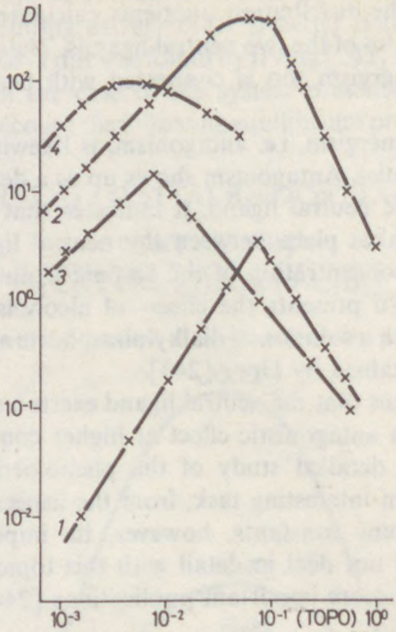

Fig. 4.47. Extraction with β-diketones in the presence of TBP (TOPO) [243].
1 — Tb^{3+}; 0.05 *M* HCl; 0.075 *M* HTTA; TBP, *2* — UO_2^{2+}; 0.05 *M* HCl; 0.2 *M* HTTA; TBP, *3* — Th^{4+}; 0.05 *M* HCl; 0.005 *M* HTTA; TBP, *4* — Lu^{3+}; 0.01 *M* HCl; 0.01 *M* acetylacetone; TOPO.
TBP = tributyl phosphate; TOPO = trioctylphosphine oxide; HTTA = thionyltrifluoroacetone
(Reproduced with permission from *Proc. 3rd Symp. Coord. Chem., Debrecen*, Akadémiai Kiadó, Budapest (1970), p. 143)

4.6.5 Specific problems of extraction equilibrium studies

The brief survey above has shown that extraction is a method that can be applied in general for complex equilibrium studies, since systems containing a metal ion can be investigated by means of competitive extraction with practically no exceptions. The method is therefore applied very widely. Nevertheless, in the course of its application, attention must be paid to a number of special problems that unavoidably accompany extraction.

The condition that the two liquids (one of which is usually water) are completely immiscible does not often hold in a strict sense. If the mutual solubility is not negligible, then the change in the medium, and the effect of this on the position of the equilibrium must be taken into account in the extraction investigations.

It may occur that the extraction is accompanied by transfer of a number of electrically neutral complexes with various compositions into the organic phase; in this case, it is not sufficient to perform calculations adequate for a single extractable complex. Attention must also be paid to side-reactions taking place in the organic phase, and to the effects of these on the position of the equilibrium. Examples will be given below, illustrating the special phenomena that may be observed during the practical application of extraction, these sometimes hampering evaluation of the results.

Kojima *et al.* [256] studied the extraction of an aqueous solution of copper(II) with carboxylic acids dissolved in chloroform, and found that the complex soluble in the organic phase is dimerized in a form containing protonated carboxylic acid. At the same time, the free carboxylic acid is also to be found in dimeric form in the organic phase. Thus, the general relationship [Eq. (4.74)] no longer holds in this system. The extraction equilibrium can be written as follows

$$2\mathrm{Cu}^{2+}_{\mathrm{aq}} + 3(\mathrm{HR})_{2\,\mathrm{org}} \rightleftharpoons (\mathrm{CuR}_2(\mathrm{HR}))_{2\,\mathrm{org}} + 4\mathrm{H}^+_{\mathrm{aq}}. \qquad (4.79)$$

Through the extraction of Zr(IV) and Hf(IV) with various hydroxamic acids in benzene and chloroform, Fouché *et al.* [257] established that the mixed complexes of composition $\mathrm{MeA}_x\mathrm{Cl}_{4-x}$ are also extracted if the HCl concentration of the aqueous phase is increased. Accordingly, mechanism (4.74) cannot be used to describe the extraction equilibrium in this case either.

Zangen and Rafaeloff [258] interpreted the results of their investigations on the Gd^{3+}–Cl^-–HSO_4^- system by assuming the formation of four different ion-pairs soluble in the organic phase.

In their study of the extraction of indium(III) with caproic acid, Tanaka *et al.* [259] found the following equilibria

$$\mathrm{In}^{3+}_{\mathrm{aq}} + 3(\mathrm{HR})_{2\,\mathrm{org}} \rightleftharpoons \mathrm{InR}_3 3\mathrm{HR}_{\mathrm{org}} + 3\mathrm{H}^+_{\mathrm{aq}}$$

$$3\mathrm{In}^{3+}_{\mathrm{aq}} + 6(\mathrm{HR})_{2\,\mathrm{org}} \rightleftharpoons (\mathrm{InR}_3 3\mathrm{HR})_{3\,\mathrm{org}} + 9\mathrm{H}^+_{\mathrm{aq}}$$

$$6\mathrm{In}^{3+}_{\mathrm{aq}} + 6(\mathrm{HR})_{2\,\mathrm{org}} + 6\mathrm{H}_2\mathrm{O} \rightleftharpoons (\mathrm{InR}_2(\mathrm{OH}))_{6\,\mathrm{org}} + 18\mathrm{H}^+_{\mathrm{aq}}.$$

Aggett [260] reported that at least two complexes with different compositions are transferred to the organic phase during the extraction of iron(III) with acetylacetone dissolved in cyclohexane.

Numerous other examples [261–269] confirm that Eq. (4.74) is often not valid, and that more than one and/or more complicated partition equilibria must be taken into consideration. The key question concerning application of the extraction method to equilibrium chemistry is the exact knowledge of the stoichiometry and constants of the partition equilibria between the organic phase and the aqueous phase. This may be followed by 'coupling' the system to the complex formation processes occurring in the aqueous phase, with the aim of determination of the equilibrium constants. Frequently, however, the extraction equilibria themselves are also very complicated, and their stoichiometry and constants can be determined only through very circumspect work. In equilibrium chemistry practice, therefore, though extraction is in principle one of the most general methods, its significance is less than that of potentiometry or the spectrophotometric methods.

If extraction studies are carried out on a given equilibrium system with a number of different organic solvents, then (within the limits of experimental errors) the logarithms of the distribution quotients must vary in the same way as functions of the free ligand concentration, i.e. identical stability constants must be obtained. If this condition is satisfied, the determined values of the constants can be regarded as reliable; any difference is an indication of the

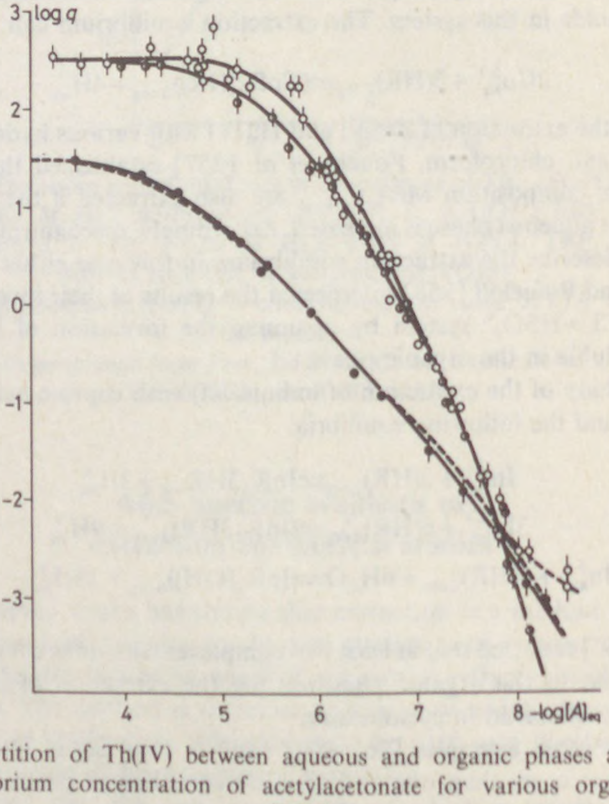

Fig. 4.48. Partition of Th(IV) between aqueous and organic phases as a function of the equilibrium concentration of acetylacetonate for various organic solvents [270]

● — Methyl isobutyl ketone; ◑ — benzene; ○ — chloroform

(Reproduced with permission from *Arkiv Kemi*, **8**, 113 (1955)) occurrence of a specific interaction between the complex undergoing extraction and the molecules of the organic solvent. Figure 4.48 shows results of extraction studies with various solvents on the thorium(IV)–acetylacetone system. The different curve found in extraction measurements with methyl isobutyl ketone could be interpreted quantitatively through the assumption that a mixed ligand complex thorium(IV)–acetylacetone–methyl isobutyl ketone is formed [270].

4.7 Solubility studies

In the stepwise complex formation reactions of metal ions and anionic ligands, the product is often an electrically neutral complex with a much lower solubility in water, or in some other solvent with a high dielectric constant, than the solubilities of cationic or anionic complexes. Through use of the expression $K_s=[\mathrm{Me}][\mathrm{L}]^{\nu}$, defining the solubility product of the sparingly soluble neutral complex MeL_{ν}, it can readily be shown that, apart from the constants K_s and β_i, the solubility depends only upon the free ligand concentration

$$S=\sum_{0}^{N} K_s\beta_i[\mathrm{L}]^{i-\nu}, \tag{4.80}$$

It is obvious that the upper limit of the range of interpretation of the functions $\log T_{\mathrm{Me}}=f(\log[\mathrm{L}])$ (discussed in Chapter 3) which supplement the concentration distribution is $T_{\mathrm{Me}}=S$; thus, the curves α_i, $\bar{n}=f(\log[\mathrm{L}])$ and $\log T_{\mathrm{Me}}=$ $=f(\log[\mathrm{L}])$ can conveniently be supplemented with the curves $\log S=f(\log[\mathrm{L}])$, indicating that the plot $\log T_{\mathrm{Me}}=f(\log[\mathrm{L}])$ has meaning only up to $T_{\mathrm{Me}}=S$ [271].

Figure 4.49 depicts the formation, distribution, total concentration and solubility curves for the Hg^{2+}–I^- system. The diagram reveals, for instance, that a precipitate of HgI_2 will separate out even from a 10^{-3} M solution of $\mathrm{K}_2[\mathrm{HgI}_4]$, but an excess of 10^{-3} M KI is sufficient to prevent precipitation. The points in the lower part of the diagram denote the T_{Hg} values that may be calculated from the K_s values alone, complex formation being ignored. The difference of the points from the actual solubility curve shows very illustratively what a serious error may result if the simplified calculation procedure usually recommended in textbooks on analytical chemistry is followed and complex formation is not taken into consideration. This has previously been pointed out by a number of authors [272–274].

Analogous curves for the Pb^{2+}–I^- system are given in Fig. 4.50. The diagram clearly shows that PbI_2 dissolves only in a very large I^- excess. The ratio interval $T_{\mathrm{I}^-}/T_{\mathrm{Pb}^{2+}}\approx 500$–$5000$ is especially interesting, for the curve $\log T_{\mathrm{Me}}=$ $=f(\log[\mathrm{L}])$ intersects the solubility curve at two points in this interval. This means, for instance, that the colourless solution containing 0.005 M $T_{\mathrm{Pb}^{2+}}$ and

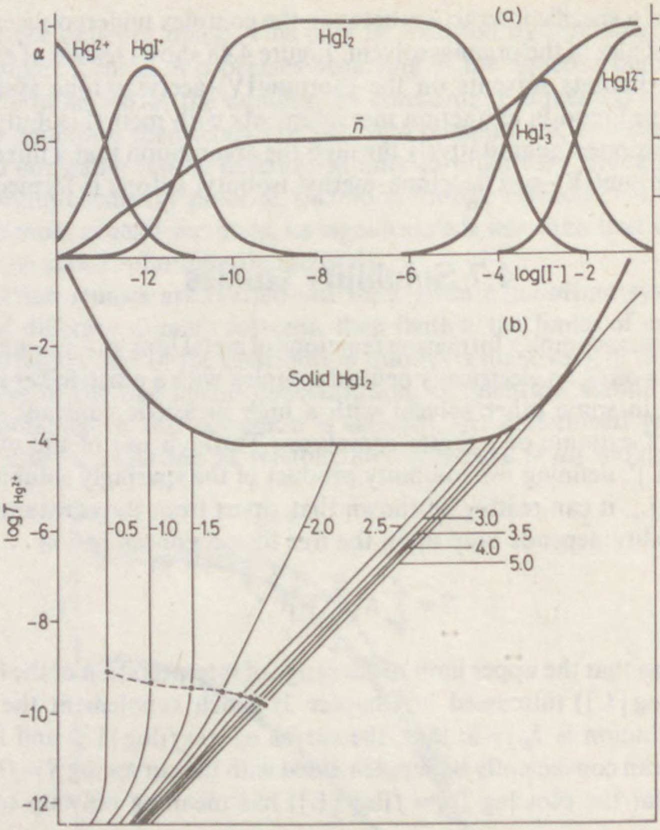

Fig. 4.49. Supplemented partition diagram of the Hg^{2+}–I^- system.
(a) Formation curve of the system, and distribution curves of the various complexes; (b) $\log T_{Hg}$ as a function of log $[I^-]$ at various concentration ratios T_I/T_{Hg} and the solubility curve. Points denoted by ● are the solubilities found by simplified calculation [271]
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3 *M* KI yields a yellow precipitate of PbI_2 on dilution. It should be emphasized that precipitation on dilution differs in principle from hydrolysis on dilution. The latter often occurs in aqueous solutions of certain metal ions, for in this case the dilution results in an increase in concentration of the reacting ionic species, the OH^- ion, whereas the concentration of I^- decreases when the Pb^{2+}–I^- system is diluted. Here, precipitate formation is a consequence of the 'dissociation'

$$PbI_4^{2-} \rightleftharpoons PbI_2 + 2I^-$$

which is shifted in the direction of the upper arrow by dilution.

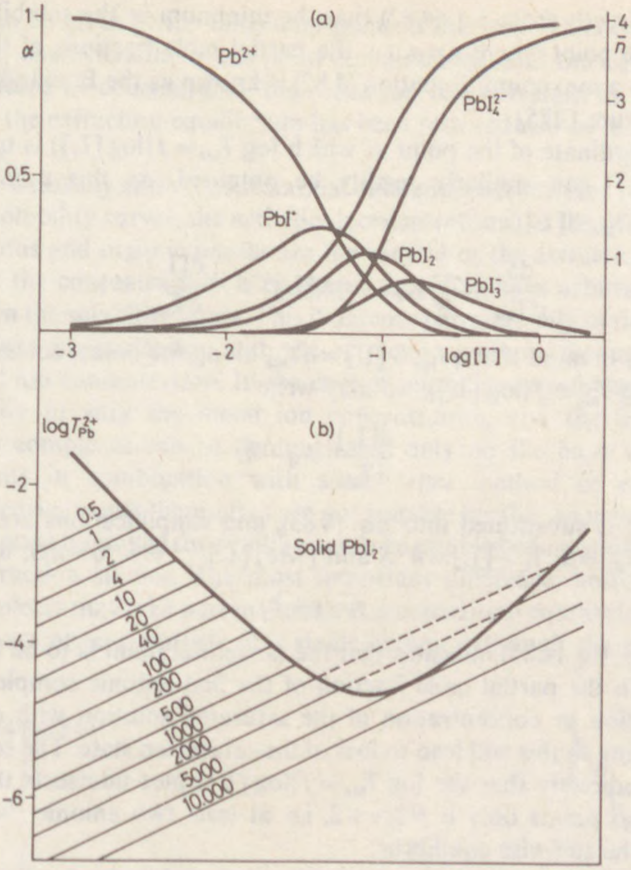

Fig. 4.50. Supplemented partition diagram of the Pb^{2+}–I^- system.
(a) Formation curve of the system, and distribution curves of the various complexes; (b) log T_{Pb} as a function of log $[I^-]$ at various concentration ratios T_I/T_{Pb}, and the solubility curve [271]
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The solubility curve has two characteristic points: the minimum point, and the point where the plot log $T_{Me} = f(\log [L])$ is tangential to the solubility curve. The coordinates of these points may be obtained by differentiation of the function log $S = f(\log [L])$. If Eq. (4.80) is differentiated with respect to [L]

$$\frac{dS}{d[L]} = \sum_{0}^{N} (i-\nu) K_s \beta_i [L]^{i-\nu-1} \qquad (4.81)$$

i.e.

$$\frac{d\log S}{d\log [L]} = \bar{n} - \nu. \qquad (4.82)$$

It follows directly from Eq. (4.82) that the minimum in the solubility is to be found at the point where $\bar{n}=\nu$, i.e. the partial mole fractions of the complex MeL_ν are at a maximum. Equation (4.82) is known as the Bodländer equation in the literature [275].

The $\bar{n}$ coordinate of the point at which $\log T_{Me}=f(\log [L])$ is tangential to $S=f(\log [L])$ can similarly readily be obtained. At this point, we have $dS/d[L]=dT_{Me}/d[L]$, i.e.

$$\frac{dS}{dT_{Me}}=\sum_{0}^{N} K_s(i-\nu)\beta_i[L]^{i-\nu-1}\frac{d[L]}{dT_{Me}}=1. \tag{4.83}$$

If it is borne in mind that $qT_{Me}-[L]=\bar{n}T_{Me}$ along the points corresponding to the plots $\log T_{Me}=f(\log [L])$, we may write

$$\frac{d[L]}{dT_{Me}}=q-\bar{n}. \tag{4.84}$$

If Eq. (4.84) is substituted into Eq. (4.83), and simplifications are made with respect to $T_{Me}=S$, $T_L-[L]=\bar{n}\cdot S$ and $[Me][L]^{\nu+1}=K_s(q-\bar{n})S$, we have

$$\bar{n}=\nu+1. \tag{4.85}$$

Accordingly, Eq. (4.85) indicates that the tangential point is to be found at the maximum in the partial mole fraction of the first anionic complex, $MeL_{\nu+1}$. Either dilution or concentration of the saturated solution with composition corresponding to this will lead to loss of the saturation state. The equation also expresses indirectly that the $\log T_{Me}=f(\log [L])$ plot intersects the solubility curve at two points only if $N\geq \nu+2$, i.e. at least two anionic complexes are formed in the stepwise equilibria.

The considerations and diagrams presented so far clearly show the direct connection of the formation, partition and solubility curves. In the application of solubility measurements in equilibrium chemistry, the data of the $S=f[L]$ or $S=f[T_L]$ plots may be determined experimentally and used to calculate the formation constants.

If the previously discussed extraction method is compared with that based on solubility measurements, they are seen to be very similar. The reason behind the similarity is that both procedures are based on the partition of the neutral complex, between two liquid phases in the extraction method, and between the solid and liquid phases in solubility measurements. The characteristic points of the plots also have similar chemical meaning. The maximum in the distribution quotient corresponds to the minimum in the solubility curve; at both characteristic points we have the correlation $\bar{n}=\nu$ for the aqueous phase.

For the extraction curves, the tangential point of $-\log q_{Me}=f(\log [L])$ and $\log T_{Me}=f(\log [L])$ is similarly found at $\bar{n}=\nu+1$. The following chemical meaning can be given to the tangential point in this case: if the concentration ratio T_L/T_{Me} characteristic of this point is maintained, and the aqueous phase is either diluted or concentrated, the metal ion concentration in the aqueous phase after the extraction equilibrium has been restored will be lower than the initial value.

There are naturally also very substantial differences between the two methods. Along the solubility curves, the activities (concentrations) of the complex MeL_v in the aqueous and organic phases are the same. For the extraction equilibria the ratio of the concentrations is constant; they may have arbitrary absolute values within the solubility limits. This difference permits study of the formation of polynuclear complexes too with the extraction method, through variation of the metal ion concentration. In the case of solubility measurements there is no possibility to vary the metal ion concentration, and the formation of polynuclear complexes can be demonstrated only on the basis of solubility measurements in combination with some other method of examination; solubility measurements themselves are not suitable for this. In general, a much longer time must be waited for equilibrium to be established in solubility studies than in extraction studies. The most important difference, however, is that several complexes may take part in the extraction partition equilibrium, whereas the solid phase always consists of a single complex (though the composition

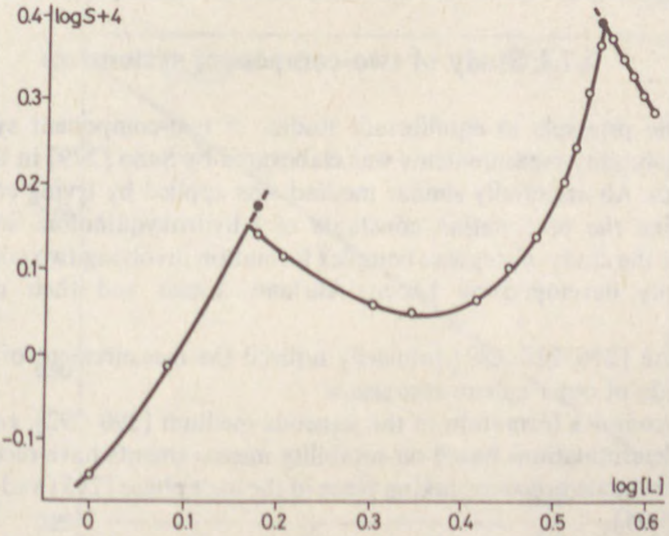

Fig. 4.51. Logarithm of solubility of $Co(NH_3)_6(ClO_4)_3$ as a function of log [Br^-] at an ionic strength $I = 4$ *M* Na(ClO_4, Br) [276]. The break-points in the curve indicate the phase transformations $Co(NH_3)_6(ClO_4)_3 \rightarrow Co(NH_3)_6Br_2ClO_4 \rightarrow Co(NH_3)_6Br_3$ (Reproduced with permission from *Acta Chem. Scand.*, **27**, 2335 (1973))

may vary). If the composition of the solid phase too changes with the variable component concentration, this shows up as a break-point in the solubility curve. An example of this phenomenon, taken from the results of Johansson [276], is presented in Fig. 4.51.

In our considerations we have so far restricted ourselves to a discussion of the solubility conditions relating to two-component precipitates, and the connection between solubility and complex formation. Haight [277] developed a method for the determination of stability constants through solubility studies on three-component precipitates. Johansson [278] has written an excellent review of solubility studies on systems where the solid phase has a more complex composition.

The methods of determining equilibrium constants via solubility measurements can be classified fundamentally into two types: those in which the solid phase is one of the complexes (generally an outer sphere complex) produced during stepwise complex formation (the studies therefore relating to two-component systems), and those in which the solubility equilibrium is connected as an 'auxiliary equilibrium' with the equilibrium system under investigation (the latter methods being known as competition solubility studies).

Of the analytical methods for the measurement of solubility, radioactive labelling, atomic absorption analysis and spectrophotometry are most generally used, but naturally any method with the desired accuracy and sensitivity can be employed.

4.7.1 Study of two-component systems

The basic principle in equilibrium studies of two-component systems by means of solubility measurements was elaborated by Sano [279] in the case of amino acids. An essentially similar method was applied by Irving *et al.* [280] to determine the protonation constants of 8-hydroxyquinoline. Procedures suitable for the study of stepwise complex formation involving two components were mainly developed by Leden, Ahrland, Lieser and their coworkers [281–287].

Johansson [276, 288, 289] primarily utilized the measurement of solubility for the study of outer sphere complexes.

Besides complex formation in the aqueous medium [290–292], equilibrium constant determinations based on solubility measurements have recently been used to investigate processes taking place in the melt phase [293] and in solvent mixtures [294].

4.7.2 Competition solubility studies

The principle behind solubility studies based on competition is that the solubility changes when a ligand L′ reacting with the metal ion is added to a saturated solution of a sparingly soluble precipitate of composition MeL (or when a metal ion Me′ is added which reacts to form a complex with the ligand). From the change of solubility, conclusions can be drawn on the interaction between Me and L′ (or between Me′ and L). The hydrogen ion must also be taken into consideration as a competition partner if the ligand L or L′ is a conjugate base of a weak acid, or if the metal ion Me or Me′ undergoes hydrolysis under the conditions of the study.

Johansson [295] used a competition method to investigate formation of the complex TlF by measuring the solubilities of $TlIO_3$ and BaF_2 as functions of the fluoride or thallium concentration. The results of his solubility measurements (Fig. 4.52) showed that, in contrast with expectations, the solubility of $TlIO_3$ does not increase, but instead decreases, with increase of the F^- concentration. He explained this unusual experimental result in that the association between Tl^+ and the ClO_4^- used as background electrolyte anion was stronger than the interaction between Tl^+ and F^-. Starting from this, the formation constants of the perchlorato complexes too may be determined [296].

Nair *et al.* [297, 298] studied the systems of Ca^{2+} and Cu^{2+} with lactic acid and malic acid through measurements of the solubilities of $Ca(IO_3)_2$ and

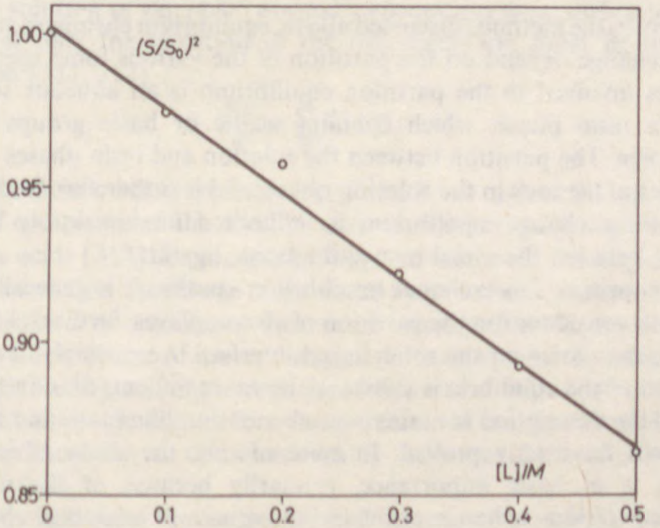

Fig. 4.52. 'Normalized' solubility of $TlIO_3$ as a function of the fluoride ion concentration [295]
(Reproduced with permission from *Acta Chem. Scand.*, **27**, 1832 (1973))

$Cu(IO_3)_2$. From the change in the solubility of silver acetate in response to $Be(NO_3)_2$, Sengupta and Adhikari [299] determined the constants of the acetato complexes of Be^{2+}. Halloff and Vannerberg [300] investigated the interaction between Ni^{2+} and Cl^- by measuring the solubility of AgCl.

With ligands that are conjugate bases of weak acids, solubility studies are naturally supplemented by pH measurement. Ilcheva and Bjerrum [301] determined the formation constants of the methylamine and dimethylamine complexes of copper(II) by measuring the solubility of gerhardtite in 2 *M* methyl- or dimethylammonium nitrate at various pH values. McDowell *et al.* [302] utilized the pH-dependent solubility of $CaHPO_4$ to draw conclusions on the solubility product and formation constant of $CaHPO_4$ and on formation of the complex $CaH_2PO_4^+$. Hedström *et al.* [303] examined the Pb^{2+}–oxalate system in a similar way.

The general introduction and the great variety of the above examples reveal that solubility studies based on competition can be applied in a very wide range. It is surprising, therefore, that the literature contains relatively few examples of such investigations (though the above listing is not complete). The probable explanation for this is that equilibrium studies based on solubility studies are much more work- and time-consuming than other methods.

4.8 Study of ion-exchange equilibria

Similarly to the methods discussed above, equilibrium chemistry studies based on ion-exchange depend on the partition of the various ionic species. One of the phases involved in the partition equilibrium is an aqueous solution; the other is a resin phase, which contains acidic or basic groups capable of ion-exchange. The partition between the solution and resin phases depends on the charges of the ions in the solution phase, and it is therefore understandable that the ion-exchange equilibrium is influenced fundamentally by complex formation between the metal ions and anionic ligands.

In the course of ion-exchange equilibrium studies, it is generally necessary to take into consideration the partition of all complexes; further, chemisorption effects too may arise on the solid–liquid interface. Accordingly, a quantitative description of the equilibria is substantially more difficult than in the previous cases, and the description contains a number of simplifications and assumptions that cannot be strictly proved. In spite of this, the study of ion-exchange equilibria is of basic importance, primarily because of the wide-ranging applications of ion-exchange resins in industrial and analytical chemistry.

Reviews are to be found on the experimental techniques in equilibrium studies based on ion-exchange, and on the descriptions of commercially-available ion-exchangers [304–306]. Detailed discussions of the principles of ion-exchange investigations of complex formation processes have been given by Marcus [307], by Inczédy [308, 309] and by Lengyel and Törkő [310].

4.8.1 Application of cation-exchangers

The partition of some metal ion between the solution and resin phases is described by the following quotient

$$\Phi = \frac{\text{no. of moles of metal ion bound on 1 g air-dry resin}}{\text{no. of moles of metal ion in 1 cm}^3\text{ solution}}. \tag{4.86}$$

Let φ_i be the ratio of the concentrations of complex MeL_i in the resin and solution phases

$$\varphi_i = \frac{[\mathrm{MeL}_i]_r}{[\mathrm{MeL}_i]_{aq}}. \tag{4.87}$$

The overall partition can then be given by means of the constants φ_i and β_i

$$\Phi = \frac{\sum\limits_0^N \varphi_i[\mathrm{L}]^i}{\sum\limits_0^N \beta_i[\mathrm{L}]^i}. \tag{4.88}$$

The general solution of Eq. (4.88) normally encounters great difficulties. If it is assumed that only the partition of the free metal ion must be taken into consideration [311, 312]

$$\frac{\varphi_0}{\Phi} = \sum_0^N \beta_i[\mathrm{L}]^i. \tag{4.89}$$

Equation (4.88) has been applied, for example, to determine the stability constants of complexes of the alkaline earth metal ions with organic di- and tricarboxylic acids [313]. Equation (4.89) can be used only if a single ligand is sufficient to neutralize the charge of the metal ion, i.e. the formation of cationic complexes need not be considered. Numerous attempts have been made to give a quantitative description of ion-exchange studies on systems forming cationic complexes [314–320], but the results must be treated with some caution. In this case it is advisable to measure the partition of the ligand too, if this is possible experimentally, as this considerably facilitates the evaluation of the experimental data.

In recent times, besides the continuation of investigations on relatively simple systems [321–323], efforts have been made to apply methods based on cation-exchange to more complicated equilibrium systems [324, 325], and even to processes taking place in the melt phase [326].

4.8.2 Application of anion-exchangers

The application of anion-exchangers for the determination of equilibrium constants was first proposed by Leden [327], and the bases of the method were put forward by Fronaeus [328]: the distribution quotient measurable on the anion-exchange resin is proportional to the partial mole fraction of the neutral complex. The theory of the method was further developed by Marcus and Coryell [329] and by Kraus and Nelson [330], who also took into account the Donnan equilibrium and defined the concept of effective ligand activity: the variation in the corrected distribution quotient according to the effective ligand activity exactly follows the variation in the mole fraction of the neutral complex. Therefore, the corrected distribution quotient varies in the same way as the solubility curve outlined in Section 4.7, or in the same way as the distribution quotient in the course of extraction based on the partition of the neutral complex. In a similar manner as for the corresponding functions of the previous methods, the differential coefficient of the logarithm of the corrected distribution quotient with respect to the logarithm of the effective ligand activity gives the value of $v-\bar{n}$.

The method can be applied if the ligands are small, so that the resulting complexes are bound on the resin without steric hindrance. Accordingly, equilibrium studies based on anion-exchange are largely used to investigate halogeno and pseudohalogeno complexes. Kraus and Nelson have studied the partitions of the chloro complexes of practically every conceivable ion; their results are presented in Fig. 4.53 [331].

The ions examined can be classified into the following four groups:

(1) Ions binding not at all, or only very weakly. These do not form anionic chloro complexes.

(2) Ions binding less strongly as the hydrochloric acid concentration is increased. These form only anionic complexes at the hydrochloric acid concentration in question.

(3) Ions exhibiting an adsorption maximum. For these, the interval of formation of the neutral complex is within the examined hydrochloric acid concentration range.

(4) Ions with an increasing ability to adsorb. An anionic chloro complex may be formed in these systems too, but the average charge number remains positive within the examined concentration range.

The starting condition in the derivation of the correlations relating to the equilibrium chemical application of anion-exchange is that, because of the very high ligand concentration of the resin phase, only a single complex, that with the maximum coordination number, binds on the resin. However, this condition

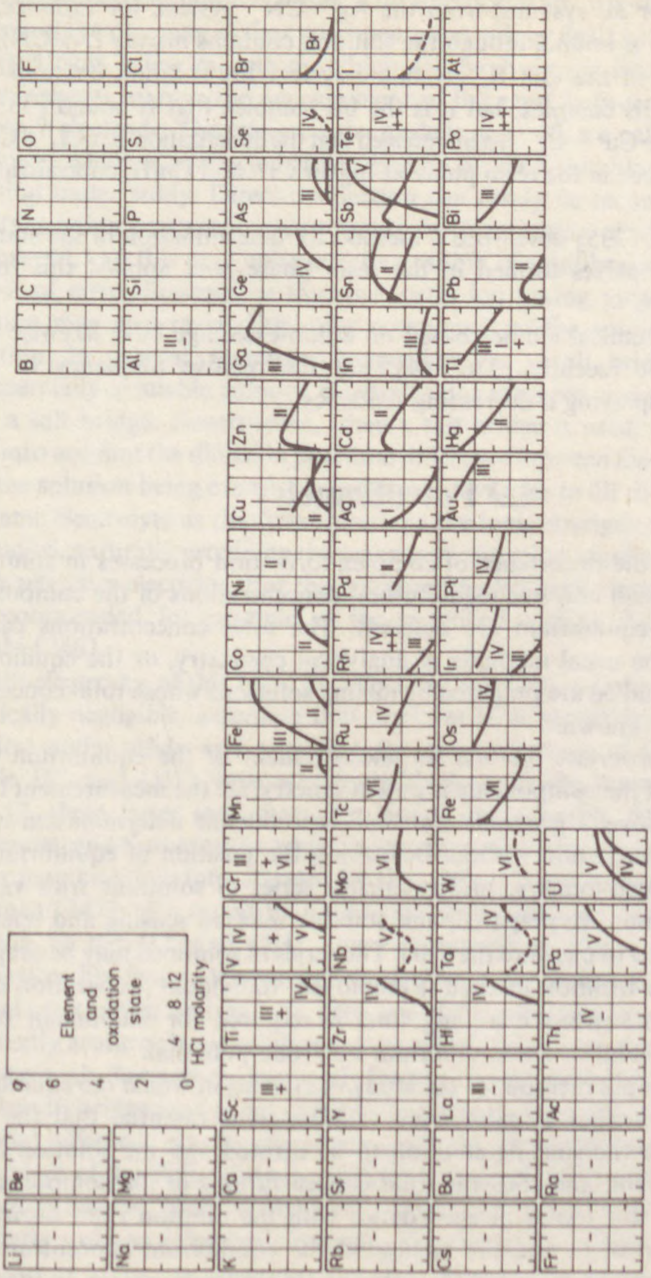

Fig. 4.53. Partition of metal ions between aqueous phase and anion-exchange resin as a function of HCl concentration of aqueous phase [331]
(Reproduced with permission from Kraus, K. A. and Nelson, F. (Eds), *Proc. Intern. Conf. Peaceful Uses of Atomic Energy*, 7, 113 (1965)

does not hold for all systems; from the Ag^+–CN^- system, for instance, the tricyano complex is bound, though the solution contains mainly $[Ag(CN)_4]^{3-}$ [332]. Similarly, in the Gd(III)–glycollate system the solution contains predominantly the tris complex, but it is the bis complex that is bound [333]. A similar study on the Cu^{2+}–Cl^- system revealed that the dimerization $2CuCl_3^- + Cl^- \rightleftharpoons$ $\rightleftharpoons Cu_2Cl_7^{3-}$ proceeds in the resin phase at higher Cl^- and Cu(II) concentrations [334].

Fronaeus *et al.* [335] developed a method for determination of the stability constants of complexes formed in the resin phase, and applied this to the Cd^{2+}–Br^- system.

Equilibrium chemical studies based on anion-exchange have likewise been carried out more recently [336–344], but the relative frequency of their application is displaying a decreasing tendency.

4.9 Potentiometry

As a result of the occurrence of complex formation processes in solutions, the total (analytical) and free (equilibrium) concentrations of the components involved in the equilibrium are different. The total concentrations can be determined by the usual methods of analytical chemistry, or the equilibrium solutions to be studied are prepared by mixing solutions whose total concentrations are already known.

The most appropriate method for measurement of the equilibrium (free) concentrations of the components is potentiometry, i.e. the measurement of the e.m.f., for this allows a generally fast, well-reproducible determination of the equilibrium concentration without disturbing the position of equilibrium. In the course of potentiometric measurements, series of solutions with various total concentrations are prepared, and suitably selected sensing and reference electrodes are used to measure the e.m.f. The series of solutions may be prepared individually, or a titration method is employed. Individual preparation of the samples is recommended if a long time is required for attainment of the equilibrium state and/or the equilibrium electrode potential.

Titration is a rapid method for the study of systems in which the equilibrium state is attained within at most a few minutes. It is essential that the total concentrations of the starting solution to be titrated and the solution in the burette are different, and thus the total concentrations of the components of solutions under study vary in accordance with the dilution rules during the stepwise addition of titrant; the change in the equilibrium concentration in question is followed by means of the appropriate electrode system. In titrations with the aim of studying equilibrium chemistry, it is very important that the concentrations of the components of the solution to be titrated and the titrant solution should be suitably chosen. This question is so important that the main aspects of the planning of the experimentation will be dealt with in detail below.

Apart from a few exceptions, which will be discussed later, potentiometric measurements involve the measurement of the e.m.f. between a sensing and a reference electrode. The reference electrode is most often a calomel or Ag/AgCl electrode, which is connected either directly or via a suitable salt bridge to the solution under study. Direct connection can rarely be recommended, for the constant anion concentration necessary for functioning of the electrode must be ensured, and this may influence the position of equilibrium. A more serious source of error, however, is that the metal ion taking part in the electrode reaction may also react with some component of the equilibrium system in question. In general, therefore, connection via a salt bridge is used. The commercially available calomel electrodes, for example, are supplied together with a salt bridge. Nevertheless, when a salt bridge is used, it is necessary to take into account the diffusion potential difference between the filling electrolyte and the solution being examined. It is most advisable to fill the salt bridge with the same electrolyte as that used to adjust the ionic strength of the solution to be studied, naturally providing the anion concentration required for functioning of the reference electrode. For this purpose, the Wilhelm electrode* [345] may be recommended, for example, or the simplified variant of this described by Ohtaki [346].

With electrodes of this type, the effect of the diffusion potential difference is practically negligible, assuming that constant ionic strength is ensured in the solution under study and also that the concentrations of the exceptionally mobile H^+ and OH^- ions are negligibly low. In the intervals $pH<2$ and $pH>12$, these latter ions may give rise to considerable diffusion potential differences, and thus exert an appreciable influence on the measured e.m.f. Their effects may be taken into account by the method devised by Biedermann and Hietanen [347], who found that the value of the diffusion potential is a linear function of the H^+ and OH^- ion concentrations. The magnitude of the proportionality factor depends on the nature and concentration of the background electrolyte, and can be determined by measurement of the e.m.f. in sufficiently acidic or basic solutions. A survey of the recent equilibrium chemical studies reveals that authors frequently forget to apply the appropriate correction.

If the salt bridge used is not of the Wilhelm type, an error due to the diffusion potential difference may appear throughout the entire pH interval. Apart from salt bridges of the Wilhelm type, a calomel electrode filled with saturated KCl, or with saturated NaCl if the background electrolyte is $NaClO_4$, is most frequently used as reference electrode. The fact that K^+ and Cl^- ions have

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* Devised in the Sillén-school and the electrode is named after the first name of the first author.

almost identical mobilities means that in the former case the error due to the diffusion potential difference is generally not appreciable, but it is not negligible! For an electrode filled with NaCl, however, the error may be even 0.1–0.2 V, and it is therefore of fundamental importance that it be determined experimentally and corrected for.

As sensing electrode (sensor) in pH-metry a glass electrode is used in general; in acidic solutions a quinhydrone electrode may be applied. The hydrogen electrode is not frequently used nowadays, partly because it is difficult to use, and partly because of the ever better quality of the glass electrodes available commercially. Measurement of the metal ion concentration may be performed with a reversibly functioning metal or amalgam electrode, or with the corresponding ion-selective electrode. Apart from these, potentiometric equilibrium studies are in some cases carried out with redox electrodes, or with two sensors connected as a concentration cell.

The activities of the species participating in the electrode reaction feature in the Nernst equation describing the potentials of the sensors. At the same time, the evaluation of equilibrium chemical measurements, among others, is based on the material balances expressed in terms of concentrations. Accordingly, in the course of the examinations, conditions must be created such that the activity and the concentration differ only by a constant multiplier, i.e. by an additive term on the logarithmic e.m.f. scale. This purpose, among others, is served by the application of a large excess of background electrolyte, whereby the ionic strength of the solution, and hence the activity coefficients of the individual ionic species, are kept constant. Experimental determination of the additive term permits calculation of the concentration from the measured e.m.f.

It may readily be seen from the foregoing that a precondition for the appropriate application of potentiometric equilibrium measurements is the suitable calibration of the electrode system. The aim of this is to determine the terms arising from the difference between the activity and the concentration and from the diffusion potential difference, i.e. terms which additively influence the measured e.m.f., and to establish the concentration interval within which the sensor shows a Nernst function. We shall return to these questions during the more detailed account of the various types of potentiometric investigations.

4.9.1 pH-metric equilibrium studies

The method most frequently applied for the study of complex equilibria is pH-metric titration. One of the reasons for this is that pH measurements with a reproducibility within ±0.005 pH unit can nowadays be performed virtually routinely with good-quality glass electrodes and modern, high-accuracy, but relatively inexpensive pH-meters. Under carefully chosen and maintained experimental conditions, it is possible to attain a reproducibility better than this by even an order of magnitude [348, 349]. Another fundamentally important reason for the widespread use of the method is that practically all equilibrium processes that take place in water or in water-containing solvent mixtures respond sensitively, either directly or indirectly, to a change in the pH.

We speak of a direct effect of the pH if the H^+ (or OH^-) ions themselves participate in the examined equilibrium process, e.g. in the case of protonation equilibria of ligands that are conjugate bases of weak acids, or the hydrolysis of metal ions.

The pH effect is indirect if the H^+ (or OH^-) ions do not take part in the association equilibria involving the components under study, but one (or more) of the components features in the protonation equilibria. The pH-metric study of metal complexes of ligands that are conjugate bases of weak acids (carboxylates, amines, amino acids, peptides, etc.) is generally based on such a pH effect.

4.9.1.1 Calibration of the electrode system

It was stated above that suitable calibration of the electrode system is a precondition of the appropriate application of pH-metry. The mode of calibration depends basically on whether the pH-meter is used to measure the pH directly, or whether potential (mV) is measured. In the former case, the pH-meter is generally calibrated by means of appropriate NBS standard buffers, the aim of the calibration being the determination of the additive term that is the difference between the measured pH and the $-\log[H^+]$ value, and the determination of the ionic product of water, expressed in terms of concentrations. The method proposed by Irving *et al.* [350] is used most generally for determination of the numerical value of the additive calibration term. The essence of this is as follows. The pH-meter is first calibrated against at least two suitable NBC standard buffers. For calibration of the electrode system, a strong acid–strong base titration is first performed, in the presence of a background electrolyte. The starting concentration of the titrated strong acid should, if possible, not exceed 3 % of the concentration of the background electrolyte. The suitable Gran functions may conveniently be used to evaluate the plot [351, 352]. If the branches calculated from the acidic and the basic intervals of the Gran functions are linear, and if the intercepts on the *x* axis coincide, this is clear-cut evidence that the solution in question does not contain acidic or basic impurity and the data obtained can be used for the reliable calculation of the additive term and the ionic product of water expressed in terms of concentrations. If there is deviation from linearity, or if the intercepts from the acidic and the basic intervals do not coincide within the limits of error, the starting materials must be purified again, and it must be ensured that the base is free of carbonate. The actual equilibrium measurements themselves can be started only when the Gran functions for the titration of the strong acid and the strong base yield the regular V-shape to be expected theoretically.

The $-\log[H^+]$ and the $-\log[OH^-]$ data may be calculated from the data relating to the acidic interval and the basic interval, respectively, in the strong acid–strong base titration. The difference between the pH measured in the acidic interval and the calculated value of $-\log[H^+]$ is constant

$$A = \mathrm{pH}_{\mathrm{measured}} + \log[H^+]\,. \qquad (4.90)$$

In accordance with the introduction to Section 4.9, the constant A includes the difference of the diffusion potential differences arising between the salt bridge of the reference electrode, the standard NBS solutions used for calibration and the salt solution used to adjust the ionic strength, and it also includes the logarithm of the activity coefficient of the H^+ ion. If the value of A is known, $-\log[H^+]$ can be calculated from the pH value measured in any solution with the same background electrolyte concentration

$$-\log[H^+] = \mathrm{pH}_{\mathrm{measured}} - A\,. \qquad (4.91)$$

The logarithm of the ionic product of water, expressed in terms of concentrations, is obtained by correcting the pH measured in the basic interval of the titration curve by the constant A, and by adding the calculated value of $-\log[OH^-]$

$$\mathrm{p}K_w^c = -\log([H^+][OH^-]) = \mathrm{pH}_{\mathrm{measured}} - A - \log[OH^-]. \qquad (4.92)$$

In connection with the above method of calibration, it must be noted that the dependence of the diffusion potential difference on $[H^+]$ and $[OH^-]$ is neglected. This is permissible only if the concentrations of H^+ and OH^- are negligible compared to the concentration of the background electrolyte. It must also be taken into consideration that equilibrium measurements with an electrode system calibrated in this way are allowed only in that pH range within which A and $\mathrm{p}K_w^c$ were determined.

In the pH range in which the concentrations of H^+ and OH^- are not negligible in comparison with the concentration of the background electrolyte, both A and $\mathrm{p}K_w^c$ vary linearly as a function of pH. This pH range should, if possible, be avoided in the course of equilibrium measurements. The accuracy of the pH measurement may perhaps be increased by taking into account the dependence of A and $\mathrm{p}K_w^c$ on $[H^+]$ or $[OH^-]$.

The method has the disadvantage that the electrode system must be lifted out of the calibration solution a number of times, and transferred to a new medium, which may lead to a small, uncontrollable alteration in the asymmetry potential of the glass electrode. This latter error may be particularly appreciable if pH measurements are performed at very high ionic strength, or in solvent mixtures containing water. In the latter case it is advisable to measure e.m.f. and to calibrate the electrode system through E_0 titration.

The essence of E_0 titration is that strong acid–strong base titration is carried out in the solvent mixture in question, and the value of E_0 is calculated from the data obtained in the acidic interval, via the relation

$$E_0 = E + 2.303\ RT/F \log[\mathrm{H}^+]\,. \tag{4.93}$$

This value of E_0 therefore means the e.m.f. relating to a solution of unit *hydrogen ion concentration* in the given medium. In the interest of the determination of pK^c_w, the e.m.f. must naturally also be measured in the basic interval, when pK^c_w can be calculated in the knowledge of E_0 and $-\log[\mathrm{OH}^-]$.

However, if we wish to study the processes of ligand protonation, the hydrolysis of the metal ion or the various complex formation reactions, then the E_0 titration is stopped before the equivalence point, the solutions of the components under examination, in the same medium, are transferred to the measuring cell without removal of the electrodes, and the titration is continued. In this way, the uncontrollable alteration of the asymmetry potential as a consequence of the lifting-out and washing of the electrodes, and their transfer to a new medium, can be avoided. A number of authors have dealt with the calibration of the electrode system, the determination of pK^c_w for various media, and calculation and elimination of the error originating from the diffusion potential differences; for the details, the reader is referred to the original publications [353–363].

4.9.1.2 Planning of pH-metric measurements

The aim of the planning of pH-metric measurements is to choose starting metal ion–ligand–proton concentrations and concentration ratios such that the titration curves will reflect as sensitively as possible the equilibrium processes taking place in the system to be investigated. Of course, the pH-metric equilibrium analysis of an unknown system cannot be planned exactly. In such a case, we can merely follow the general principle that conclusions on the processes occurring in the system are drawn from the results of measurements in relatively wide ranges of concentration and pH.

pH-metric titrations are most often carried out with a basic solution. In some cases, the correct choice of the basic solution may be important. For example, Al-Niaimi and Al-Saadi [364] studied the protonation of thiosalicylic acid and the formation of its metal complexes in a 75 vol.% dioxane–water solvent mixture at 30°C. When the titration was performed with tetramethylammonium hydroxide without the use of a background electrolyte, the protonation constants were found to be 7.17 and 13.57, whereas titration with KOH solution in the presence of 0.02 *M* KCl led to values of 6.50 and 11.95. Although the activity coefficients too may be very different in the two media, the difference of more than 1.5 orders of magnitude in the second protonation constant is primarily a consequence of the interaction between the K^+ ion and thiosalicylic acid, which may be particularly marked in a medium with a very small dielectric constant. In a solvent mixture with a low dielectric constant, therefore, it is preferable to use as background electrolyte the tetraalkylammonium salts, which are less prone to complex formation, and to carry out the titrations with tetraalkylammonium hydroxide. There is an appreciable complex formation reaction between Na^+ and polyaminocarboxylic acids in aqueous medium too, and thus the use of sodium salts as background electrolyte and of NaOH as titrant in studies on the complexes of polyaminocarboxylic acids is to be avoided.

4.9.1.2.1 Determination of protonation constants

Numerous authors have investigated the possibilities and accuracy of the determination of protonation constants. On the examples of nitrilotriacetic acid and ethylenediaminetetraacetic acid, for instance, Irving *et al.* [350] showed that the determination is uncertain in the intervals $\log K_p < 3$ and $\log K_p > 11$. McBryde [365] reached similar conclusions. Nagypál and Gergely [366] made an analysis of the function $\mathrm{d}\log K_p/\partial \mathrm{pH}$, which characterizes the possibility of determination; they studied how the value of the function varies at different $\log K_p$ values, concentrations and concentration ratios. The correlation

$$K_p = \frac{[\mathrm{HL}]}{[\mathrm{H}][\mathrm{L}]} = \frac{aT_L - [\mathrm{H}^+] + [\mathrm{OH}^-]}{[\mathrm{H}^+]\{T_L(1-a) + [\mathrm{H}^+] - [\mathrm{OH}^-]\}} \tag{4.94}$$

defines one-step protonation processes; it was used as the starting-point in the calculations, and the following equation was derived

$$\frac{\partial \log K_p}{\partial \mathrm{pH}} = 1 + \frac{T_L([\mathrm{H}^+] + [\mathrm{OH}^-])}{\{aT_L - [\mathrm{H}^+] + [\mathrm{OH}^-]\}\{(1-a)T_L + [\mathrm{H}^+] - [\mathrm{OH}^-]\}} \tag{4.95}$$

where $a = T_H/T_L$.

The equation reveals that a given a and $[\mathrm{H}^+]$ pair relate to the same $\partial \log K_p/\partial \mathrm{pH}$ as the corresponding $(1-a)$ and $[\mathrm{OH}^-]$ pair, i.e. at $a = 0.5$ the curve $\partial \log K_p/\partial \mathrm{pH} = f(\mathrm{pH})$ is symmetrical about $\mathrm{pH} = \mathrm{p}K_w/2$. From the aspect of the planning of the experimental work, the $\partial \log K_p/\partial \mathrm{pH} = f(\log K_p)$ data should be available, as the expected pK value of some ligand can be estimated with greater certainty than the pH of solutions with various compositions. Figure 4.54 shows the shapes of the function $\partial \log K_p/\partial \mathrm{pH} = f(\log K_p)$ at different T_L values in a solution with $a = 0.5$, i.e. half neutralized.

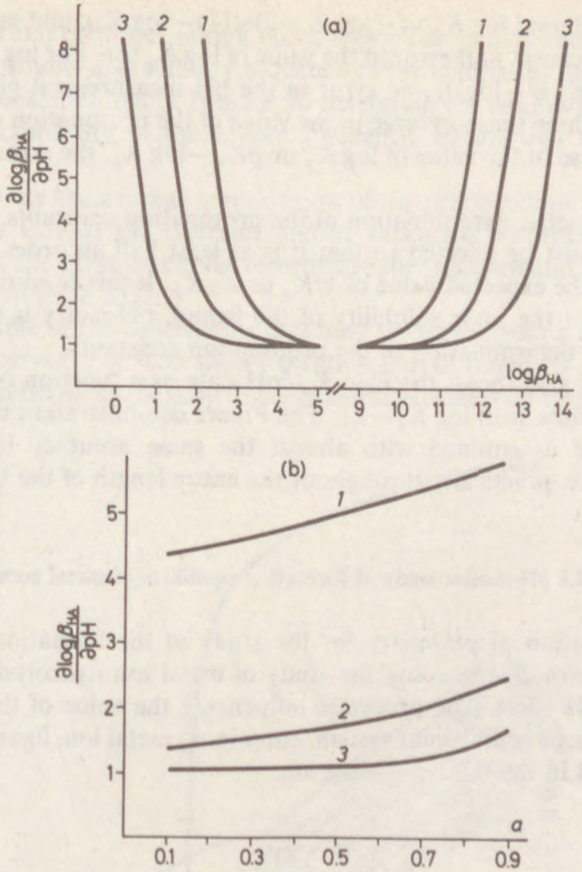


Fig. 4.54 (a) Shapes of the function $\partial \log K_{HA}/\partial pH = f[\log \beta_{HA}]$ at various total ligand concentrations, for $a = 0.5$.

1 — $T_L = 0.001$ *M*; 2 — $T_L = 0.01$ *M*; 3 — $T_L = 0.1$ *M*

(b) Shapes of the function $\partial \log \beta_{HA}/\partial pH = f(a)$ at $\log \beta_{HA} = 2.5$ and various ligand concentrations.

1 — $T_L = 0.001$ *M*; 2 — $T_L = 0.01$ *M*; 3 — $T_L = 0.1$ *M* [366]

(Reproduced with permission from *Magyar Kémiai Folyóirat*, **78**, 18 (1972))

The most important conclusions that can be drawn from the Figure are as follows.

(a) At given T_L, with $a = 0.5$, the $\log K_n = X$ and $\log K_p = (pK_w - X)$ values relate to the same value of $\partial \log K_p/\partial pH$.

(b) The smaller the value of $\log K_p$ or of $pK_w - \log K_p$, the higher the ligand concentration must be in the solution in which the determination is performed.

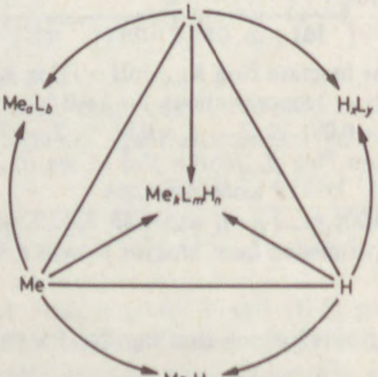
(c) In the interval $\log K_p > (-\log T_L + 2) < (14 - \log K_p)$, unit error in the pH measurement causes unit error in the value of $\log K_p$ too. For $\log K_p \approx -\log T_L$ or $pK_w - \log K_p \approx -\log T_L$, an error in the pH measurement gives rise to an error almost three times as large in the value of the protonation constant; with further decrease of the value of $\log K_p$ or $pK_w - \log K_p$, the error rises rapidly.

In the pH-metric determination of the protonation constants, therefore, the value of T_L must be selected so that it is at least half an order of magnitude smaller than the expected value of $1/K_p$ or $K_w K_p$. If this condition can not be met because of the poor solubility of the ligand, pH-metry is not a suitable procedure for determination of the protonation constants.

Figure 4.54 also shows the $\partial \log K_p / \partial pH$ data as a function of $a = T_H / T_L$ at various T_L values, with $\log K_p = 2.5$. The Figure demonstrates that the value of $\log K_p$ can be determined with almost the same accuracy in the interval $0.1 < a < 0.9$, i.e. practically throughout the entire length of the titration curve.

4.9.1.2.2 pH-metric study of formation equilibria of metal complexes

The application of pH-metry for the study of the formation equilibria of metal complexes (disregarding the study of metal ion hydrolysis) is based on an indirect pH effect. The processes influencing the value of the pH in some three-component equilibrium system, containing metal ion, ligand and proton, are illustrated in the following diagram:



Study of the metal complexes is generally preceded by study of the H–L interaction and of metal ion hydrolysis. The titration curves obtained at the same initial total hydrogen ion and total ligand concentrations, in the presence and in the absence of the metal ion, provide an extremely illustrative reflection of the equilibrium processes taking place; they often yield reliable information on the compositions and stability sequence of the complexes formed.

In many cases, no attempt is made to determine the equilibrium constants; indeed, the complexity of the system frequently means that this would be hopeless.

Instead, merely the average composition of the predominant complexes are determined in various pH intervals and at various concentration ratios, by comparison of the titration curves recorded in the presence and in the absence of the metal ion [367–372].

As an example of the conclusions that may be drawn from a comparison of the titration curves, Fig. 4.55 shows titration curves found by Brücher *et al.* [373] in rare earth metal–hexamethylenediaminetetraacetate systems. It clearly

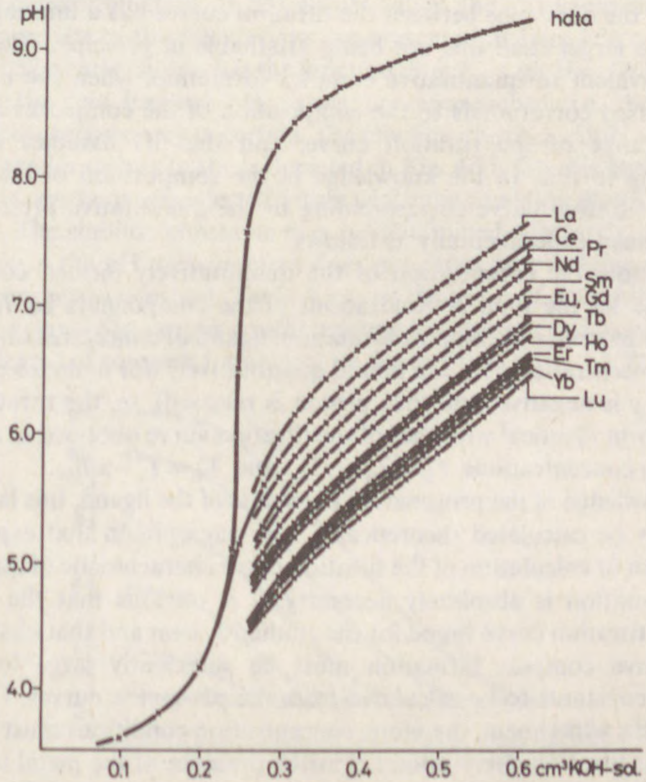


Fig. 4.55. Titration curves of K_2H_2hdta in the presence and in the absence of rare earth metal ions. For La and Lu, $T_{\mathrm{hdta}} = 9.14 \times 10^{-3}$ M; for Ce–Yb, $T_{\mathrm{hdta}} = 9.52 \times 10^{-3}$ M; $T_{\mathrm{Ln}} = 2 \times 10^{-3}$ M; [KOH] = 0.207 M; $V_0 = 25$ cm³, hdta = hexamethylenediaminetetraacetic acid [373]

(Reproduced with permission from *Magyar Kémiai Folyóirat*, **81**, 339 (1975)) follows from the Figure that an appreciable extent of complex formation must be taken into account at $\mathrm{pH} > 5$, and the stability of the resulting complexes increases with increase of the atomic number of the rare earth metal.

The Figure also demonstrates that the difference between the pH-metric curves obtained in the presence and in the absence of the metal ion serves as the basis of the determination of the stability constants. This principle was utilized as long ago as 1954 by Rossotti and Irving [374], who developed a general procedure for calculation of the formation curves of metal complexes via the difference in the pH-metric curves.

On the above basis, it is obvious that, when pH-metry is applied, the concentrations must be chosen such that the difference between the curves measured in the presence and in the absence of the metal ion should be several orders of magnitude larger than the largest possible experimental errors.

Naturally, the difference between the titration curves has a limiting value, a pH difference larger than this not being attainable in principle. The limiting value is equivalent to quantitative complex formation, when the number of protons released corresponds to the composition of the complexes formed in the whole range of the titration curve, and the pH assumes the value corresponding to this. In the knowledge of the composition of the complex formed, the titration curve corresponding to the quantitative proton release may be obtained experimentally as follows.

Let us denote the composition of the quantitatively formed complex by $\mathrm{MeL}_x\mathrm{H}_y$, and let the total concentrations of the components be T_H, T_L and T_Me. As a consequence of complex formation, ligand of concentration xT_Me and proton of concentration yT_Me are bound quantitatively (for hydroxo complexes the value of y is negative, and thus proton is released), i.e. the titration curve will have a form identical with that of the titration curve obtained in a solution with starting concentrations $T'_\mathrm{H} = T_\mathrm{H} - yT_\mathrm{Me}$ and $T'_\mathrm{L} = T_\mathrm{L} - xT_\mathrm{Me}$.

In the knowledge of the protonation constants of the ligand, this latter curve can naturally be calculated theoretically. It is our opinion that experimental determination or calculation of the titration curve characteristic of quantitative complex formation is absolutely necessary: it is obvious that the difference between the titration curve found for the studied system and that characteristic of quantitative complex formation must be sufficiently large for reliable equilibrium constants to be calculated from the pH-metric curves. During the planning of the experiment, therefore, concentration conditions must be chosen such that the titration curve obtained in the presence of the metal ion should differ both from the titration curve obtained in the absence of the metal ion and from that characteristic of quantitative complex formation to an extent considerably in excess of the maximum possible value of the experimental error. In the opposite case, merely the fact of complex formation, and the possible lower and upper limiting values of stability of the complex formed can be established, but exact evaluation can not be carried out.

In connection with the application of pH-metry to equilibrium chemistry, on the examples of the bipyridyl and phenanthroline complexes of Cu(II), in 1967 McBryde [365] drew attention to the fact that if the equilibrium process

$$\mathrm{Me} + \mathrm{HL} \rightleftharpoons \mathrm{MeL} + \mathrm{H}$$

is shifted considerably to the right, the method can not be utilized. Nevertheless, even in recent times publications have appeared which reveal that the authors disregarded this circumstance [375–377].

With the assumption that only the associations HL and MeL are formed in some equilibrium system, Nagypál and Gergely [366] calculated the functions $\log K_{\mathrm{MeL}} = f(\mathrm{pH})$ and $\mathrm{d}\log K_{\mathrm{MeL}}/\mathrm{dpH} = f(\mathrm{pH})$, which is characteristic of the possibility of determination, at various pH values and at various concentration ratios. The results of the calculations are presented in Figs 4.56 and 4.57.

Figure 4.57 clearly shows that the function $\mathrm{d}\log K_{\mathrm{MeL}}/\mathrm{dpH} = f(\mathrm{pH})$ rises very steeply as the two limiting pH values are approached, i.e. the pH-metric measurements become very uncertain. The function $\mathrm{d}\log K_{\mathrm{MeL}}/\mathrm{dpH} = f(\log K_{\mathrm{MeL}})$ gave very similar curves to those depicted in Fig. 4.57. On this basis, the range of formation constants was selected within which the condition $\mathrm{d}\log K_{\mathrm{MeL}}/\mathrm{dpH} < 3$ is satisfied. The stability constants may be determined accurately in this range, for an error in the pH measurement does not cause an overlarge difference in the logarithm of the constant. Table 4.3 gives the range of determination of the stability constants for various concentrations and concentration ratios, but for a similar degree of complex formation, i.e. for identical $(T_{\mathrm{L}} - T_{\mathrm{H}})/T_{\mathrm{Me}} = b$ values.

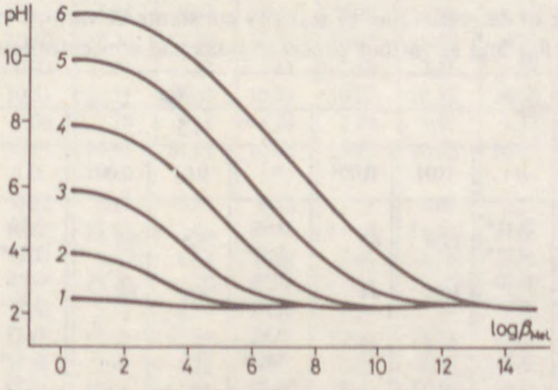


Fig. 4.56. Shapes of the function $\mathrm{pH} = f(\log \beta_{\mathrm{HL}})$ at $T_{\mathrm{A}} = T_{\mathrm{M}} = 0.01$ and $a = 0.6$ for various protonation constant values.

1 — $\log \beta_{\mathrm{HL}} = 2$; *2* — $\log \beta_{\mathrm{HL}} = 4$; *3* — $\log \beta_{\mathrm{HL}} = 6$; *4* — $\log \beta_{\mathrm{HL}} = 8$; *5* — $\log \beta_{\mathrm{HL}} = 10$; *6* — $\log \beta_{\mathrm{HL}} = 12$ [366]

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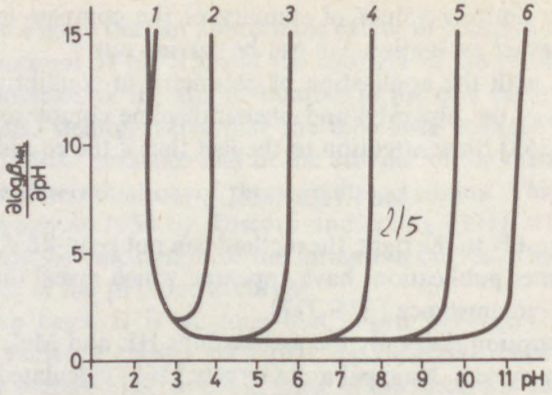

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Fig. 4.57 Shapes of the function $\partial \log \beta_{MeL}/\partial pH = f(pH)$ at $T_A = T_{Me} = 0.01$ and $a = 0.6$ for various protonation constant values.
1 — $\log \beta_{HL} = 2$; *2* — $\log \beta_{HL} = 4$; *3* — $\log \beta_{HL} = 6$; *4* — $\log \beta_{HL} = 8$; *5* — $\log \beta_{HL} = 10$; *6* — $\log \beta_{HL} = 12$ [366]
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When the dlog $K_{MeL}/\partial pH$ values do not attain the fixed limit of 3, but the minimum is below 10, the $\partial \log K_{MeL}/\partial pH < 10$ limiting values are denoted by a star in the Table. When the minimum of $\partial \log K_{MeL}/\partial pH$ does not even attain 10, a single datum is given: the value of $\partial \log K_{MeL}/\partial pH$ at the minimum.

The following main conclusions may be drawn from the data in Table 4.3:

Table 4.3 Range of determination of stability constants at various values of $\log K_p = \log \beta_{HL}$ and at various concentrations and concentration ratios

		T_L/T_{Me}								
		1			1.5			2		
$\log K_p$	b \ T_b	0.1	0.01	0.001	0.1	0.01	0.001	0.1	0.01	0.001
2	0.2	0.41* 3.23*	11.6	65	0.69 2.87*	15.5	85	0.89 2.56*	19.7	107
	0.4	0.30 3.38*	10.8	64	0.59 2.90*	14.8	84	0.81 2.57*	19.2	106
	0.6	0.24 3.56*	10.1	63	0.52 2.93*	14.3	83	0.75 2.57*	18.7	105
	0.8	0.22 3.79*	2.02 2.60*	62	0.48 2.91*	13.9	82	0.70 2.56*	18.2	105
	0.2	0.79 3.87	1.99 3.80	2.41 5.23*	0.99 3.75	2,36 3.58	2.69 4.87*	1.16 3.62	2.79 3.23	2.89 4.56*
		0.84	1.92	2.30	1.03	2.21	2.59	1.17	2.49	2.81

		T_L/T_{Me}								
		1			1.5			2		
log K_p	b \ T_b	0.1	0.01	0.001	0.1	0.01	0.001	0.1	0.01	0.001
4	0.4	4.19	4.14	5.39*	4.01	3.88	4.90*	3.84	3.60	4.57*
	0.6	0.93	1.98	2.24	1.12	2,23	2.52	1.25	2,48	2,75
		4.50	4.45	5.56*	4.21	4.07	4.93*	4.00	3.73	4.57*
	0.8	1.07	2.10	2.22	1.25	2.35	2.48	1.38	2.60	2.70
		4.90	4.82	5.79*	4.38	4.15	4.90*	4.10	3.69	4.55*
6	0.2	0.76	1.76	2.79	0.93	1.94	2.99	1.06	2.07	3.16
		5.88	5.88	5.87	5.76	5.76	5.75	5.45	5.65	5.62
	0.4	0.83	1.83	2.84	1.01	2.01	3.03	1.13	2.14	3.17
		6.20	6.20	6.19	6.02	6.02	6.01	5.87	5.86	5.84
	0.6	0.93	1.93	2.93	1.11	2.11	3.12	1.23	2.23	3.25
		6.51	6.51	6.50	6.23	6.23	6.21	6.03	6.03	6.00
	0.8	1.06	2.06	3.07	1.24	2.24	3.25	1.36	2.37	3.38
		6.91	6.91	6.90	6.42	6.41	6.38	6.17	6.16	6.10
8	0.2	0.76	1.76	2.76	0.93	1.93	2.93	1.06	2.06	3.06
		7.88	7.88	7.88	7.76	7.76	7.76	7.65	7.65	7.65
	0.4	0.83	1.83	2.83	1.01	2.01	3.01	1.13	2.13	3.13
		8.20	8.20	8.20	8.02	8.02	8.02	7.87	7.87	7.87
	0.6	0.93	1.93	2.93	1.11	2.11	3.11	1.23	2.23	3.23
		8,51	8.51	8.51	8.23	8.23	8.23	8.03	8.03	8.03
	0.8	1.06	2.06	3.08	1.24	2.24	3.24	1.36	2.36	3.37
		8.91	8.91	8.91	8.42	8.42	8.42	8.17	8.17	8.17
10	0.2	0.76	1.76	2.82	0.93	1.94	2.99	1.06	2.06	3.11
		9.88	9.88	9.88	9.76	9.76	9.76	9.65	9.65	9.65
	0.4	0.83	1.85	2.93	1.01	2.02	3.08	1.13	2.14	3,20
		10.20	10.20	10.20	10.02	10.02	10.02	9.87	9.87	9.87
	0.6	0.93	1.96	3,12	1.11	2.12	3.21	1.23	2.24	3.31
		10.51	10.51	10.51	10.23	10.23	10.23	10.03	10.03	10.03
	0.8	1.08	2.18	3.51	1,24	2.26	3.41	1.37	2.38	3.48
		10.91	10.91	10.91	10.42	10.42	10.42	10.17	10.17	10.17
12	0.2	0.82	2.12	3.87	0.99	2.28	4.02	1.11	2.39	4.13
		11.88	11.88	11.88	11.76	11.76	11.76	10.65	11.65	11.65
	0.4	0.93	2.30	4.04	1.08	2.41	4.16	1.20	2.51	4.25
		12.20	12.20	12.20	12.02	12.02	12.02	11.87	11.87	11.87
	0.6	1.12	2.55	4.29	1.21	2.59	4.33	1.32	2.66	4.40
		12.51	12.51	12.51	12.23	12.23	12.23	12.03	12.03	12.03
	0.8	1.51	2.99	4.72	1.41	2.85	4.60	1.48	2.87	4.62
		12.01	12.01	12.01	12.42	12.42	12.42	12.17	12.17	12.17

(1) At $\log K_{HL} = 2$, there is no concentration range within which the constants can be measured well.

(2) With increase of the $(T_L - T_H)/T_{Me}$ values, both the lower and the upper limit of the range of determination of the stability constants increase, i.e. more reliable data can be calculated from relatively low $\bar{n}$ values when weak complexes are studied, and from relatively large $\bar{n}$ values when stable complexes are studied. The lower limit of the range of determination of the stability constants varies almost in proportion to the total concentration of the ligand, i.e. it is preferable to use solutions with relatively high concentration when weak complexes are studied.

(3) Increase of the ratio T_L/T_{Me} narrows the range of stability constants that can be measured pH-metrically.

These findings naturally also follow from a qualitative consideration of complex equilibria; the data merely support the above conclusions quantitatively.

An example of the pH-metric study of an almost stoichiometric complex formation is provided by the Cu(II)–bipyridyl system [378]. The protonation constant of bipyridyl in 1 *M* KCl at 25 °C is 4.63, while the stability constant of the complex Cubipy^{2+} in the same medium is about 8.0. Accordingly, the 1 : 1 complex does not dissociate to an appreciable extent even in 1 *M* acid solution, and at $\mathrm{pH} > 1$ complex formation can be regarded as stoichiometric. The logarithm of the equilibrium constant for the process

$$\mathrm{Cubipy}^{2+} + \mathrm{bipy} \rightleftharpoons \mathrm{Cubipy}_2^{2+}$$

is about 6.0; when the pK value is taken into consideration, this similarly means nearly stoichiometric complex formation.

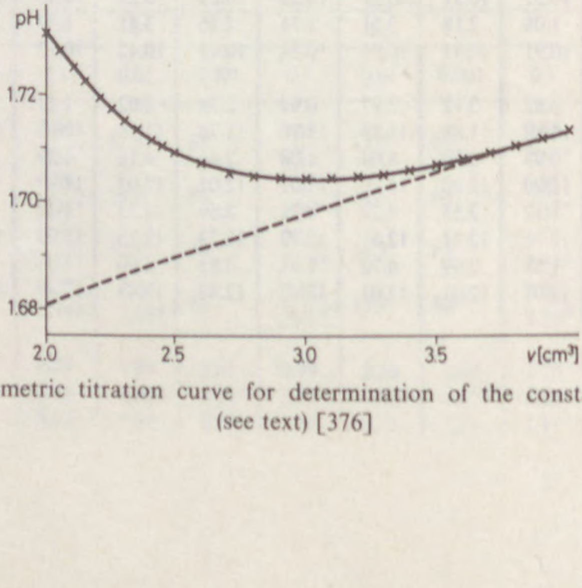

Fig. 4.58. pH-metric titration curve for determination of the constant $\log K^{\mathrm{Cubipy}}_{\mathrm{Cubipy}_2}$ (see text) [376]

Figure 4.58 illustrates results obtained when a solution with an initial volume of 25 cm^3 and with initial concentrations $T_H = 0.0234$ and $T_{bipy} = 0.020$ was titrated with 0.1268 M $CuCl_2$ solution. For the final points of the curve, $T_{Cu}/T_{bipy} < 1$, i.e. the complex formation can be considered definitely stoichiometric; calibration of the electrode system can be carried out on this section of the curve, therefore, since the H^+ concentration is known at every point. The theoretical titration curve characterizing stoichiometric $Cubipy_2^{2+}$ formation can be constructed on this basis (dashed line). Although the difference from this is very small in the interval $2 > T_{bipy}/T_{Cu} > 1$, it can be measured well in the given experimental set-up, and is suitable for the calculation of $\bar{n}$. This is illustrated in Fig. 4.59 too, which shows formation curve segments calculated from the data of titration curves obtained in a similar manner at various initial concentrations. The formation curve yields $\log K^{Cubipy}_{Cubipy_2} = 5.90$.

In connection with the application of pH-metry, it is to be noted that elevation of the pH leads to an increase not only in the free concentration of the ligand, but also in the OH^- concentration, i.e. studies of the complexes of metal ions liable to hydrolysis may run into difficulties. It is frequently necessary to apply a very high ratio T_L/T_{Me} in order to suppress hydrolysis.

Bjerrum [22] investigated ammine complexes in 2 M NH_4NO_3, i.e. at an extremely high value of T_L/T_{Me}. Nevertheless, pH-metric equilibrium studies in a high ligand excess (more than 10-fold) may be regarded as very rare exceptions [379]. The reason is that increase of the ligand excess has the consequence that the pH effect of the protonation equilibria increasingly approximates to, and may even exceed, the pH effect of formation of the metal complexes, and thus

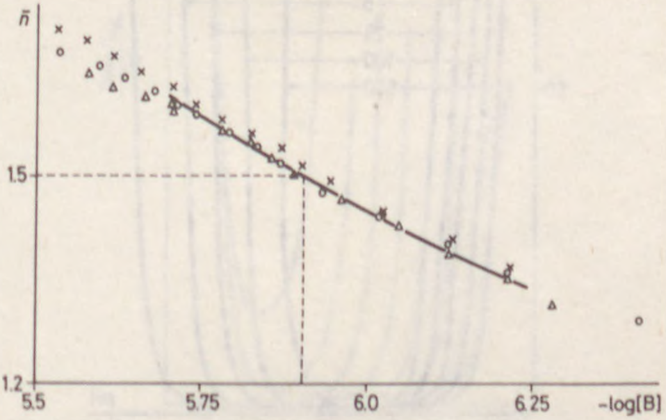

Fig. 4.59. Formation curve of the copper(II)-bipyridyl system in the interval $2 > \bar{n} > 1$ [376]

B = Bipyridyl, $T_{bipy} = 0.02$ M, $T_H/T_{bipy} = 1.20$ (×), 1.44 (○), 1.68 (△)

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the evaluation of titration curves for samples containing the metal ion becomes increasingly more uncertain.

The correctness of the above, qualitative considerations is beyond dispute, but the results of mathematical analysis show [380] that, under favourable conditions, pH-metry can be utilized successfully even when there is a ligand excess of more than 100-fold. With the assumptions that the ligand is to be found in the form HL in some equilibrium system, and that the metal in question forms only the complex MeL, Fábián and Nagypál [380] derived the following relationships

$$\frac{\partial \log \beta_{\mathrm{MeL}}}{\partial \mathrm{pH}} = -\left(1+\frac{[\mathrm{H}]+[\mathrm{OH}]}{[\mathrm{HL}]}\right)\left(1+\frac{[\mathrm{L}]}{\bar{n}(1-\bar{n})T_{\mathrm{Me}}}\right)-\frac{[\mathrm{H}]+[\mathrm{OH}]}{\bar{n}(1-\bar{n})T_{\mathrm{Me}}} \tag{4.96}$$

$$\frac{\partial \log \beta_{\mathrm{MeL}}}{\partial T_{\mathrm{H}}} = -\frac{2.303}{[\mathrm{MeL}]}-\frac{2.303}{\bar{n}(1-\bar{n})T_{\mathrm{Me}}\bar{n}_{\mathrm{H}}} \tag{4.97}$$

where $\bar{n}=[\mathrm{MeL}]/T_{\mathrm{Me}}$ and $\bar{n}_{\mathrm{H}}=[\mathrm{MeL}]/([\mathrm{L}]+[\mathrm{MeL}])$.

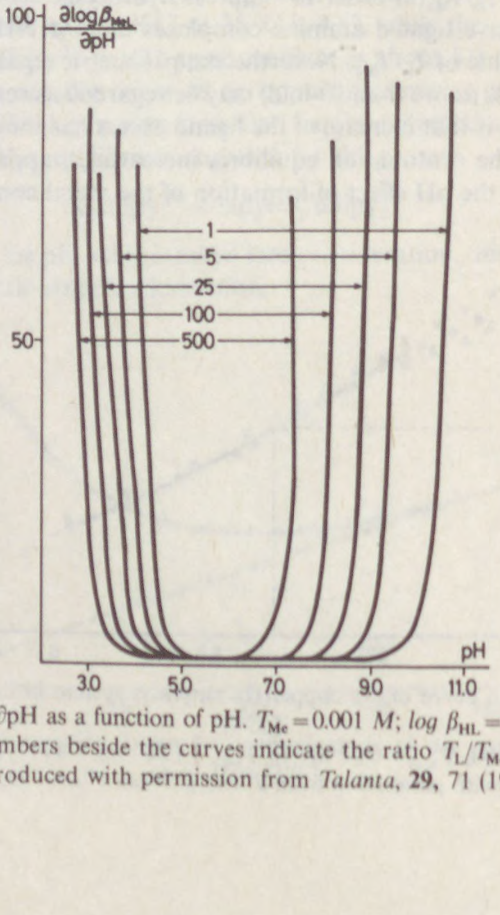

Fig. 4.60. $\partial \log \beta_{\mathrm{MeL}}/\partial \mathrm{pH}$ as a function of pH. $T_{\mathrm{Me}}=0.001$ *M*; *log* $\beta_{\mathrm{HL}}=12.0$; log $\beta_{\mathrm{MeL}}=8.0$. The numbers beside the curves indicate the ratio $T_{\mathrm{L}}/T_{\mathrm{Me}}$ [380]
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As an example, Fig. 4.60 presents $\partial \log \beta_{\mathrm{MeL}}/\partial \mathrm{pH}$ curves obtained at $\log \beta_{\mathrm{HL}} = 12$, $\log \beta_{\mathrm{MeL}} = 8$, $T_{\mathrm{Me}} = 0.001$ and various concentration ratios $T_{\mathrm{L}}/T_{\mathrm{Me}}$.

The Figure reveals that, as the ratio $T_{\mathrm{L}}/T_{\mathrm{Me}}$ is increased, the interval in which complex formation occurs and can be investigated pH-metrically shifts towards ever lower pH values. However, even with a ligand excess of 500-fold, the data obtained can be evaluated well in the range pH 4–6.

Figure 4.61 depicts the function $\partial \log \beta_{\mathrm{MeL}}/\partial \mathrm{pH} = f(\mathrm{pH})$ for a given value of the equilibrium constant for the process $\mathrm{HL} + \mathrm{Me} \rightleftharpoons \mathrm{MeL} + \mathrm{H}$, i.e. for the same differences $\log K_{\mathrm{HL}} - \log K_{\mathrm{MeL}}$, with a 250-fold ligand excess.

It may be observed from the Figure that the extremely high ligand excess can be employed only at $\log K_{\mathrm{HL}} > 7$, i.e. primarily in studies on metal complexes of ligands containing aliphatic amine and/or phenolic OH donor groups.

Figure 4.62 confirms that the value of $\partial \log \beta_{\mathrm{MeL}}/\partial T_{\mathrm{H}}$, i.e. the extent of the inaccuracy due to the error in addition of base solution, is not appreciably influenced by the large ligand excess.

Equations (4.96) and (4.97) and the presented Figures indicate two important conditions for the application of a large ligand excess:

(1) The ligand must be added to the system in a form such that the ratio $T_{\mathrm{H}}/T_{\mathrm{L}}$ should be strictly fixed in accordance with the rules of stoichiometry,

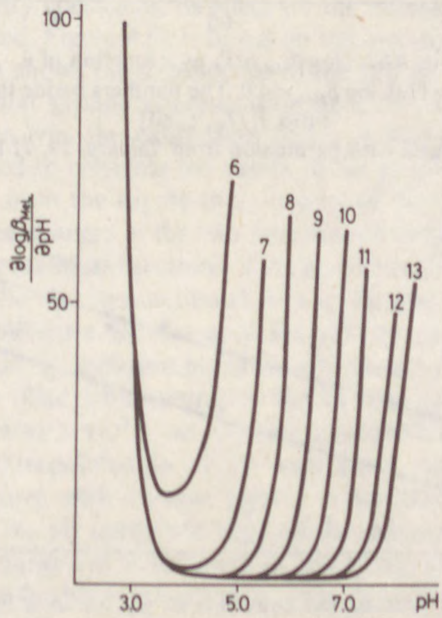

Fig. 4.61. $\partial \log \beta_{\mathrm{MeL}}/\partial \mathrm{pH}$ as a function of pH at fixed $\log \beta_{\mathrm{HL}} - \log \beta_{\mathrm{MeL}} = 4$, in a 250-fold ligand excess, for various values of $\log \beta_{\mathrm{HL}}$ [380]
(Reproduced with permission from *Talanta*, **29**, 71 (1982))

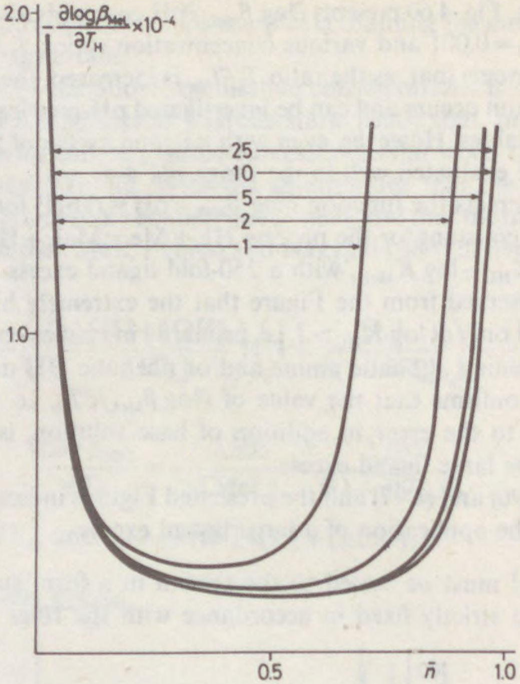

Fig. 4.62. $\partial \log \beta_{MeL}/\partial T_H$ as a function of $\bar{n}$.
$T_{Me} = 0.001$ *M*; $\log \beta_{HL} = 11.0$; $\log \beta_{MeL} = 4.0$. The numbers beside the curves indicate the ratio T_L/T_{Me} [380]
(Reproduced with permission from *Talanta*, **29**, 71 (1982))

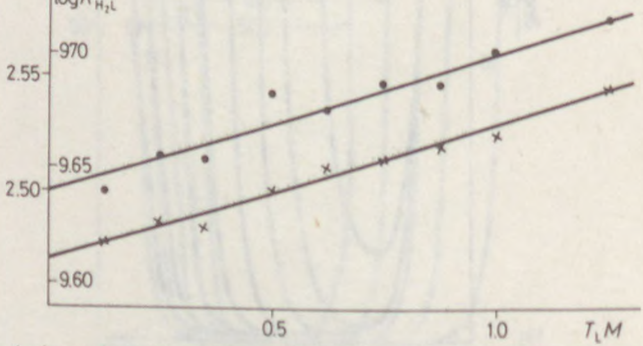

Fig. 4.63. Variation of protonation constants of glycine as a function of the ligand concentration, in 1 *M* $NaClO_4$ at 25 °C.
● — $-\log \beta_{HL}$; × — $-\log K^{HL}_{H_2L}$ [380]
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and thus, even if an error of some tenths of a per cent in the concentrations becomes comparable with the value of T_{Me}, the difference $T_H - T_L$ should be negligible compared to T_{Me}.

(2) Complex formation should occur in the pH interval in which the system is not buffered by the protonation equilibria of the ligand, i.e. when even the addition to the system of a quantity of base comparable to the quantity of the metal ion results in a considerable pH change. In the presence of metal ion, the pH change due to the same amount of base will be substantially smaller, because of the proton release accompanying complex formation, and a well measurable difference in the pH change, in the above manner, allows an exact evaluation of the titration curves.

Naturally, application of an extremely large ligand excess is justified only if the system under consideration can not be studied at the customary concentration ratios (1 : 1–1 : 10) because hydrolysis is accompanied by precipitate formation.

At an extremely large ligand excess, if the ligand concentration is not negligible compared to the concentration of the background electrolyte, the validity of the calibration of the electrode system also comes into question. Although a high concentration of the neutral ligand HA has scarcely any influence on the value of the activity coefficient, its effect on the diffusion potential difference cannot be neglected. Figure 4.63 is based on the investigations by Fábián and Nagypál [380]. It shows the dependence of the two protonation constants of glycine on the total glycine concentration at 25 °C, with 1 *M* $NaClO_4$ as background electrolyte, the calibration factor *A* found in glycine-free 1 *M* $NaClO_4$ being used to calculate the values of the protonation constants.

It may be seen from the Figure that, in spite of the fundamental difference between the charge changes in the two protonation processes, the protonation constants vary in parallel as functions of the glycine concentration. This finding lends support to the assumption that change of the glycine concentration does not appreciably influence the value of the activity coefficient, but it has a substantial effect on the diffusion potential difference for the given electrode, a calomel electrode filled with saturated NaCl. In a pH-metric study of the complex of glycine with VO^{2+}, an ion very susceptible to hydrolysis, protonation constants extrapolated to $T_L \to 0$ were used, but the titration curves recorded in solutions with various glycine concentrations were taken into consideration via the pH correction read off the diagram.

Only a few examples are to be found of pH-metric studies at an extremely large ligand excess; further work is required for the possibilities of the method to be elucidated more exactly.

The pH-metric analysis of more complicated systems and the pH-metric demonstration of complex formation demands even more careful experimental

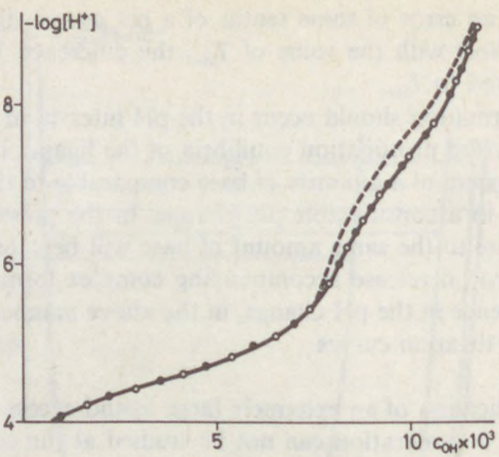

Fig. 4.64. pH-metric titration curve of the Ni(II)–glycine–L-histidine system at $T_{Ni} = T_{gly} = T_{hist} = 0.004\ M$.

●, ○ experimental points; ——— theoretical titration curve calculated with mixed complex formation considered; --- theoretical titration curve calculated with neglect of mixed complex formation [381]

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planning. This often necessitates 'theoretical' titration curves that can be calculated by neglecting the formation of some complex. Figure 4.64, based on work by Daniele and Ostacoli [381], presents the titration curve obtained experimentally in the Ni(II)-glycine-L-histidine system, and that calculated by neglecting mixed complex formation. Figure 4.64 shows clearly that mixed complex formation becomes significant at $pH > 6$, and the relevant formation constants are best calculated from the data around $pH \sim 7$.

In Fig. 4.65, the pH-metric titration curve recorded for the Cu(II)–asparagine system is compared with a theoretical titration curve [382] calculated on the assumption that only the complexes MeA and MeA_2 are formed in the system, and that following this the value of the pH is governed merely by the protonation equilibrium of the excess ligand. It is obvious from the difference between the curves that the complex CuA_2 loses proton at $pH > 10$, yielding the complex CuA_2H_{-1}, or possibly CuA_2H_{-2}. These latter complexes probably contain the acid amide group in deprotonated form; in other words, complex formation leads to the loss of proton from a ligand group which does not undergo dissociation in the measurable pH interval in the absence of metal ion.

The literature contains a very large number of examples of the application of pH-metry in equilibrium chemistry; the scope of this book does not permit us to mention all of the important work. Accordingly, we refer the reader only

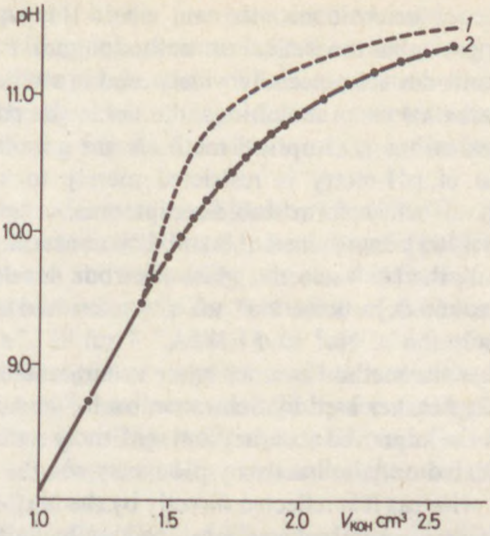

Fig. 4.65. Titration curve of copper(II)–asparagine system in the interval pH 8–11.5 [382]. *1* — Theoretical titration curve, assuming formation of HL, H_2L CuL and CuL_2; *2* — experimental titration curve. $T_L = 8.00 \times 10^{-3}$ *M*; $T_{Cu} = 2.50 \times 10^{-3}$ *M*; [KOH] = 0.1351 *M*; $V_0 = 25$ cm³ [382]
(Reproduced with permission from *J. Inorg. Nucl. Chem.*, **37**, 551 (1975))

to some of the original publications, which are particularly noteworthy for various reasons: the novelty of the technical or computational solutions, the complexity of the system in question, or the nature of the interactions [383–396].

4.9.2 Application of metal and ion-selective electrodes

The use of ion-selective electrodes in equilibrium chemistry has become general only in the past 10 years, whereas metal electrodes (amalgam electrodes) have been applied in equilibrium chemistry for a much longer period. The basic principle of application is the same as in the case of pH-metry: in the knowledge of the total concentrations, the equilibrium concentrations are measured, and the differences between the two quantities are used to draw conclusions on the compositions and stabilities of the complexes formed. We shall not dwell on the technical details of work with ion-selective electrodes, for their importance in analytical chemistry has led to this field being dealt with in a number of reviews [397–400], while the methods of preparation and handling of metal electrodes or amalgam electrodes are also well known [401–402]. In this section we shall primarily discuss examples of application where the basic aim was the determination of equilibrium constants, and where this was attained by the introduction of appreciable theoretical or methodological innovations.

Ion-selective electrodes are especially widely used in studies on complexes of alkali metal and alkaline earth metal ions; the noble gas configuration of the electronic structure means that optical methods are generally not applicable here, and the use of pH-metry is restricted merely to studies concerning polyfunctional ligands which form stable complexes.

In 1963, Palaty [403] determined the stability constant of the Na–EDTA complex by utilizing the Na^+-selective glass electrode developed by Eisenman *et al.* [404]. Figure 4.66 depicts the Na^+ activity measured as a function of pH in an equimolar solution of Na^+ and EDTA.

Palaty stated that the method is much more accurate and sensitive than the pH-metric procedure earlier used by Schwarzenbach and Ackerman [405]. An obvious reason for the improved accuracy and sensitivity is that the Na^+–EDTA interaction is indicated only indirectly by pH-metry, via the competition chain Na^+–EDTA–H^+, whereas it is reflected directly by the Na^+-selective electrode.

A potential-comparison method was developed by Rechnitz and Zamochnick [406] for study of the Na^+–citrate and Na^+–malate interactions. The essence of the method is that concentrated NaCl solution was added to a solution containing the dissociated forms of the ligands until the measured potential agreed exactly with the potential of a solution of known Na^+ concentration, not containing ligand. The formation constants of the 1:1 complexes can be calculated by means of a direct formula from the titration data and the quantities added.

Dunsmore and Midgley [407] calculated the formation constant of the Na^+–tartrate complex directly from the data relating to titration with NaCl

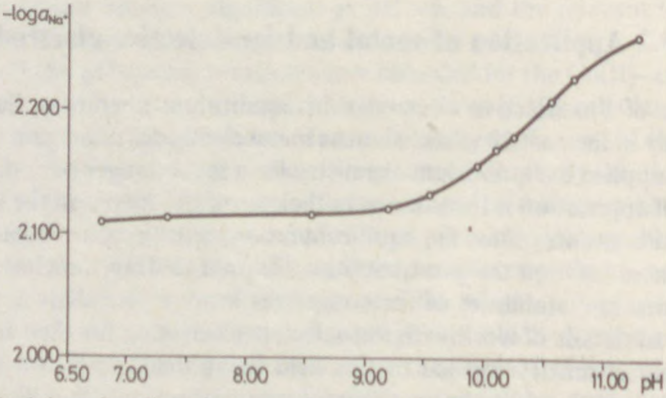

Fig. 4.66. Activity of sodium ion as a function of pH in the presence of equimolar EDTA (10^{-2} *M*) [403]
(Reproduced with permission from *Can. J. Chem.*, **41**, 18 (1963))

solution. Their paper, which provides detailed experimental data, clearly demonstrates the difficulties encountered in the study of the weak Na^+–tartrate interaction, even when use is made of an ion-selective electrode reflecting the interaction directly; the e.m.f. change due to complex formation is generally about 1 mV, while the standard deviation of the individual measurements is 0.33 mV.

Ion-selective electrodes were employed by Frensdorff [408] to determine the stabilities of complexes of alkali metal ions with cyclic polyethers (crown ethers) with various ring sizes and containing various substituents. He found that the number of ring atoms necessary for formation of the most stable complexes was 15–18 for Na^+, 18 for K^+, and 18–21 for Cs^+. Replacement of the ring oxygen donor by nitrogen or sulphur resulted in decreased affinities for the alkali metal ions, and in an increased affinity for the Ag^+ ion. A surprising, but clear-cut finding from Fig. 4.67 is that K^+ and Cs^+ ions in methanolic medium undergo coordination to two molecules of crown ethers with ring sizes smaller than the optimum.

In an investigation of the Ca^{2+}–ATP system with a Ca^{2+}-selective electrode, Mohan and Rechnitz [409] demonstrated the formation of the binuclear complex Ca_2ATP.

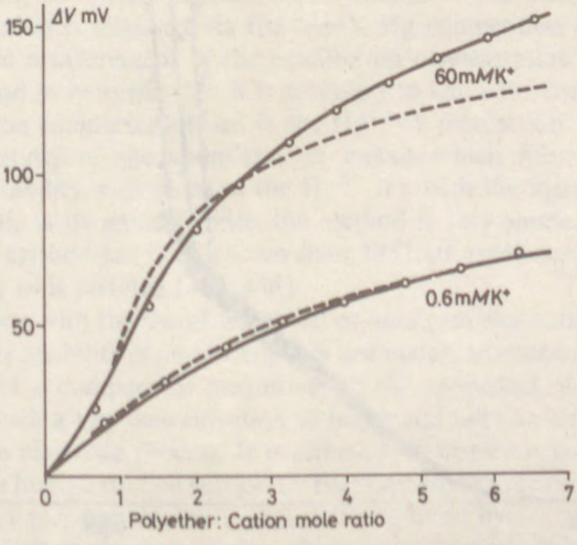

Fig. 4.67. Titration of KCl with the macrocycle cyclohexyl-15-crown-5. The numbers on the curves denote the starting concentrations of KCl. The points are experimental data. The continuous line is the best-fitting theoretical curve calculated with $K_1 = 3900$ and $K_2/K_1 = 0.02$, while the dashed line is that calculated with $K_1 = 4500$ [408] (Reproduced with permission from *J. Am. Chem. Soc.*, **93**, 600 (1971))

Nakamura *et al.* [410, 411] utilized Li^+ and Na^+-selective glass electrodes to study the 'transsolvation' equilibria with various solvents of Li^+ and Na^+ dissolved in acetonitrile. The diagrams they report convincingly show that the process of transsolvation, at least in the first 2–3 steps, can be described satisfactorily with the equilibrium constants and functions characterizing stepwise complex formation. Apart from cation-selective electrodes specific for alkali metal and alkaline earth metal ions, the copper(II)-selective electrode finds very important applications in equilibrium chemistry. It is surprising that use of the copper(II)-selective electrode initially led to findings in contradiction with the fundamental rules of solution equilibrium chemistry [412, 413], and these were therefore rightly criticized [414]. Thanks to the work by Hansen and Ruzicka [415], Nakagawa *et al.* [416], McBryde *et al.* [417] and Baumann [418], the possibilities, advantages and limitations of the application of copper(II)-selective electrodes in equilibrium chemistry are now well known.

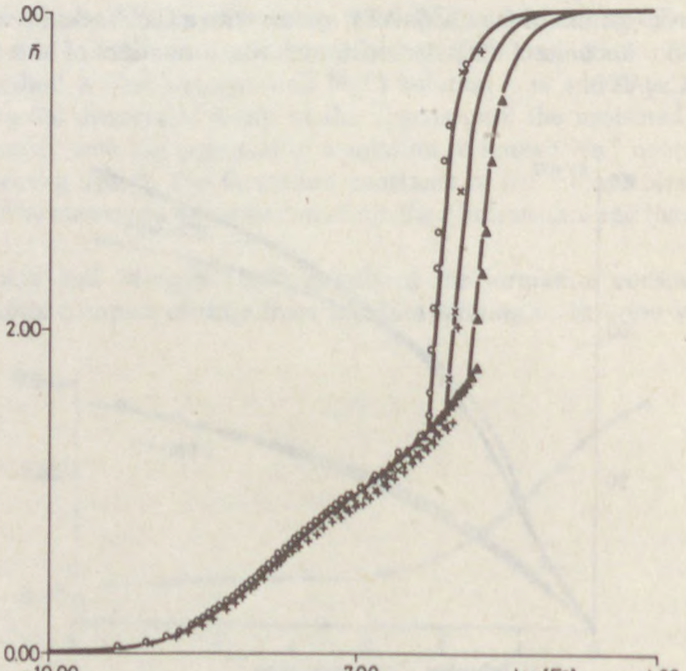

Fig. 4.68. Experimentally measured formation curves for the Th(IV)–F^- system [420]. The points are the experimental data for various metal ion concentrations. The continuous lines denote the theoretical curves in which the solubility equilibrium of ThF_4 and stepwise complex formation are taken into account simultaneously (Reproduced with permission from *Inorg. Chem.*, **10**, 740 (1971))

As concerns the anion-selective electrodes, the most generally applied is the F^--selective electrode, which is ideally suited for the study of fluoro complexes [419–427]. Through the use of a F^--selective electrode, Klotz *et al.* [420] determined not only the equilibrium constants of the stepwise complex formation processes in the Th^{4+}–F^- system, but also the solubility product of ThF_4. Their experimentally found formation curves, and those calculated theoretically by taking into consideration simultaneously stepwise complex formation and the solubility equilibrium, are depicted in Fig. 4.68. The break-points in the curves lie at that solution composition where the heterogeneous equilibrium appears besides the homogeneous equilibria, i.e. ThF_4 begins to precipitate out.

Of the anion-selective electrodes, the Cl^-, Br^- and I^--selective electrodes are also suitable for equilibrium analysis [428, 429], but secondary Ag/AgX electrodes too may be used to measure the activities of these ions or, in the event of appropriate calibration, their concentrations [430].

Only a few metals, primarily with an electronic configuration close to the d^{10} structure, are suitable for the preparation of metal or amalgam electrodes which function reversibly and display a reproducible potential. Of the various possibilities of application of metal or amalgam electrodes in equilibrium chemistry [431–457], the pHg method devised by Schwarzenbach and Anderegg [457] is worthy of special attention. The essence of the method is that the Me–Y interaction is followed via the Me–Y–Hg competition chain, through potentiometric measurement of the equilibrium concentration of Hg^{2+} ions. For the method to be applicable, it is necessary to know the compositions and stabilities of the complexes formed in the Hg^{2+}–Y interaction. The method is suitable for study of the complexes of metals which form complexes of comparable stability with those of the Hg^{2+} ion with the ligand in question. It is clear that, as its name implies, the method is very similar to pH-metry. Although the method has been known since 1957, its application has not been as widespread as is justified [442, 458].

In connection with the use of metal ion or amalgam electrodes, doubts may arise as to the possibility of measuring very low metal ion concentrations, which are at times of a comparable magnitude to the reciprocal of the Avogadro number, for such a low concentration of free metal ion can clearly not result in a reversible electrode process. It is self-evident, however, that it is not the free metal ions but the studied complexes that take part in the electrode reaction governing the e.m.f.; consequently, the e.m.f. expressed by the Nernst equation varies *as if* the electrode were immersed in a solution with the very low metal ion concentration concerned. This finding, which also follows from thermodynamic considerations, must be stressed, for the possibility of measuring very low metal ion concentrations has led to debate even very recently [444, 459].

The field of application of redox electrodes is restricted to studies on the complex-forming processes of merely a few metal ions. The principle of the method is presented on the basis of the work of Dellien [460], who investigated the Fe(III)–oxalate and Fe(III)–malonate systems by measuring the potential of the Fe^{2+}/Fe^{3+} redox system. As a consequence of the relatively low stability of Fe^{2+} complexes in these systems, the stabilities of the oxalato and malonato complexes could be determined pH-metrically via the H^{+}–L^{2-}–Fe^{2+} competition chain. The Fe^{3+} ion reacts practically stoichiometrically with these ligands in the measurable pH interval, however, and it is also very susceptible to hydrolysis, so that its complexes can not be examined pH-metrically. The e.m.f. measurable in a solution containing known concentrations of Fe^{2+}, Fe^{3+}, ligand and proton depends not only on the stabilities of the Fe^{2+} complexes and the pK values of the ligands, but also on the stabilities of the Fe^{3+} complexes. In the knowledge of the above data, the stabilities of the Fe^{3+}-oxalato and Fe^{3+}-malonato complexes can be calculated. It is obvious that, similarly to pH-metry and the pHg method, the application of redox electrodes is based on competition, but the ions participating in this competition are ions of the same element in different oxidation states [461–463].

The use of concentration cells for the study of equilibrium processes has achieved prominence in the past 10 years. Tedesco and Anon [464], for instance, employed the following concentration cell to investigate the acetato and propionato complexes of the Th^{4+} ion, which is very prone to hydrolysis and can therefore not be studied pH-metrically

$$\begin{array}{c|c||c|c} \mathrm{Hg/Hg_2Ac_2} & \mathrm{Acetate} & \mathrm{Acetate} & \mathrm{Hg/Hg_2Ac_2} \\ & \mathrm{Propionate} & \mathrm{Propionate} & \\ \mathrm{Hg_2Pr_2} & T_1 & T_2 & \mathrm{Hg_2Pr_2} \end{array}$$

Pr = propionate; T_1 and T_2 = total concentrations; pH = 2.00. If T_2 is varied at constant T_1, each individual T_2 defines an e.m.f. Thus, in the knowledge of the pH and the dissociation constant of the corresponding acid, the correlation can be given between the e.m.f. and the free ligand concentration in the sample. When Th^{4+} ion is added to the sample, the free ligand concentration decreases; the change can be followed by measurement of the e.m.f., and hence all of the data necessary for calculation of the formation constants are available. This method allowed determination of the stability constants of the relatively not too stable Th-acetato and Th-propionato complexes at a 5–15-fold ligand excess without the disturbing effect of hydrolysis. The method has the obvious advantage over pH-metry that the L^{-}–Th^{4+} interaction is followed not indirectly, via the H^{+}–Ac^{-} equilibrium at the given concentrations, i.e. relatively insensitively, but directly, via comparative measurements of the L^{-} concentrations. A similar principle was utilized by Koul and Dubey [465] to determine the formation constants of the bis-thiosalicylato–Hg(II) complexes with Hg electrodes, and by Molina and Tabak [466] to determine those of the Ag(I)–pyridine complexes with Ag electrodes.

Gal *et al.* [467–470] studied the formation of halide complexes of Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} in aqueous melts of NH_4NO_3 and $Ca(NO_3)_2$–NH_4NO_3, with the appropriate Ag/AgX electrodes connected as concentration cell.

4.9.3 Measurements with two electrodes

Potentiometric measurements with two electrodes generally provide much more reliable information than do studies with a single electrode on the system in question. Although measurements with two electrodes of the changes in the equilibrium concentrations of two different components must be in correlation with one another, it frequently occurs (an example has already been seen above) that in a certain range of the total concentrations the potential of some electrode does not respond sensitively to the processes taking place, particularly if the process in question exerts its effect not directly, but via a competition chain. When two electrodes are used, the danger of this is much less, and thus equilibrium measurements may be made in a much wider concentration interval.

One of the two electrodes is usually the glass electrode or, during studies of the interactions of F^- ions, some other pH-sensitive electrode [471]; there are barely any examples of the combined application of metal ion and ligand-sensitive electrodes [472]. The basic principles of measurements with two sensing electrodes do not generally differ from those of equilibrium measurements with a single electrode. Accordingly, we refer only to a few of the representative publications [473–490], and give a somewhat more detailed account of the potentiostatic method developed by Österberg [491], which is of outstanding importance in its conceptions and from the aspects of measurement and computation. The essence of the method is that the total concentrations of two components are varied in the course of the titration, but in such a way that the equilibrium concentration of one of the components should always remain constant. When the pH-static method is used, for instance, metal ion is added to a starting ligand solution adjusted to some constant pH. As a result of the addition, of course, the pH too changes. Subsequently, the initial pH is restored with base solution or with an appropriate buffer solution prepared from the ligand, and the equilibrium concentration of the metal ion is measured. The titration is then continued by the addition of the next dose of metal ion solution. The procedure is altered accordingly when the pMe-static method is applied.

The method clearly has the great advantage that, in the quantitative description of titration curves obtained at constant pH (or pMe), all associations the concentrations of which can be expressed by the relation $\beta_{pqr}[H]^p[A]^q[Me]^r$

can be accounted for in the form $\beta'_{qr}[A]^q[Me]^r$, since $\beta_{pqr}[H]^p$ = constant. Hence, the behaviour is similar to that observed if the system contains one fewer component. This description mode simplifies both the evaluation and the survey of the equilibrium conditions in the system. The method has primarily been utilized to study very complicated equilibrium systems [492–496]. Its widespread application is certainly impeded by the fact that an instrument suitable for the experimentation is not available commercially, though it can be built in the laboratory comparatively simply.

4.10 Polarography

There are certain similarities between the applications of polarography and potentiometry in equilibrium chemistry, although the redox processes occurring on the surface of the dropping mercury electrode are generally much more complex than those in the case of potentiometry. Because of the simplicity of the polarographic measurement technique and the great variety of possibilities for its application, this method too is used very widely; a number of reviews have appeared on this topic [497–500].

If a reversible electrode process is assumed, the potential of the dropping mercury electrode may be given by the Heyrovsky–Ilkovič equation:

$$E=(E_{1/2})_s-\frac{RT}{zF}\ln\frac{i_d}{i_d-i} \tag{4.98}$$

where $(E_{1/2})_s$ is the half-wave potential relating to the solvated (hydrated) metal ion, z is the change in electron number in the electrode process, i_d is the diffusion current, and i is the current strength relating to the given potential E. Heyrovsky and Ilkovič observed and correctly interpreted the phenomenon that complex formation gives rise to a shift of the half-wave potential towards more negative values. Lingane [501] found that the following correlation holds between the potential shift and the composition and stability of the complex MeL_n that is formed

$$E_{1/2}=(E_{1/2})_s-(E_{1/2})_c=\frac{2.303\,RT}{zF}\log\beta_n+\frac{2.303\,RT}{zF}n\log[L] \tag{4.99}$$

where $(E_{1/2})_c$ is the half-wave potential characterizing the complex in question at the given free ligand concentration. Equation (4.99) indicates that a plot of $E_{1/2}$ vs. $\log[L]$ yields a straight line, from the intercept and slope of which $\log\beta_n$ and n, respectively, can be determined. In the derivation of the equation, it is assumed that the hydrated (solvated) metal ion and the complex MeL_n have identical diffusion coefficients, and that the values of the activity coefficients do not change either. If the diffusion coefficient does change, which can be followed through measurement of i_d, an appropriate correction must be made. Equation (4.99) can be used only if a single complex is formed (generally that with maximum coordination number). If complex formation proceeds in a stepwise manner, in steps that are well separated from one another, the $E_{1/2}$ vs. log [L] diagram can be broken down into several linear sections. When the complex formation steps overlap, however, the $E_{1/2}$ vs. log [L] curve varies continuously; in this case, the method devised by DeFord and Hume [502] can be used, the basic equation of this being

$$\text{antilog}\left(\frac{0.4343\ zF}{RT}\Delta E_{1/2}+\log\frac{I_s}{I_c}\right)=\sum_0^N \beta_i[\text{L}]^i \qquad (4.100)$$

where I_s and I_c are the diffusion constants characterizing the free metal ion and the complex equilibrium system at the given [L], respectively. It can readily be seen that the right side of Eq. (4.100) expresses the value of T_{Me}/[Me], i.e. the free concentration of the metal ion can also be calculated from the polarographic data if T_{Me} is known. If the numerical values of I_s and I_c are assumed to be the same, it can further be seen that the change in the polarographic half-wave potential corresponds exactly to the potential change exhibited by a metal ion-selective or amalgam electrode when the metal ion concerned passes from a solution with concentration T_{Me} into a solution of the complex equilibrium system with free metal ion concentration [Me].

Besides the above similarity, there is another essential analogy between polarography and potentiometry: a reversible polarographic step is displayed by those metal ions with an electronic structure close to the d^{10} configuration from which a reversibly functioning metal or amalgam electrode too can be prepared. The majority of polarographic equilibrium measurements involve studies of the stepwise complex formation of metal ions that undergo reversible reduction on the surface of the dropping mercury electrode [503–517]. Since the left-hand side of Eq. (4.100) gives T_{Me}/[Me] not only in the case of stepwise complex formation, but also in more complicated systems, the method may logically be extended to the determination of the equilibrium constants of mixed ligand complexes [518–522].

Apart from determination of the numerical values of the formation constants in certain complex equilibrium systems, polarography is also suitable for studies on the kinetics of exchange reactions in these systems [523, 524]. It can also be used to study complexes of outer sphere type [525–527], and as an analytical chemical method to determine the individual concentrations of the ionic species present in the equilibrium system, which similarly permits calculation of the equilibrium constant [528].

Tamamushi and Tanaka [529] attempted to utilize the polarographic method for the investigation of complexes of irreversibly reducing metal ions. Their procedure has not become widespread, however, primarily because the ion-

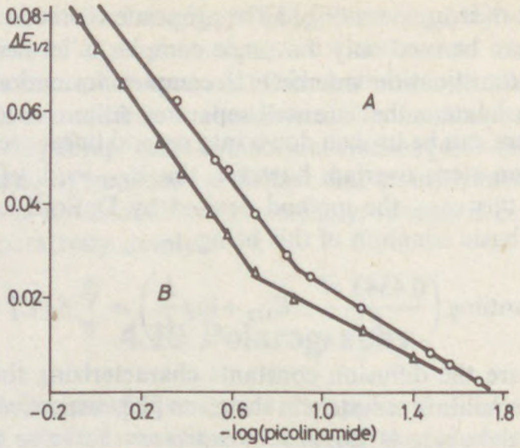

Fig. 4.69. $\Delta E_{1/2}^{\mathrm{Cd}}$ vs. $-\log$ (picolinamide).
A — $T_{\mathrm{Cd}} = 5 \times 10^{-4}$ M; B — in the presence of 0.05 M $\mathrm{Ni(NO_3)_2}$ [532]
(Reproduced with permission from *J. Coord. Chem.*, **2**, 281 (1973))

indication method put forward by Ringbom and Eriksson [530] proved of much more general validity. The method is essentially based on competition, in which the irreversibly reducing metal ion to be studied, $\mathrm{Me_1}$, the ligand in question, L, and a metal ion reducing reversibly at a more positive potential than the metal ion under study, $\mathrm{Me_2}$, take part. Polarographic examination of the interaction $\mathrm{Me_2}$–L is followed by study of the system $\mathrm{Me_2}$–L–$\mathrm{Me_1}$; because of the presence of $\mathrm{Me_1}$, a change occurs in the half-wave potential of $\mathrm{Me_2}$, and from this conclusions can be drawn as to the interaction $\mathrm{Me_1}$–L. It was recently proved by Tedesco [531] that it is not necessary to know the equilibrium constants for the system $\mathrm{Me_2}$–L in order to determine those for the system $\mathrm{Me_1}$–L. As an illustration of the method, based on the work by Ma *et al.* [532], Fig. 4.69 shows $\Delta E_{1/2}$ vs. log [L] functions obtained in a solution containing 5×10^{-4} M T_{Cd} in the presence and in the absence of 0.05 M $\mathrm{Ni(NO_3)_2}$.

In the absence of $\mathrm{Ni^{2+}}$, the total picolinamide concentration practically agrees with the free concentration (Curve A). In the presence of $\mathrm{Ni^{2+}}$, however, this relation no longer holds; for some $\Delta E_{1/2}$ value relating to Curve B, the free ligand concentration too can be read off Curve A, and the value of $\bar{n}$ may be calculated from the difference between the total and free concentrations. This method has recently been employed mainly by Tedesco *et al.* [533–535]; the possibilities afforded by the method are probably not yet sufficiently well known.

4.11 Other methods

Besides the generally used methods described in the previous sections, numerous other physico-chemical methods of measurement are suitable, or may be adapted so as to be suitable, for the determination of equilibrium constants. The possibilities for their application are limited, however, as they each relate only to a well-defined group of equilibrium systems; accordingly, we give only a very brief account of the individual procedures, and refer the reader to the original publications for the details.

Interactions between anionic ligands and metal ions are accompanied by changes in the conductivities of the solutions. Thus, measurement of the conductivity is one of the most obvious methods of studying equilibrium processes. An excellent survey of the equilibrium chemical aspects of the method has been published by Davies [536]. The method has the unavoidable drawback that a background electrolyte ensuring the standard state can not be used, and changes in the equilibrium concentrations are therefore always accompanied by changes in the activity coefficients. For this reason, if more than one complex is formed, quantitative evaluation of the experimental data encounters virtually insoluble theoretical and computational difficulties. Even when only a single ion-pair is formed, three parameters must be calculated from the conductivity–concentration data pairs: the molar conductivity relating to an infinitely dilute solution, the formation constant of the ion-pair, and the "distance of closest approach" of the individual ions within the ion-pair. It was pointed out by Beronius [537, 538] that this calculation does not always lead to a clear-cut result: the deviations calculated from the measured and calculated conductivities may display two minima corresponding to fittings with almost the same goodness at considerably different parameter values. Figure 4.70 gives level diagrams obtained during the evaluation of experimental results relating to tetrabutylammonium perchlorate dissolved in propanol [537]. It can readily be seen that the experimental data can be described with nearly the same accuracy at two essentially different values of *R*, the distance of closest approach.

In spite of the above difficulties, the measurement of conductivity is used widely, e.g. for the quantitative study of ion association in various solvents [539–545], for determination of the stoichiometric compositions of the complexes formed [546, 547], for the detection of associations formed between coordinately saturated metal complexes through the 'residual coordination strength' [548], for comparison of the basicities of peptide bonds [549], etc.

High-frequency conductometry can similarly be used for determination of the stoichiometric composition in stable complexes [550–552].

An obvious method for the equilibrium study of complexes containing optically active ligands is polarimetry. The relation describing the rotatory power of a solution is formally exactly the same as the Bouguert–Lambert–Beer

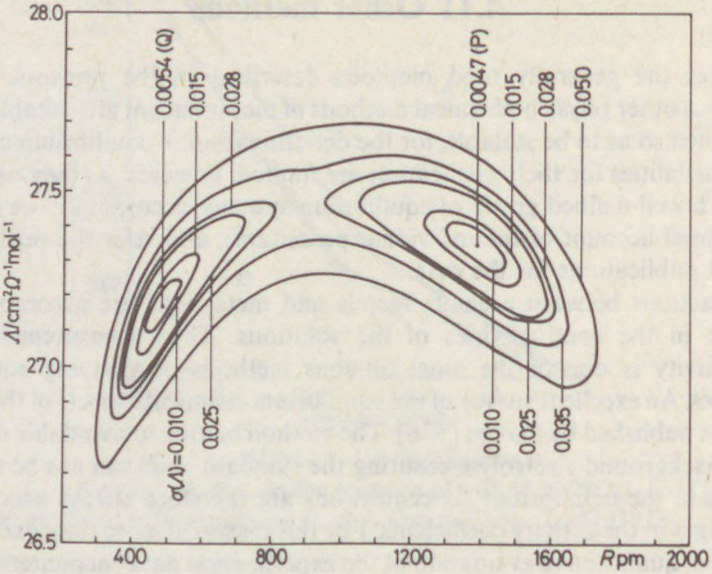

Fig. 4.70. Level diagram obtained during evaluation of conductivity data on tetrabutyl perchlorate dissolved in propanol [537]
(Reproduced with permission from *Acta Chem. Scand.*, **A29,** 289 (1975))

equation, the difference being merely that the proportionality factor is the molar rotatory power instead of the molar absorbance. Thus, polarimetry can be applied under the same conditions and according to the same considerations as those discussed in connection with spectrophotometry. The theoretical difference is that in photometry the change taking place in the electronic structure of the metal ion is generally, but not exclusively, responsible for the change in the spectrum, whereas in polarimetry the change in the rotatory power is caused by the change in the electronic structure of the ligand.

Polarimetry has been employed, for example, to determine the dissociation constants of the carboxyl and OH groups of tartaric acid [553–555], the dissociation constants of some amino acids, and the stability constants of certain metal complexes [556–563]. The equilibrium chemical aspects of the method were recently reviewed by Petit-Ramel and Paris [564].

Infrared spectrophotometry is essentially a similar method to visible-ultraviolet photometry, though the measurement technique is substantially different. Its great advantage over visible-ultraviolet photometry is that the bands relating to the individual associations formed in the equilibrium processes are generally much better separated; thus, the concentration ratios can be directly calculated from the ratios of the integrated intensities, which simplifies the evaluation considerably. A further advantage is that valuable information on the structures of the complexes formed may be obtained from the band shifts. However, it has the unavoidable drawback that the bands of the solvent may overlap an appreciable part of the spectrum, so that the method can be applied only under very favourable conditions. If the bands due to the individual species overlap one another extensively, evaluation of the results may be promoted by band resolution or by the various methods discussed in section 4.2. Infrared spectrophotometry has been utilized primarily to determine the formation constants of cyano and thiocyanato complexes [565–569], and of hydrogen-bonded associations formed in water [570] and in non-aqueous solvents [571, 572].

Raman spectroscopy is applied relatively widely for equilibrium investigations. Following discovery of the method, it was used by Rao [573] to study the dissociation of nitric acid. It was first utilized for the study of complex equilibria by Delwaulle *et al.* [574–578]. The bands of the individual associations generally appear separate from one another in the Raman spectra, and following band resolution the equilibrium constants may be calculated from the ratios of the integrated intensities via a direct formula. The method has the disadvantage that it is usually necessary to work at very high concentration, and thus the standard state can not always be ensured. The method is extensively applied for the investigation of various parent and mixed ligand halogeno complexes [574–591] and the complexes of other simple anionic ligands [592–601], in aqueous, non-aqueous and melt phases, and also for equilibrium studies on associations linked by hydrogen-bonds [602, 603].

Very narrow bands are observed in the infrared and Raman spectra (compared to the bands appearing in the visible-ultraviolet region), and this permits calculation of the concentration ratios following band resolution. However, it is known that very narrow absorption bands (which vary sensitively in response to complex formation) also appear in the low-intensity electronic excitation spectra of certain rare earth metals. Accordingly, the bands resolved by Gaussian analysis in these systems too may be suitable for the direct calculation of the concentration ratios, or the integrated intensities (oscillator strengths) of the bands arise as the sum of the molar integrated intensities relating to the individual complexes, weighted in accordance with the concentrations. This was utilized by Bukietynska *et al.* [604] to devise a method based on measurement of the oscillator strength, which is suitable for equilibrium studies on the complexes of lanthanides with electronic structures f^2–f^6 or f^7–f^{12}.

The electrophoretic migration rate depends to a large extent on the charges of the ions, which vary as a consequence of complex formation or other equilibrium processes. Hence its measurement can similarly be used to determine equilibrium constants [605–607].

Wallace [608] developed a procedure for the equilibrium study of metal complexes of anionic ligands, based on the shift of the Donnan equilibrium as an effect of complex formation. The results obtained on the UO_2^{2+}–SO_4^{2-} system agreed well with the data found with other methods.

In addition to what has been discussed above, a few examples are to be mentioned where equilibrium constants are determined via other means: measurement of the polarographic diffusion current [609], chronopotentiometry [610], cyclic voltammetry [611], gas chromatography [612–617], density measurement [618–623], magnetic susceptibility measurement [624], emission titration [625], measurement of the self-diffusion coefficient [626], positronium annihilation [627], and pressure measurement in the case of gaseous ligands [628, 629].

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Chapter 5

Evaluation of experimental data

By the evaluation of the experimental data, we mean the series of calculations whereby various mathematical and computational methods are used to determine the compositions and stability constants of the complexes exerting significant effects on the measured data. We shall not deal in this chapter with evaluation of the constants from chemical aspects; certain questions relating to this will be discussed in the next chapter.

Before giving an account of the details of the numerical evaluation, we must define when the effect exerted on the experimental data by the formation of some complex can be regarded as significant. It is obvious that this is not merely dependent on the maximum mole fraction of the species in question; it also depends on how sensitively the experimental data vary in response to a change in the mole fraction. For instance, if one of the complexes is formed in very low concentration because of the various disproportionation reactions (discussed in Section 3.3), but if its molar absorbance or its catalytic effect on some indicator reaction is several orders of magnitude higher than those of the other complexes, then its formation constant may possibly be determined accurately in spite of the low concentration. At the same time, if the spectrum of one of the complexes coincides with the average of the spectra of the complexes containing one fewer and one more ligand, for example, then it is not certain that the complex in question can be detected at all, even if it is formed in appreciable concentration. As a consequence of stepwise complex formation, the electronic structure of the metal ion also varies in a 'stepwise' manner, and this possibility cannot simply be ignored if one of the complexes cannot be detected spectrophotometrically.

If a system H–L–Me is studied in a ligand excess with a pH-potentiometric method, the effect of reaction

$$\mathrm{MeLH_{-1} + L \rightleftharpoons MeL_2H_{-1}}$$

occurring in the pH range higher than the pK value of the ligand, will be scarcely detectable pH-metrically, even if other equilibrium processes need not be considered. The reason is that the coordination of L in this pH range is not accompanied by the release of hydrogen ion, so that the above equilibrium influences the experimental data only indirectly and to a very slight extent. In contrast, if a complex is formed at pH ~ 7, for instance, and the protonation equilibria of the ligand do not display a significant buffer effect in this range, there will be a well-measurable change in the pH of the solution even if complex formation proceeds to only a very slight extent.

To summarize, it may be stated that the effect of a complex is significant if its formation causes the directly measured data to change to an essentially larger extent than (3–10-fold) the limit of experimental error.

The aim of equilibrium studies is to determine the compositions and stability constants of the species formed in appreciable concentration in the system in question. However, as demonstrated by the earlier examples, the compositions and stabilities of those complexes that significantly influence the measured data can be calculated via the methods of numerical analysis. The two series of complexes defined as above do not always coincide. In such cases it is necessary to apply different experimental methods simultaneously. We are much more likely to obtain correct results in this way than if we attempt to refine the mathematical and computational aspects of the evaluation.

Numerous authors have dealt with this topic in the past 20 years [1–20], and the results have been discussed in several reviews [21–23]. A number of general programs are available [24–30], by means of which practically any type of equilibrium chemical measurement series can be evaluated. In this chapter, therefore, we shall merely touch on the various computational methods and programs. We shall concentrate mainly on questions concerning the choice of the appropriate equilibrium model, the strategy of the evaluation, and the correlations between the experimental and the evaluation methods, and we shall also discuss the possibilities of error if the general methods and programs are not applied with sufficient circumspection.

5.1 Determination of compositions of complexes formed

5.1.1 Experimental considerations

During the discussion of the individual experimental methods in Chapter 4, it emerged that a reliable equilibrium model and constant series is to be expected only if the aspects relating to the later evaluation are already taken into consideration in the course of the planning of the experiments. Moreover, the experimental technique, the measurement method, the concentration ranges, etc. should also be chosen carefully for reliable numerical evaluation of the direct experimental data. At the same time, it is obvious that optimization of the experiment is possible only if the compositions and stability constants of the complexes formed are already known, i.e. when no further experimental work is required. This contradiction can be resolved by planning the preliminary experiments on the basis of previously known data on similar systems, or other chemical considerations. A more exact series of experiments can be planned after evaluation of the preliminary results and, if necessary, the entire procedure can then be repeated.

It should be noted that not even this procedure leads to unambigous results in all cases in the study of relatively complicated equilibrium systems. It frequently happens that the effect of the formation of some complex is sufficiently large to disturb the evaluation, but still too small for the composition of the complex to be identified exactly. In such cases it is necessary to extend the range of the ratios of the total concentrations, so that the composition and stability of the complex concerned can be determined. As a consequence of the change in the concentration ratios, however, new complexes may appear in the system, the compositions of these not being identifiable exactly. Variation of the concentrations is further limited by the fact that the ionic strength must be kept constant, and precipitate formation may mean still another limitation.

In a tabulation of the formation constants in these cases it is advisable to give not only the ionic strength, the temperature and the method of measurement, but also the range of total concentrations of the components in which the data in question were determined. For the sake of completeness, it should be noted that, through variation of the total concentrations, it is not possible to regulate the concentrations of all complexes and their effects on the experimental data. For instance, if the effect of the complex MeL in a complex formation process is insignificant because the reaction

$$2\mathrm{MeL} \rightleftharpoons \mathrm{Me} + \mathrm{MeL}_2$$

has a large equilibrium constant, then the maximum partial mole fraction of MeL and its effect on the experimental data cannot be increased by any means. Regulation of the maximum partial mole fractions by varying the total concentrations is generally possible only if protonated, mixed hydroxo, or polynuclear complexes are formed.

5.1.2 Application of auxiliary functions

The data of the auxiliary functions are calculated from the directly measured experimental data, in order to obtain correlations and graphs which illustrate the equilibrium conditions and the compositions and stabilities of the complexes formed more descriptively than the direct experimental data. Calculation of the auxiliary functions therefore essentially means function transformation.

Numerous auxiliary functions were presented in the course of the discussion of the experimental methods in Chapter 4, and the possibilities and limitations of their application were analysed (see Figs 4.5, 4.6, 4.7, 4.8, 4.9, 4.10, 4.16, 4.17, 4.19, 4.40 and 4.41). It was necessary to deal with the auxiliary functions presented in the Figures in the previous chapter since the choice of the experimental conditions was automatically determined by the auxiliary functions. In the present section, therefore, we shall not give any further account of the application of the previously discussed functions. However, we shall deal in detail with the formation function that can be determined via various experimental methods, and we shall present some other function transformations, serving primarily for determination of the compositions of the complexes formed.

5.1.2.1 Application of the formation function

The formation function discussed in Section 3.5 is of fundamental importance as concerns the choice of the appropriate chemical model. The basis of application is the comparison of the shapes of the curves calculated from the experimental data and those to be expected theoretically.

It was demonstrated earlier that, in the event of the formation of mononuclear complexes with $N=1$ or $N=2$, the curves are symmetrical about their mid-point. It was seen that the shape of a curve with $N=1$ is independent of the value of the formation constant; the formation constant determines merely the position occupied by the curve on the $-\log[\mathrm{L}]$ scale. The value of the formation constant can be calculated from any point of the curve, via a direct formula

$$\beta_1 = \frac{\bar{n}}{(1-\bar{n})[\mathrm{L}]}. \tag{5.1}$$

The fact that the β_1 values calculated from the various points agree within the limits of experimental error is convincing evidence that only a single complex, with composition MeL, is formed in the system.

In contrast, if it is found that the points calculated from the experimental data do not lie on the curve to be expected theoretically, this indicates that, besides the formation of ML, further equilibrium processes must be taken into consideration in the system.

Figure 5.1, based on the studies by Gorton and Jameson [31], shows the formation curve obtained in the system Mg^{2+}–L-β-(3,4-dihydroxyphenyl)alanine.

The diagram reveals that in the interval $\bar{n} \sim 0.2$–0.8 the measured points can be described well by assuming formation of the complex MeL only. At $-\log[\mathrm{L}] > 5.0$ (at lower pH values), however, the difference is already appre-

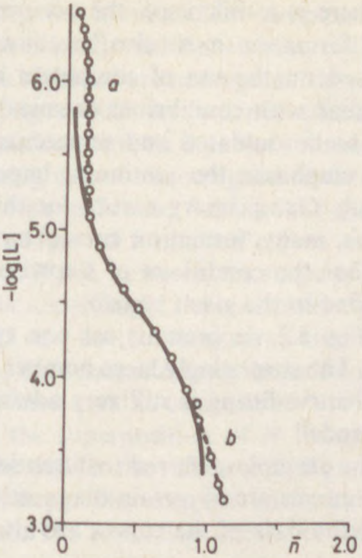

Fig. 5.1. Formation curve of the Mg^{2+}–DOPA (L-β-(3,4-dihydroxyphenyl)alanine) system. The differences between the experimental data and the calculated curve are indicative of formation of the protonated complex *(a)* and coordination of the second ligand *(b)* [31]
(Reproduced with permission from *J. Chem. Soc.*, 310 (1972))

ciable, while at high ligand concentrations the points of the curve rise above $\bar{n}=1$. The former difference points to the formation of a protonated complex, MeLH, and the latter difference to the formation of a bis complex, MeL_2. Further calculations by Gorton and Jameson lent support to the assumptions made from the shape of the curve, viz. that the complexes MeLH, MeL and MeL_2 are formed.

The formation curve for a mononuclear complex with $N=2$ is also symmetrical about the mid-point. The shape of the curve is determined by the quotient of the stepwise constants, and its position on the $-\log[L]$ scale by the value of $\log\beta_2$. Recognition of this was used in the 1950's as the basis of the correction term [32], projection strip [33] and curve-fitting [34] methods. The importance of these methods has naturally declined during the past decades. With a view to selecting the appropriate model, however, it is still advisable to utilize graphical curve-fitting. The essence of this is that the theoretical curves for $\log\beta_2=0$ and various ratios K_1/K_2 are plotted on transparent paper. If the set of curves is placed over the experimentally determined plots of the points, it can be visually observed which interval of the points corresponds to the theoretically expected curve shape, and in which interval deviates from that.

In an interval where there is a difference, the occurrence of processes other than stepwise complex formation must also be considered. Currently, when numerical methods based on the use of computers have gained ground so rapidly, specialists familiar with equilibrium chemical analysis may consider graphical curve-fitting to be outdated and unnecessary. In spite of this, we regard it as essential to emphasize the continuing importance and significance of graphical curve-fitting. Our primary reason for this is the fact that, even during the past 10 years, many 'formation curves' have been reported which reveal at first glance that the conditions of stepwise mononuclear complex formation are not satisfied in the given system.

As an example, in Fig. 5.2 we present just one typical unrealistic set of 'formation curves' [35]. The surprisingly large number of similar cases [36–52] confirms that graphical curve-fitting is still very advisable for selection of the appropriate chemical model!

In connection with the examples referred to, attention must be drawn to the fact that the formation curves are of certain diagnostic value when $N=1$ and $N=2$. This means that the data of the curves are always calculated with the

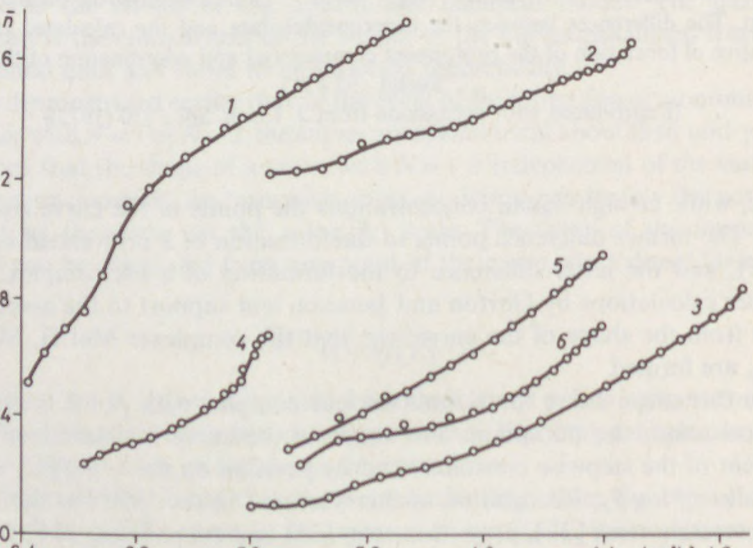

Fig. 5.2. 'Formation curves' of complexes of Fe(III), La(III) and Nd(III) with dl- and meso-tartaric acid [35].
1 — Fe(III) — meso-tartaric acid; 2 — Fe(III) — dl-tartaric acid; 3 — La(III) — meso-tartaric acid; 4 — La(III) — dl-tartaric acid; 5 — Nd(III) — meso-tartaric acid; 6 — Nd(III) — dl-tartaric acid
(Reproduced with permission from *J. Inorg. Nucl. Chem.*, **34**, 1977 (1972))

assumption that only stepwise mononuclear complex formation occurs in the system. This assumption is confirmed if the shape of the curve is regular.

However, if the curves obtained are not regular, then they lose their chemical meaning, for the starting conditions are not satisfied in the system. An irregularly-shaped 'formation curve' is thus not suitable for further evaluation, as a real chemical meaning can not be assigned to the quantities given on the axes. We have already seen in Section 3.6 that the shapes of the distribution curves and the closely connected formation curves are functions only of the quotients K_i/K_{i+1}. When $N>2$, however, the shape of a curve is influenced by several of these quotients; accordingly, the correctness of the assumptions made prior to the calculations can not be checked so simply as in the cases $N=1$ and $N=2$. If the K_i/K_{i+1} data characterizing the individual steps of the complex formation process each have a value of about 10^3–10^4, then the curve can be handled in practice as the superposition of N formation curves relating to single-step processes. The smaller the values of K_i/K_{i+1}, the greater the overlap between the individual steps. The steepest formation curve is obtained for systems with $K_i/K_{i+1}=0$. The formation curves for systems with $K_i/K_{i+1}=0$ are defined by

$$\bar{n}=\frac{N\beta_N[\mathrm{L}]^N}{1+\beta_N[\mathrm{L}]^N}\,. \qquad (5.2)$$

Analysis of this equation readily yields that the value $[\mathrm{L}]=1/\sqrt[N]{\beta_N}$ is associated with the point $\bar{n}=N/2$, and the maximum slope characteristic of the mid-point is $\mathrm{d}\bar{n}/\mathrm{d}(-\log[\mathrm{L}]_{\bar{n}=N/2}=2.303(N/2)^2$. If the maximum slope is less than this, then, besides formation of the complex MeL_N, the formation of complexes with a lower coordination number must also be taken into account. A maximum slope greater than the above value clearly reflects that the initial experimental or calculation conditions do not hold. Agreement with the maximum slope to be expected theoretically is evidence of the exclusive formation of MeL_N. To exemplify this latter case, Fig. 5.3 depicts the formation curve obtained by Persson [53] in a pH-metric study of the Ni^{2+}–CN^- system. We have supplemented the curve with the straight line with the theoretically expected maximum slope. The correspondence of the straight line and the slope of the experimental points relating to $\bar{n}=2$ illustratively shows that only the tetracyanonickel(II) complex is formed in significant concentration in this system.

It may be seen in Fig. 5.3 that Persson carried out his experiments at various metal ion concentrations. The agreement between the curves clearly demonstrates that no polynuclear complexes are formed in the system. It is rather surprising that confirmation of the assumption of the stepwise formation of mononuclear complexes on the basis of the coincidence of the formation curves

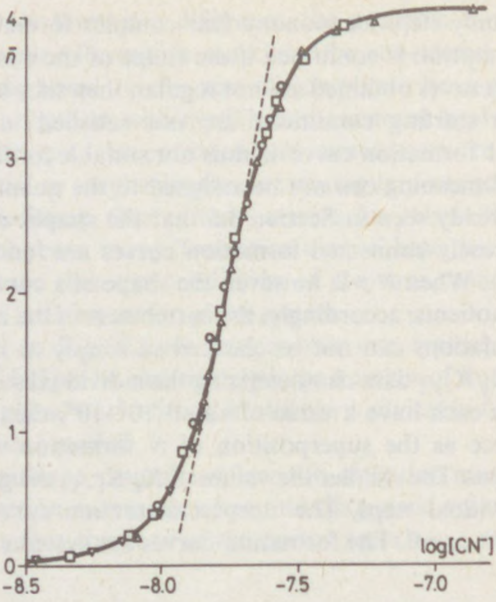

Fig. 5.3. pH-metrically obtained formation curve of Ni(II)–CN⁻ system [53], calculated from data found in solutions with various compositions. The dashed line indicates the maximum slope calculated for the exclusive formation of $Ni(CN)_4^{2-}$
(Reproduced with permission from *Acta Chem. Scand.* **A28**, 885 (1974))

measured at various metal ion concentrations has become general practice in relatively few laboratories.

There are fundamentally two possible reasons for a systematic difference between the formation curves calculated at various total metal ion and total ligand concentrations:

(1) The formation of protonated or mixed hydroxo complexes.
(2) The formation of polynuclear complexes.

If both processes occur simultaneously, then the systems are classified in group (1).

Case (1) in the sense of the classification discussed in Section 3.6 means that the system is not additive, i.e. the correlations (3.150) used to calculate the data of the formation curves are not valid. In such cases the calculated 'formation curves' have no chemical meaning; the individual $\bar{n}$ vs. log [L] points are merely computational artefacts. The shapes of the calculated curves in systems of this type also depend on the total metal ion concentration and the total ligand concentration. Nevertheless, calculation of the 'formation curves' is not always a waste of time. As an example, Fig. 5.4 shows 'formation curves' calculated from the pH-metric titration curves for the Cu^{2+}–aspartic acid system. The agreement for the upper sections of the curves clearly demonstrates that interfering processes need be considered only below $\bar{n} \sim 1.5$, i.e. in the range of formation of CuL.

Investigations on this system [54, 55] have shown that, in accordance with Fig. 5.4, only the protonated complex CuLH is formed besides CuL and CuL_2.

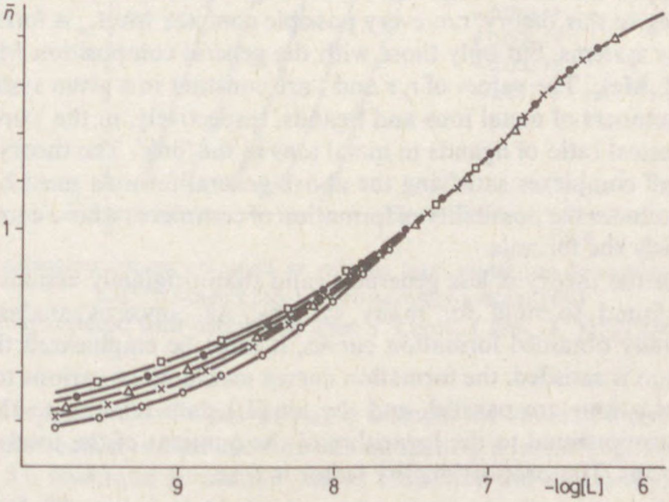

Fig. 5.4. Calculated 'formation curves' for the Cu^{2+}–aspartic acid system at a total ligand concentration of 0.01 *M* and various total metal ion concentrations. Symbols: □-□-□ $T_{Me} = 0.001\ M$; ●-●-● $T_{Me} = 0.002\ M$; △-△-△ $T_{Me} = 0.003\ M$; x-x-x $T_{Me} = 0.005\ M$; ○-○-○ $T_{Me} = 0.010\ M$

It should be mentioned that Corrie *et al.* [56] developed a complete system of model selection on the basis of the 'apparent formation curves' calculated for systems of type (1), as exemplified in Fig. 5.4. The method is primarily based on the observations and experience acquired by the authors in calculations on a large number of systems; the theoretical basis of the method is that of $\bar{n} - \log[L]$ curves being coincident for mononuclearity; any spread observed is caused by protonated, hydroxy or polynuclear species.

In case (2), i.e. if only polynuclear complexes are formed, but not protonated or hydroxo complexes, the system is additive, and the conditions used for calculation of the curves are valid. In this case, although the shape of the formation curve depends on the total metal ion concentration, at a given total metal ion concentration it is independent of the total concentration of the ligand. In this case the data of the real formation curve are calculated, and conclusions as to the compositions of the predominant polynuclear complexes may be drawn from the dependence of the shapes and positions of the formation curves on the total concentration of the metal ion.

Numerous authors have dealt with the correlations between the shapes of the formation curves for equilibrium systems involving polynuclear complexes and the compositions of the predominant complexes. Work of pioneering importance on the hydrolysis of metal ions was performed by Sillén [57, 58], who developed the 'core + links' theory through analysis of the curves.

According to this theory, not every possible complex Me_qL_p is formed in the polynuclear systems, but only those with the general composition $Me_s(L_tMe)_n$ and/or $L_r(L_tMe)_n$. The values of r, s and t are constant in a given system. s and r are the numbers of metal ions and ligands, respectively, in the 'core', while t is the numerical ratio of ligands to metal ions in the 'link'. The theory does not state that all complexes satisfying the above general formula must be formed; it merely excludes the possibility of formation of complexes whose compositions do not satisfy the formula.

Although the theory is less generally valid than originally assumed [59], it has been found to hold for many systems. As concerns analysis of the experimentally obtained formation curves, it must be emphasized that, when the condition is satisfied, the formation curves measured at various total metal ion concentrations are parallel, and the log [L] data relating to the same $\bar{n}$ value are proportional to the logarithm of the quotient of the total metal ion concentrations. The proportionality factor is t, i.e.

$$\frac{\Delta \log [L]}{\Delta \log T_{Me}} = t \,. \tag{5.3}$$

Figure 5.5 shows the parallel formation curves found for the Cd(II)-3-mercapto-1,2-propanediol system by De Brabander and Van Poucke [60]. Analysis of the curves yielded a value of $1.66 = 5/3$ for t, i.e. the system can be described by the assumption of the formation of complexes $Cd(L_{5/3}Cd)_3 = Cd_4L_5$, $Cd(L_{5/3}Cd)_6 = Cd_7L_{10}$, etc.

The formation curves for polynuclear equilibrium systems frequently intersect one another at a single point. A fair number of authors have dealt with the interpretation of the phenomenon, and with the discovery of correlations between the position of the point of intersection and the compositions of the predominant complexes [61–65]. Special attention should be paid to the work by Van Poucke and De Brabander, who discuss separately the real and the apparent intersection points and the possibilities of applying these to determine the composition. The reader is referred to the original publications for the details of their considerations [64, 65]. As concerns their results, we shall mention only that a point of intersection is always to be found in the formation curves if, besides the series of parent complexes MeL, ..., MeL_N, only a single

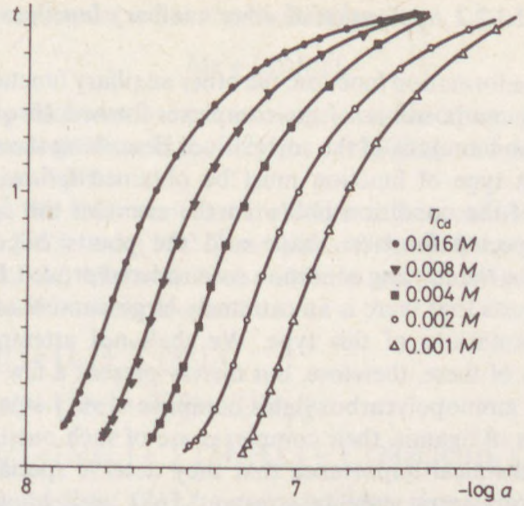

Fig. 5.5. Formation curves obtained at various total metal ion concentrations in the Cd^{2+}–3-mercapto-1,2-propanediol system [60]
(Reproduced with permission from *J. Coord. Chem.*, 3, 301 (1974))

complex Me_qL_p (and/or its polymer(s)) is formed; the value of $\bar{n}$ relating to the point of intersection is equivalent to the quotient q/p (assuming that $q/p<N$).

Figure 5.6 illustrates formation curves found for the Zn(II)–thiolactic acid system [66]. The value of $\bar{n}$ relating to the point of intersection of the curves is 1.3; accordingly, it could be assumed that, besides the mononuclear complexes, a polynuclear complex of composition Zn_3L_4 ($q/p=1.33$) is formed in major concentration. Formation of the complex Zn_2L_2 ($q/p=1$) was also assumed, to explain the slight deviation from the point of intersection to be expected theoretically. In accordance with the conclusions drawn from the shape of the curve and from the position of the point of intersection, the experimental data could be described best by the assumption that the complexes ZnL, ZnL_2, Zn_2L_2 and Zn_3L_4 are formed. The continuous lines in Fig. 5.6 denote the theoretical curves corresponding to the best fitting; a systematic difference can not be observed anywhere within the set of curves.

In spite of the deep theoretical and experimental analysis of the formation processes of polynuclear complexes, selection of the appropriate model encounters substantially greater difficulties than in the case of the stepwise formation of mononuclear complexes. Theoretical and experimental work of fundamental importance was carried out on polynuclear equilibrium systems by Sillén, who in 1964 made the following remark [67]: "The more I work with polyions, the more I think we must be cautious with claims to have proved the existence of any particular species." This is still true more than 20 years later.

5.1.2.2 Application of other auxiliary functions

Similarly to the formation function, the other auxiliary functions are obtained by assuming the compositions of the complexes formed; through appropriate transformation and analysis of the correlations describing the system, it is then established what type of function must be obtained following the function transformation if the condition holds. In the event of the agreement of the theoretically expected function shape and the points calculated from the experimental data, the starting condition is considered proved. Even this general description suggests that there is an extremely large number of possibilities for function transformations of this type. We shall not attempt to survey the complete system of these, therefore, but merely present a few examples.

Although the aminopolycarboxylates comprise a very small proportion of the total number of ligands, their complexes are of such outstanding practical and analytical chemical importance that they deserve special attention. The concept of the 'apparent stability constant' [68], well known in analytical chemistry was introduced to characterize the complexes of the aminopolycarboxylates, and on this basis Ringbom and Harju [69, 70] developed a general method for determination of the compositions of the complexes formed. Naturally, the method is also suitable for the study of complexes of other polyfunctional ligands.

The aminopolycarboxylates primarily form 1:1 complexes with the various metal ions. However, the equilibrium conditions are complicated by the fact

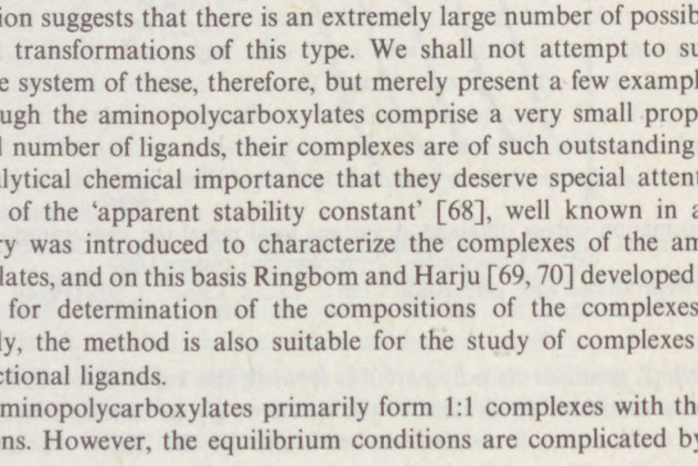

Fig. 5.6. Formation curves obtained at various total metal ion concentrations in the Zn^{2+}–thiolactic acid system [66]
(Reproduced with permission from *J. Inorg. Nucl. Chem.*, 37, 799 (1975))

that all three species involved in the equilibrium

$$\mathrm{Me} + \mathrm{L} \rightleftharpoons \mathrm{MeL}$$

may additionally take part in various side-reactions. Thus, depending on the conditions, the associations H_jL, MeH_iL, $MeL(OH)_k$ and $Me(OH)_n$ may be formed too, for example.

The effects of the side-reactions are taken into account in terms of the quantities [L′], [M′] and [MeL′], which are the sums of the equilibrium concentrations of L, Me and MeL and the concentrations of the other associations formed in the side-reactions

$$[\mathrm{L}'] = [\mathrm{L}] + \sum [\mathrm{H}_j\mathrm{L}]$$

$$[\mathrm{Me}'] = [\mathrm{Me}] + \sum [\mathrm{Me(OH)}_n]$$

$$[\mathrm{MeL}'] = [\mathrm{MeL}] + \sum [\mathrm{MeH}_i\mathrm{L}] + \sum [\mathrm{MeL(OH)}_n] .$$

The constants defined by L′, Me′ and MeL′ are termed 'apparent stability constants'. It is obvious that the value of the apparent stability constant depends on the pH, for the pH governs the concentration distribution within all three series of species.

On this basis, the following correlation arises between the apparent stability constant and the formation constant for the process $\mathrm{Me} + \mathrm{L} \rightleftharpoons \mathrm{MeL}$

$$K_{\mathrm{MeL}'}^{\mathrm{Me}',\mathrm{L}'} = K_{\mathrm{MeL}}^{\mathrm{Me},\mathrm{L}} \cdot \frac{\alpha_{\mathrm{MeL}}}{\alpha_{\mathrm{L}}\alpha_{\mathrm{Me}}} \tag{5.4}$$

where $\alpha_{\mathrm{MeL}} = [\mathrm{MeL}]/[\mathrm{MeL}']$, $\alpha_{\mathrm{L}} = [\mathrm{L}]/[\mathrm{L}']$ and $\alpha_{\mathrm{Me}} = [\mathrm{Me}]/[\mathrm{Me}']$.

Through simultaneous measurement of the pH and the equilibrium concentration of the metal ion, there is also a possibility for calculation of the equilibrium constant defined by the following correlation

$$K_{\mathrm{MeL}'}^{\mathrm{Me},\mathrm{L}} = \frac{[\mathrm{MeL}']}{[\mathrm{Me}][\mathrm{L}]} = \frac{[\mathrm{MeL}] + \sum [\mathrm{MeH}_i\mathrm{L}] + \sum [\mathrm{MeL(OH)}_k]}{[\mathrm{Me}][\mathrm{L}]} . \tag{5.5}$$

If the logarithm of the constant is plotted as a function of the pH, the slope of the curve can be used to draw conclusions on the numbers of protons bound in the complexes formed in the various pH intervals.

Figure 5.7 depicts the results of the calculations of Ringbom and Harju [70] based on the data of Österberg [71]. The tangents denoted by dashed lines permit the finding that complexes of composition MeH_2L, MeHL, MeL and MeL(OH) are formed in the Cu^{2+}–O–phosphorylserylglutamic acid system. The original publications [69, 70] give further details of the composition determination, based on the pH-dependence of the other variously defined and measured 'apparent' constants.

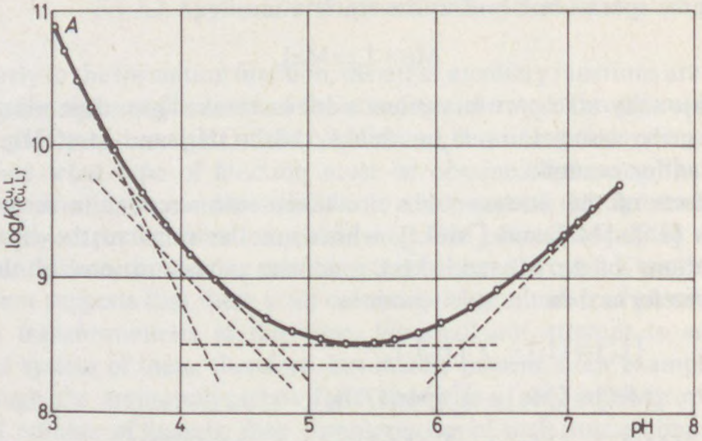

Fig. 5.7. The function $\log K_{(\mathrm{CuL})'} = f(\mathrm{pH})$ for the Cu^{2+}–O-phosphorylserylglutamic acid system, calculated on the basis of pH and $p[\mathrm{Cu}]$ measurements [71] (Reproduced with permission from *Anal. Chim. Acta*, **59**, 33 (1972))

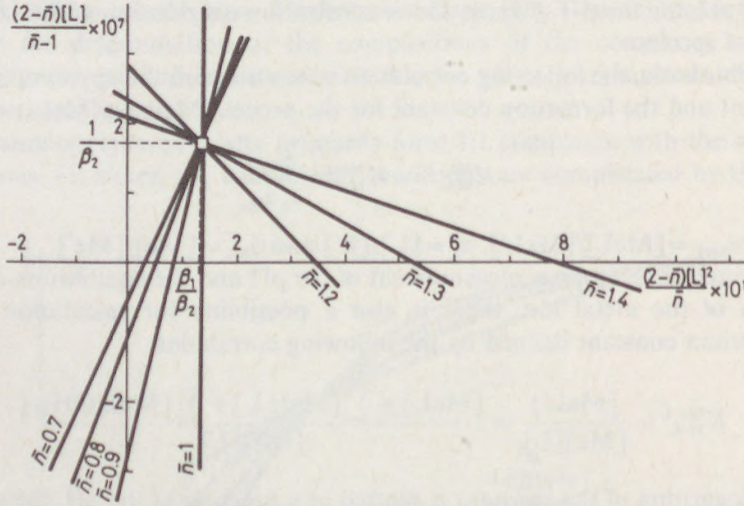

Fig. 5.8. Variants of the formation curve of the Cu^{2+}–threonine system, linearized in accordance with Eq. (5.6) [72]

Many of the other auxiliary functions arise from further transformation of the formation function. When $N = 2$, for instance, there is a possibility for (among others) the following transformation

$$1 = \frac{\beta_1}{\dfrac{\bar{n}}{(1-\bar{n})[\mathrm{L}]}} + \frac{\beta_2}{\dfrac{\bar{n}}{(2-\bar{n})[\mathrm{L}]^2}}. \tag{5.6}$$

According to this equation, the straight lines connecting the related points $\bar{n}/(1-\bar{n})[L]$ and $\bar{n}/(2-\bar{n})[L]^2$ on the abscissa and the ordinate intersect one another at one point, and the coordinates of the point of intersection are given by the values of β_1 and β_2.

Figure 5.8 shows the diagram obtained by transformation of the formation curve for the Cu^{2+}–threonine system in accordance with Eq. (5.6) [72]. The diagram reveals that the straight lines really do intersect at one point, i.e. only the complexes CuL and CuL_2 are formed in the system.

The work of Dunsmore and Midgley [73] can essentially be regarded as a further development of transformations of this type; by means of a computer, they performed a transformation which yields a straight line only if the complex MeLH is formed besides MeL and MeL_2, and they gave the formation constant of this correctly (Fig. 5.9).

When two species of unknown composition are formed simultaneously, then a correlation similar to Eq. (5.6), but not always linear, can be derived between

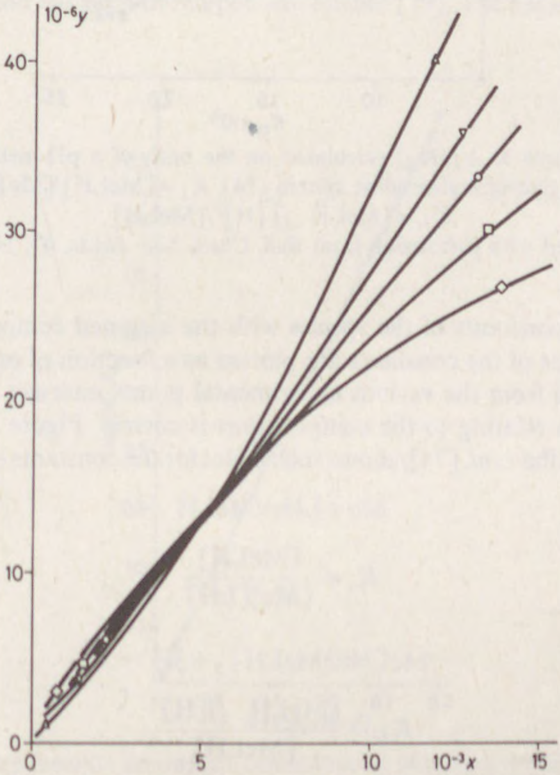

Fig. 5.9. Functions $y=\beta_{MeL}\cdot x+\beta_{MeL_2}$ calculated at various values $\beta_H=[MeLH]/[Me][HL]$ [73]. △ — $\beta_H=50$; ▽ — $\beta_H=150$; ○ — $\beta_H=200$; □ — $\beta_H=250$; ◇ — $\beta_H=300$. (Reproduced with permission from *Anal. Chim. Acta*, **67**, 341 (1973))

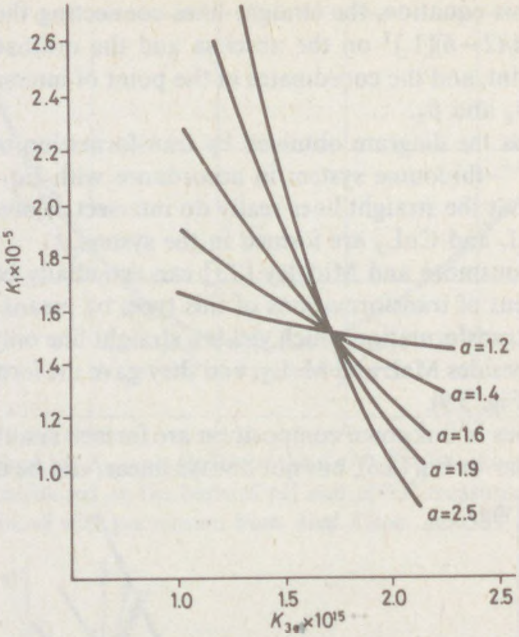

Fig. 5.10. Functions $K_1 = f(K_{3c})$ calculated on the basis of a pH-metric study of the Cu^{2+}–glycylglycylhistidine system [74]. $K_1 = [MeLH]/[Me][LH]$; $K_{3c} = [MeLH_{-2}]\,[H]^3/[MeLH]$
(Reproduced with permission from *Bull. Chem. Soc. Japan*, **47**, 1437 (1974))

the formation constants of the species with the assumed compositions. If the numerical values of the constants are plotted as a function of one another, the plots calculated from the various experimental points intersect at one point if the assumption relating to the compositions is correct. Figure 5.10, based on the studies by Aiba *et al.* [74], shows such a plot for the constants of the processes

$$Me + LH \rightleftharpoons MeLH$$

$$K_1 = \frac{[MeLH]}{[Me][LH]}$$

and

$$MeLH \rightleftharpoons MeLH_{-2} + 3H^+$$

$$K_{3c} = \frac{[MeLH_{-2}][H]^3}{[MeLH]}$$

in the Cu^{2+}–glycylglycylhistidine system.

It can be seen that the $K_1 = f(K_{3c})$ curves calculated from the various points of the pH-metric titration curves intersect at one point. This is clear-cut evidence that only the complexes CuLH and $CuLH_{-2}$ are formed in appreciable concentration in the given pH-range. The dissociation of the three protons is not a successive process, but proceeds in one step during structural rearrangement of the complex.

It must be noted that the methods illustrated in Figs 5.7–5.10 were originally proposed for the calculation of formation constants. If the recent development of computer methods is taken into account, however, these and similar graphical methods with an optionally wide range of application could be used advantageously to establish primarily the compositions of the complexes formed and to calculate the starting data for the general programs.

On the basis of a photometric study of the polymerization of complexes and of the formation of polynuclear complexes, Klausen and Langmyhr [75] developed a general method for the determination of composition. This method is essentially a further-developed variant of the 'straight line' method of Asmus [76], which has recently been utilized in its original or in a slightly modified form [77, 78] and has been developed still further [79]. The basis of the method

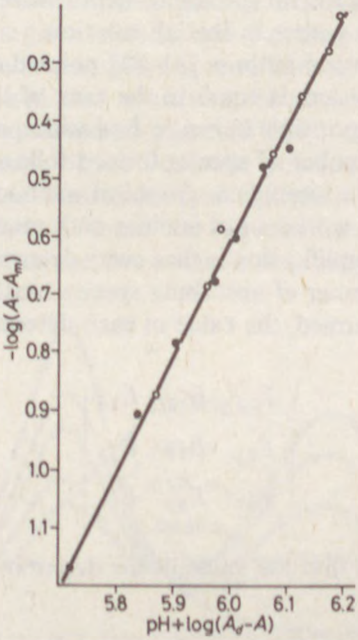

Fig. 5.11. Auxiliary function serving for determination of the degree of polymerization of the complex $(CuLH_{-1})_n$ formed in the Cu(II)–histidylglycine system. The slope of the function gives the value of n (=2) [80]
(Reproduced with permission from *J. Inorg. Nucl. Chem.*, **37**, 1097 (1975))

is that the function transformation gives a straight line only if the composition is correctly assumed, or the function transformation performed gives a straight line with slope equal to the degree of polymerization [80] (see Fig. 5.11).

5.1.3 Direct methods

The fundamental difference between the direct methods and those based on auxiliary functions is that the number and compositions of the species formed in significant concentration are determined by starting from the general correlations describing equilibrium systems, without any preliminary conditions.

In the study of equilibrium systems by means of photometry (or any other additive method), the measured quantity is a linear combination of the concentrations of the individual species, i.e.

$$E_{k,j} = \sum_{i=1}^{n} \varepsilon_{ij}[\mathrm{A}_i]_k \tag{5.7}$$

where $E_{k,j}$ is the absorbance in the kth solution at the jth wavelength, $\varepsilon_{i,j}$ is the molar absorbance of the ith species at the jth wavelength, and $[\mathrm{A}_i]_k$ is the concentration of the ith species in the kth solution.

During the 1960's, several authors [81–84] pointed out that the number of species formed in the system is equal to the rank of the matrix formed from the elements $E_{k,j}$. This principle began to find widespread application for the determination of the number of species formed following the publication by Coleman *et al.* [85] of a simplified, graphical method that could readily be understood by research workers not familiar with matrix algebra.

The essence of the simplification is that every determinant with a dimension one larger than the number of absorbing species must be zero. For instance, when two species are formed, the value of each determinant

$$\begin{vmatrix} E_{11} & E_{12} & E_{13} \\ E_{21} & E_{22} & E_{23} \\ E_{31} & E_{32} & E_{33} \end{vmatrix}$$

must be zero. It follows that the value of the determinant

$$\begin{vmatrix} 1 & 1 & 1 \\ E_{21}/E_{11} & E_{22}/E_{12} & E_{23}/E_{13} \\ E_{31}/E_{11} & E_{32}/E_{12} & E_{33}/E_{13} \end{vmatrix}$$

is also zero. Thus, if the data pairs E_{21}/E_{11} and E_{31}/E_{11}, E_{22}/E_{12} and E_{32}/E_{12}, and E_{23}/E_{13} and E_{33}/E_{13} are plotted in the x vs. y coordinate system, a straight line passing through the origin is obtained. It can readily be seen that the data pairs E_{2j}/E_{1j} and E_{3j}/E_{1j} obtained at any other solution composition also lie on this straight line. Accordingly, if three different wavelengths are chosen, the absorbances measured at two of the wavelengths are divided by the absorbance measured at the third wavelength, and the quotients are plotted versus one another, then the points will lie on a straight line if two species are formed. Coleman *et al.* derived essentially similar correlations to demonstrate the formation of three, four, etc. species.

As illustrations of the method, Fig. 5.12 depicts spectra recorded at various solution compositions in the Ni^{2+}–CN^- system [86], while Fig. 5.13 shows the straight lines obtained with the outlined method.

Figure 5.13 clearly reveals that the absorbance quotients at the various wavelengths describe straight lines as functions of one another, i.e. only two species are simultaneously present (cf. Fig. 5.3).

In fact, the presence of two absorbing species is to be expected from the fact that the spectra pass through an isosbestic point. If more than two species are present simultaneously, an isosbestic point is observed only in special cases. Through extension of the given method, however, the presence of several species can be demonstrated, and the number of complexes formed can be determined.

It should be mentioned that a number of authors have dealt with the diagnostic value of the isosbestic point [87–89]; indeed, a sharp dispute concerning the significance of the isosbestic point emerged in the literature [90, 91] as a consequence of misunderstandings relating to the microconstants.

Even without a detailed account of the relevant literature, it is clear that the isosbestic point itself is not decisive evidence that only two absorbing species

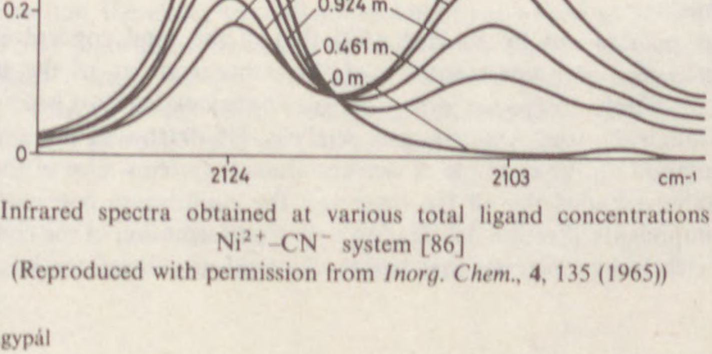

Fig. 5.12. Infrared spectra obtained at various total ligand concentrations in the Ni^{2+}–CN^- system [86]
(Reproduced with permission from *Inorg. Chem.*, 4, 135 (1965))

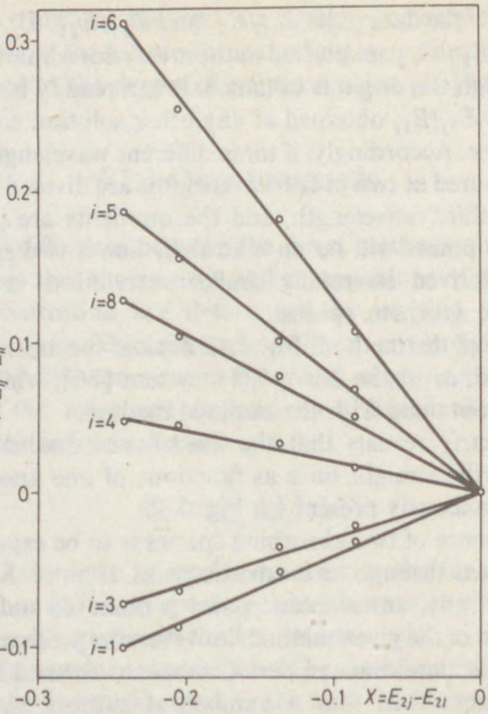

Fig. 5.13. Straight lines calculated from the spectra of the Ni^{2+}–CN^- system, confirming the formation of two light-absorbing ionic species: $Ni(CN)_4^{2-}$ and $Ni(CN)_5^{3-}$ [85] (Reproduced with permission from *Inorg. Chem.*, 9, 1015 (1970))

are present in the given system, but it is natural that this obvious assumption is the first step of the evaluation if an isosbestic point is observed. However, the assumption can be regarded as confirmed only if it is supported by Coleman graphical analysis or matrix rank analysis extending to the entire wavelength interval. At the same time, it may occur that the spectra do not intersect one another, so that an isosbestic point does not result even though two species are formed.

It was pointed out by Vadasdi [92] that, if the total concentrations are interpreted as linear combinations of the concentrations of the individual species, the number of species formed can also be calculated from potentiometric data through the use of matrix rank analysis. He illustrated the applications of the method on the example of two-component systems. Use of the method necessitates a knowledge of the total and the equilibrium concentrations of both components. (Section 3.2, dealing with transformation of the composition matrix, clearly demonstrates that, besides the total concentrations, it is sufficient to know the equilibrium concentrations of any two species, and not only those of the components.)

The essence of the method is that the number of species participating in the equilibrium is given by the rank of the matrix of any one total concentration defined at several different, but fixed equilibrium concentrations of one of the components (a higher number of concentrations than the number of species formed), and at the several related, but similarly fixed equilibrium concentrations of the other component. The method has not become as widespread as might be expected from its potentialities. However, an increasing number of authors [93–96] have begun to study, interpret and utilize the method originally proposed by Hedström [97] and McKay [98] for determination of the equilibrium concentrations of each of the components. Accordingly, extension of the utilization of the Vadasdi method is to be expected, together with detailed analyses of the possibilities of its application and its limitations.

5.2 Computer evaluation of equilibrium measurement data

In our discussion of computer-based methods of evaluation, it is assumed that the reader is familiar with the various methods of numerical analysis for the solution of linear and non-linear equation systems, and with the bases of parameter fitting involving application of the least squares principle. Details on these topics and on the computational principles are to be found in a whole series of excellent monographs [99–105], and a number of reviews have also been published on the programs used in equilibrium chemistry [21–23]. The volume *Computational Methods for the Calculation of Stability Constants*, edited by Leggett, recently appeared in the Plenum Press series *Modern Inorganic Chemistry* [106]. Besides an account of the methods of numerical analysis connected with equilibrium chemistry, this volume contains detailed descriptions of eight programs by different authors, with complete documentation and the input–output systems, and concrete examples of the possibilities of application are presented.

In this section, therefore, we shall not attempt to give even an outline account of all of the algorithms. Instead, we shall trace the main aspects of the development during the past 20 years. Unless otherwise mentioned, our comments relating to the various numerical methods and to the possibilities of solution will be based primarily on our own experience.

5.2.1 Historical survey

Up to the middle of the 1960's, the evaluation of equilibrium measurements was based on the different graphical methods. These methods were reviewed in considerable detail by Rossotti and Rossotti [107] in their book *The Determination of Stability Constants*, which appeared in 1961. Starting from the middle of the 1960's, computers acquired ever greater importance in the evaluation of equilibrium measurement data.

Initially, computers too were used only to accelerate the mechanical calculations necessary for the application of graphical methods. The next stage in the development was when the experimental data were first transformed to the auxiliary functions customary for the graphical methods, and the values of the constants were calculated via numerical fitting of the auxiliary functions. First among the larger, generally applicable fitting programs was the LETAGROP program family [24]. It is worth noting that the title of the series of publications presenting the various LETAGROP program variants and the work of the Sillén school relating to certain computational aspects was *High Speed Computers as a Supplement to Graphical Methods.* This title clearly indicates that the authors considered graphical analysis to be of fundamental importance. Computers primarily served to make more exact the model and the equilibrium data resulting from graphical analysis, and to support these with statistical parameters. The authors of subsequently published general programs no longer stressed to such an extent the importance of preliminary graphical analysis. In our view, it is not absolutely necessary to subject every series of experimental data to such preliminary graphical analysis. At the same time, research workers active in equilibrium chemistry must be sufficiently familiar with this field too, in order to be able to avoid the pitfalls associated with the mechanical application of the general procedures (see Refs. [35–52]).

As a consequence of the development of the evaluation methods, the use of the various auxiliary functions has lost much of its importance. The calculations nowadays generally set out from the basic correlations described and analysed in detail in Chapter 3. A high proportion of the programs published in the 1960's and 1970's were designed for the large computers situated in computer centres. The progress made in electronics, however, has led to the availability of relatively cheap, slower desk-computers, with smaller memories, that can be programmed in a simplified language, but which can nevertheless be utilized for the control of the measuring instruments, for automatic data collection, etc. Accordingly, there is currently an increase in the number of publications describing generally interactive programs and program packages that have been prepared for smaller computers.

Below, we shall deal with three main topics relating to computer-based evaluation: methods based on the auxiliary functions; the calculation of equilibrium concentrations; and questions concerning the fitting of parameters (equilibrium constants, molar absorbance, etc.).

5.2.2 Evaluation methods based on auxiliary functions

It was seen in Section 5.1 that the various auxiliary functions provide a very illustrative picture of the system examined, and are of fundamental importance in the determination of the compositions of the complexes formed. If they are utilized to calculate the equilibrium constants, however, it must always be taken into account that transformation of the direct experimental data into auxiliary functions is accompanied by transformation of the experimental errors too, and in an unfavourable case the transformation of the errors may lead to unrealistic results. This phenomenon was pointed out very descriptively by Cumming *et al.* [5]. Figure 5.14 shows the formation curve of the Cu^{2+}–ethylenediamine system, together with the errors ascribed to the individual points. (For purposes of illustration, the actual errors have been magnified ten-fold.) Figure 5.15 [5] depicts the function linearized in accordance with the equation

$$\frac{(\bar{n}-1)[L]}{\bar{n}} = \frac{(2-\bar{n})[L]^2}{\bar{n}} K_2 - \frac{1}{K_1} \tag{5.8}$$

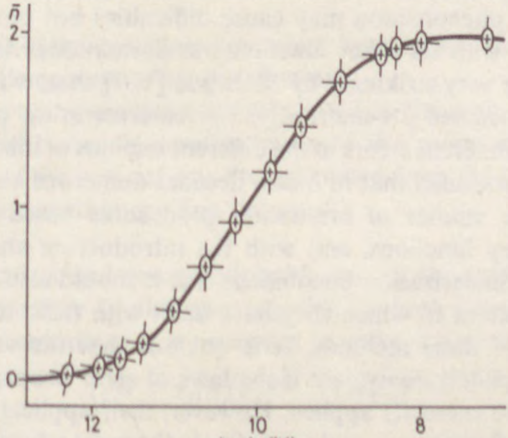

Fig. 5.14. Formation curves of the Cu^{2+}–ethylenediamine system in a methanol–water mixture. For clarity, the ellipses characterizing the errors in the points are magnified 10-fold [5]

(Reproduced with permission from *J. Chem. Soc. Dalton Trans.*, 2652 (1972))

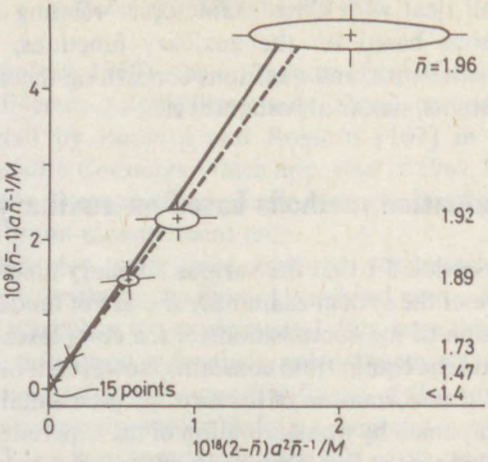

Fig. 5.15. Straight lines relating to the data from Fig. 5.14, transformed in accordance with Eq. (5.8), together with the transformed errors in the individual points [5] (Reproduced with permission from *J. Chem. Soc. Dalton Trans.*, 2652 (1972))

together with the transformation of the errors. The dashed line is the straight line calculated by neglecting the laws of error propagation, while the continuous line is that calculated when these laws are taken into consideration. The difference between the constants calculated from the two straight lines may attain even 0.3 log unit.

Naturally, this phenomenon may cause difficulties not only in the case of linearization, but with all other function transformations. As an example, it was demonstrated very strikingly by McBryde [129] that, when the Cu^{2+}–bipyridyl system is studied pH-metrically, a given error in the pH measurement leads to basically different errors in the different sections of the formation curve.

It should be mentioned that in recent decades numerous authors have dealt with comparative studies of evaluation procedures based on the various linearized auxiliary functions, and with the introduction and application of newer and newer linearization possibilities, but it should also be stated that in many cases the extent to which they have dealt with these topics far exceeds the significance of these methods. It is obvious that the various linearized variants are completely equivalent if the laws of error propagation and error transformation are correctly applied. However, their application considerably increases the calculation time, and accordingly the great advantage of linearization, the rapidity, is lost. In our view, it is more advisable to use the auxiliary functions to select the appropriate equilibrium model only, and to fit the theoretical curves to the direct experimental data in the calculation of the equilibrium constants.

5.2.3 Calculation of equilibrium concentrations

Each iteration step in the majority of the procedures for evaluation of the data of equilibrium measurements can be separated into two stages:

(1) Calculation of the equilibrium concentrations with the aid of the assumed (or known) constants.

(2) Calculation of the increments of the assumed constants on the basis of the least squares principle.

A method that differs in principle is to calculate the equilibrium concentrations of the components from the experimental data via differential correlations, but without a knowledge of the equilibrium model.

Finally, for the sake of completeness, it must be mentioned that the equilibrium concentrations and the constants of the assumed equilibrium model can be calculated simultaneously too; this was pointed out by Sabatini and Vacca [8] in 1972, and the possibility has been utilized in the development of numerous programs.

5.2.3.1 Calculation of equilibrium concentrations when the stability constants are known

The expression 'when the stability constants are known' may in fact cover two different cases:

(1) The values of the constants are indeed known, and the aim is simply the calculation of the concentration distribution.

(2) The values of the constants are calculated on the basis of the least squares principle, and within each iteration cycle of the procedure the equilibrium concentrations of the components are calculated from the prevailing values of the constants (assumed in the first iteration).

The mathematical and computational bases are the same in the two cases, and they will therefore be discussed together. In both cases, in the knowledge of the total concentrations it is necessary to solve the equation system

$$\begin{aligned} T_1 &= \sum \alpha_{j1}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}\ldots.[\mathrm{k}_m]^{\alpha_{jm}} \\ &\vdots \\ T_m &= \sum \alpha_{jm}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}\ldots.[\mathrm{k}_m]^{\alpha_{jm}} \end{aligned} \tag{5.9}$$

for $[\mathrm{k}_1], \ldots, [\mathrm{k}_m]$. It may occur that the equilibrium concentrations of the other components are calculated at a fixed value of one of the equilibrium concentrations (e.g. at given pH), but this does not change the task essentially; it merely decreases the number of unknowns. Various methods have been devised and utilized to solve the equation system. The HALTAFALL program [23], for instance, calculates the equilibrium concentrations by means of successive approximations reminiscent of the halving method. Since the condition $0 < [\mathrm{k}_i] < T_i$ clearly always holds as concerns the equilibrium concentration of the components (with the exception of the hydrogen ion), the method is always convergent, and the convergency does not depend on the starting values.

In the course of the development of the COMICS program [108], and later the SCOGS program [109], Sayce introduced an original iteration formula not discussed among the general methods of numerical analysis

$$[\mathrm{k}_i]_{j+1} = [\mathrm{k}_i]_j (T_i / T_{i,j}^{\mathrm{calcd.}})^{1/2} . \tag{5.10}$$

In this equation, $[\mathrm{k}_i]_j$ and $T_{i,j}^{\mathrm{calcd.}}$ are the equilibrium and the calculated total concentrations, respectively, of the i-th component in the j-th iteration cycle. In our experience, the method is always convergent; at a distance from the solution it is relatively fast, but in the vicinity of the solution it slows down considerably.

According to May *et al.* [110], this slow convergence in the vicinity of the solution can be avoided by using the formula

$$[\mathrm{k}_i]_{j+1} = [\mathrm{k}_i]_j (T_i / T_{i,j}^{\mathrm{calcd.}}) . \tag{5.11}$$

This formula can not be used at any appreciable distance from the solution, for it demonstrably diverges.

Essentially the Sayce method was used several years later by Nagypál [28] and Cumme [111].

Ginzburg [112] modified the Sayce method by using $1/p$ in place of $1/2$ as the exponent on the right-hand side of Eq. (5.10), where p is the largest stoichiometric number used in the given mass balance equation.

The method may primarily be used to calculate the concentration distribution at constant, known pH. It is not always suitable for calculation of the pH, as the total concentration relating to the hydrogen ion may be negative, and it may occur that the root of a negative number should be extracted during the iteration.

Maggiore *et al.* [113] reported the successful application of an original iteration formula

$$[\mathrm{k}_i]_{j+1} = [\mathrm{k}_i]_j (T_i / T_{i,j}^{\mathrm{calcd.}} + 1)/2 . \tag{5.12}$$

It is surprising that one of the longest-known methods, the Newton–Raphson method, was first applied in solution equilibrium calculations only in 1972. On the basis of this, the EQUIL program was developed by Ting–Po I and

Nancollas [25], and the LEAST NR program by Sabatini and Vacca [8]. This method later became much more general.

In our experience, if appropriate checking instructions are inserted, the correct solution can always be obtained with the Newton–Raphson method [114]. If the equations

$$(T_i^{\text{calcd.}} - T_i) = 0 \tag{5.13}$$

are interpreted as function of log [k$_i$] and solved, in the course of the iteration it is possible to avoid divergency and the calculation of chemically unrealistic negative concentrations.

The solution of

$$\log \frac{T_i^{\text{calcd.}}}{T_i} = 0 \tag{5.14}$$

by the Newton–Raphson method, similarly via interpretation as a function of log [k$_i$], has proved particularly fast and efficient at a comparatively large distance from the solution.

However, Eq. (5.14) is not applicable to the hydrogen ion, and in the PSEQUAD program, therefore, it was modified as follows

$$\ln \frac{T_{+\mathrm{H}}^{\text{calcd.}} + \dfrac{\operatorname{sign}(T_{\mathrm{H}}^{\text{exp.}}) - 1}{2} T_{\mathrm{H}}^{\text{exp.}}}{T_{-\mathrm{H}}^{\text{calcd.}} + \dfrac{\operatorname{sign}(T_{\mathrm{H}}^{\text{exp.}}) + 1}{2} T_{\mathrm{H}}^{\text{exp.}}} = 0 \tag{5.15}$$

where sign denotes the sign function.

$T_{-\mathrm{H}}^{\text{calcd.}}$ and $T_{+\mathrm{H}}^{\text{calcd.}}$ are the total hydrogen ion concentrations calculated on the basis of the concentrations of the species with negative and positive stoichiometric numbers respectively. This modification makes the method suitable for the calculation of pH too.

Besides the fundamental iteration formulae, from a computational aspect the assumptions relating to the starting values are of great importance, as are the safety instructions promoting convergency.

In the SCOGS program, for instance, the calculation begins at the point with the lowest pH in the titration curves, where complex formation is not yet appreciable. Thus, the starting value for the equilibrium metal ion concentration is the total concentration of the metal ion, while the starting value for the equilibrium concentration of the ligand can be calculated via a direct formula, neglecting the effect of complex formation.

Naturally, when calculations are made for successive points, it is reasonable to set out from the solution obtained for the previous point, the accuracy of the starting equilibrium concentrations possibly being further improved by linear extrapolation [114].

In the solution of Eq. (5.13)–(5.15), the PSEQUAD program sets out from the $[k_i]_0 = T_i/2$ values (if the hydrogen ion concentration is negative, $[H]_0 = 10^{-6}$), and determines the starting values at the successive points by linear extrapolation, using the analytical derivatives.

In some programs a step-length control too is inserted, to avoid divergency and the unrealistic range of the equilibrium constants.

5.2.3.2 Calculation of the equilibrium concentrations when the equilibrium model is unknown

The method is based on the differential correlations between the mass balance equations, discussed in detail in Chapter 3. The essence is that the equilibrium concentrations of all of the components may be calculated from the appropriately planned and executed series of experiments, with measurement of the concentration of only a single ionic species, without a knowledge of the compositions and stability constants of the complexes formed.

Before a brief account of the correlations and the diagrams, it is worthwhile surveying the main stages in the recent development in this field. It was first pointed out by Bjerrum [115] that the differential of the function $\log \alpha_{Me} = f(p[L])$ gives the value of $\bar{n}$, i.e. the equilibrium concentration of the metal ion can be calculated by integration of the formation curve, even without a knowledge of the stability constants. The procedure was later generalized to iso- and heteropoly acids by Souchay [116], Bye [117] and Lefebrve [118]. With a different mathematical formalism, McKay [98], Hedström [97], Sillén [119] and Österberg [120] reached essentially the same result. The equivalence of the two different approaches was demonstrated in 1969 by Martin [121], who also extended the procedure to the very involved, four-component equilibrium system Cu(II)–histidine–threonine–proton [122].

Sarkar and Kruck [93] also reached virtually the same result by setting out from the Gibbs–Duhem equations, and successfully applied their procedure to a number of systems. The possibilities of application of the method have since been investigated by various authors [94–96] (the generalization is usually attributed to Sarkar and Kruck instead of to Martin). The most important of these results were those of Avdeef and Raymond [95], who introduced the total system of differential correlations, including the possibility of the analytical calculation of the fundamentally important differential quotients during the determination of the various experimental data and the stability constants. This latter possibility was also pointed out by Nagypál *et al.* [123], who utilized a different mathematical formalism. Both derivations are essentially based on the differentiation laws of implicit function systems, which are to be found in any textbook on mathematical analysis. These rules have been applied for many years by research workers dealing with studies on the fundamental thermodynamic correlations in equilibrium chemistry [124]. They were first used in the field of the chemistry of equilibria in solution by Bugaevsky *et al.* [125–127]. Nevertheless, they began to find wider application only after the appearance of the publication by Nagypál *et al.* [123].

If the equilibrium concentration of a single component is measured, without a knowledge of the equilibrium model, the differential connections treated in detail in Chapter 3 allow calculation of the equilibrium concentrations of the other components. The total correlation system has been discussed most generally by Avdeef and Raymond [95]; here, we present only two equations used in the pH-metric study of systems H–L–Me

$$-\log[\mathrm{L}] = -\log[\mathrm{L}]_0 - \int_{\mathrm{pH}_0}^{\mathrm{pH}} \left(\frac{\partial T_{\mathrm{H}}}{\partial T_{\mathrm{L}}}\right)_{T_{\mathrm{Me}},[\mathrm{H}]} \partial\mathrm{pH} \qquad (5.16)$$

$$-\log[\mathrm{Me}] = -\log[\mathrm{Me}]_0 - \int_{\mathrm{pH}_0}^{\mathrm{pH}} \left(\frac{\partial T_{\mathrm{H}}}{\partial T_{\mathrm{Me}}}\right)_{T_{\mathrm{L}},[\mathrm{H}]} \partial\mathrm{pH}. \qquad (5.17)$$

We shall illustrate the interpretation of these correlations, and the difficulties arising in the course of application, with calculations based on Eq. (5.16). With a view to the determination of $(\partial T_{\mathrm{H}}/\partial T_{\mathrm{L}})_{T_{\mathrm{Me}},[\mathrm{H}]}$, the pH-metric titration curves recorded at different total ligand concentrations, but at the same total metal ion concentration, are transformed to $\mathrm{pH} = f(T_{\mathrm{H}})_{T_{\mathrm{L}},T_{\mathrm{Me}}}$ curves, as can be seen in Fig. 5.16, which presents the example of the Cu^{2+}–O-phosphorylethanolamine system, investigated by Österberg [128].

From Fig. 5.16, a $T_{\mathrm{H}} = f(T_{\mathrm{L}})_{\mathrm{pH}}$ diagram is constructed (Fig. 5.17), if necessary via interpolation; the $(\partial T_{\mathrm{H}}/\partial T_{\mathrm{L}})_{\mathrm{pH}}$ values are read off, and are then plotted as a function of the pH (Fig. 5.18). Finally, the curve depicted in Fig. 5.18 is integrated graphically or numerically. As the starting-point of the integration, it is necessary to choose a very low pH_0 value at which complex formation can be neglected; thus, $\log[\mathrm{L}]_0$ can be calculated through a direct formula, the protonation equilibrium being taken into consideration. If the equilibrium concentration of the metal ion is to be calculated, the above procedure is modified appropriately.

Even from this description it is readily possible to appreciate the difficulties involved in applying the method.

(1) For the calculation of $\log[\mathrm{L}]_0$, the pH-metric titration must be begun at a low pH where the effect of complex formation is still negligible. This means that the effects of the equilibria under examination are insignificant over a considerable section of the titration curve, while at the same time even a very

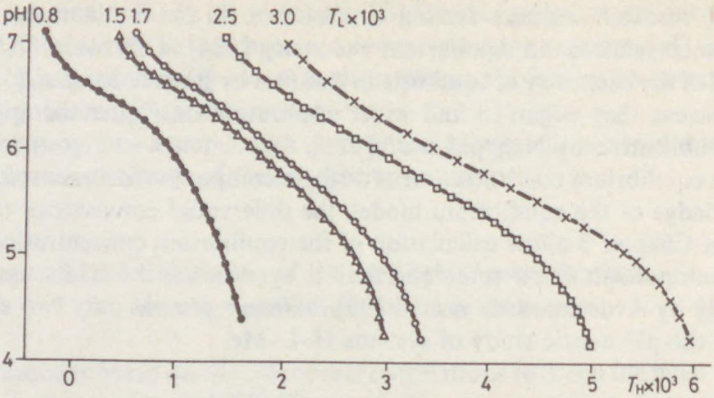

Fig. 5.16. Functions $pH = f(T_H)$, obtained experimentally at various total ligand concentrations in the Cu^{2+}–O-phosphorylethanolamine system [128]
(Reproduced with permission from *Acta Chem. Scand.*, **14**, 471 (1960))

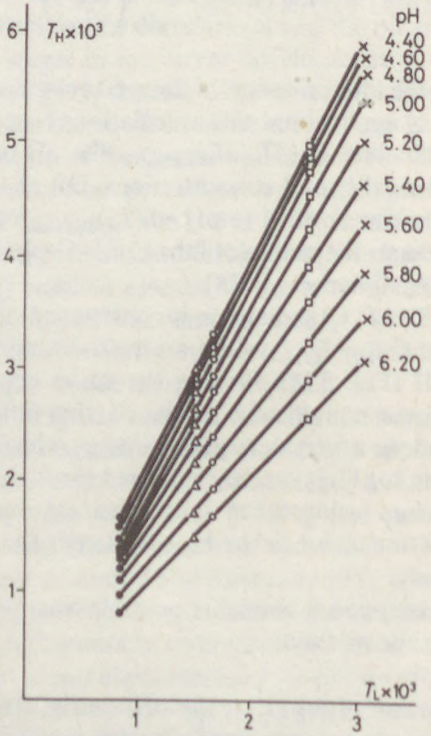

Fig. 5.17. Functions $T_H = f(T_L)$, calculated by interpolation from the data of Fig. 5.16 at various pH values [128]
(Reproduced with permission from *Acta Chem. Scand.*, **14**, 471 (1960))

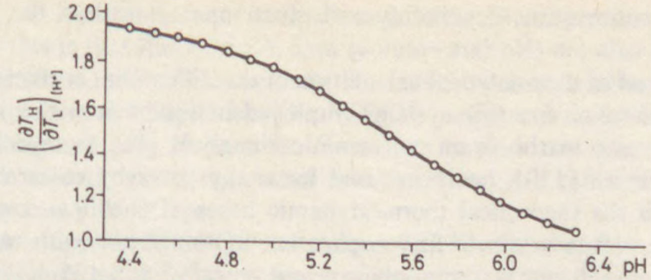

Fig. 5.18. Functions $(\partial T_H/\partial T_L)_{pH} = f(pH)$, calculated on the basis of Fig. 5.17 [128] (Reproduced with permission from *Acta Chem. Scand.*, **14**, 471 (1960))

small error made experimentally in the total concentrations may become highly significant in the pH interval sensitive to the complex formation processes.

(2) A very large number of experimental data are required for the method to be applicable, in order that the unavoidable interpolations and the graphical or numerical differentiation and integration may be carried out reliably.

Nevertheless, the method also has the obvious tremendous advantage that, if the equilibrium concentrations of all of the components are known, the other calculations can be simplified considerably, and the compositions of the complexes formed in predominant concentrations can be identified with a high degree of certainty.

In our opinion, therefore, this procedure would best be used primarily for determination of the correct chemical model, possibly in combination with the Vadasdi [92] procedure discussed in connection with two-component systems, but appropriately extendable to multicomponent systems. When the very probable model is known, it is possible to plan with very high certainty titrations that are sufficiently sensitive to the formation of every complex. Through the fitting of these, by means of the methods surveyed in the following section, the formation constants can in all probability be determined more exactly.

5.2.4 Calculation of formation constants

The vast majority of programs constructed to calculate formation constants operate on the basis of the least squares principle, and the minimum in the target function is generally calculated by the Gauss–Newton method or by modified variants of this. In the course of the calculations, there is always a need for the differential coefficients of the experimental data to be fitted with respect to the parameters to be calculated. It is surprising that these differential coefficients are calculated numerically in the large majority of the programs; as a consequence of the repeated solution of the mass balance equations, this is obviously more time-demanding and more inaccurate than the analytical method.

The method of the analytical calculation of the differential coefficients in the case of the implicit function systems employed in equilibrium chemistry is to be found in any textbook on mathematical analysis and, as revealed in the review by Smith [130], has been used for many years by research workers dealing with the theoretical thermodynamic bases of chemical equilibria. In spite of this, it has begun to find application in connection with calculations on solution equilibrium systems only in recent years [95, 123, 125–127, 131, 132].

The theoretical computational principles of the Gauss–Newton method and its modifications have been detailed in a number of publications; accordingly, in this section we shall deal primarily with

(1) selection of the function to be minimized;
(2) checking of the goodness of the fit, and its meaning;
(3) certain questions or error estimation.

5.2.4.1 Selection of the function to be minimized

We completed our review of methods based on the auxiliary functions with the statement that the constants are most advisably calculated through fitting of the direct experimental data. In Chapter 4, dealing with the experimental methods, we saw that there may be very many types of direct experimental data, e.g. the total concentrations, the e.m.f.-s (which are directly connected with the equilibrium concentrations), pH values, the volume of titrant solution, the distribution coefficient, the absorbance, the half-step potential, the NMR band-width, etc. In principle, the function to be minimized may be any of these, or any optional combination of them.

In most of the generally applicable programs, the function to be minimized is fixed and cannot be regulated with the input data. The target functions used in the programs published up to 1976 are given in the review by Gaizer [23]. In programs written for the evaluation of photometric measurements, for instance, the square sum of the differences between the measured and calculated absorbances is minimized. The program of Lingane and Hugus [133] is an exception for, besides the absorbances, it also interprets the total concentrations of the metal ion and of the ligand as data to be fitted.

The SCOGS program [109] serves for the evaluation of pH-metric titration curves, and minimizes the square sum of the differences between the measured and calculated volumes of titrant base. It is obvious, however, that both, the volume of titrant and the pH contain experimental errors during pH-metric titrations, and it is therefore preferable to use orthogonal regression [134]. The essence of this is that the X and Y data (volume and pH) are also regarded as containing errors, and the function to be minimized is a combination of the differences in the two variables. The SCOGS program was modified in this sense by Nagypál [28]. A number of authors have drawn attention to the importance of orthogonal regression in connection with other methods and other programs [135–137].

The widely applied MINIQUAD program [27] minimizes the square sum of the differences of the total concentrations of all of the components. This provides a possibility for a very fast, efficient algorithm. The specific feature of the program is that the solution of the balance equations and the refinement of the constants are not separated, but can be performed in a single iteration cycle. The differential coefficients necessary for the simultaneous refinement of the equilibrium concentrations and the constants are calculated analytically, but separately for each balance equation; this circumstance makes it unavoidable that the differences in the concentrations of all of the species be taken into consideration in the function to be minimized.

The minimization of $\sum(\Delta T_i)^2$ is obviously correct if the individual samples are made up separately. However, if pH-metric titration is performed, then T_L and T_{Me} are practically constant (they vary only with the dilution), so that the error in T_L and T_{Me} can only be a systematic error; merely the T_H and pH data are subject to experimental error. Accordingly, in our view, the fitting employed in the MINIQUAD programs is incorrect in principle in the case of pH-metric titrations. With well-planned, accurate measurements, however, this error of principle affects the values of the constants to a negligibly small extent, as demonstrated by the agreement of the results of calculations on the same systems with the SCOGS [109] and LETAGROP [24] programs and with the LEAST program [8], which operates on a similar principle to the MINIQUAD program.

The PSEQUAD program [114] permits the simultaneous evaluation of the data of potentiometric and spectrophotometric measurements. The function to be minimized in this program is

$$F = \sum_{q=1}^{n_d} F_q \tag{5.18}$$

$$F_q = w_l \sum_{i=1}^{r} (\Delta x_1)^2 + \sum_{i=1}^{r} \sum_{l=2}^{m} v_l (\Delta x_l^P)^2 + w_A \sum_{i=1}^{r} \sum_{l=m+1}^{p} (\Delta x_l^A)^2 \tag{5.19}$$

where r is the number of experimental points; x_l is the total concentration of the species denoted by l, or the volume of titrant solution; $x_2^P, \ldots, x_m^P$ are the measured potentials; $x_{m+1}^A, \ldots, x_p^A$ are the measured absorbances; w_l is the weighting factor of the total concentration of component l, or the titrant solution volume; w_l are the weighting factors of the potentials; and w_A is the weighting factor of the absorbance values. F_q may be any function set up in accordance with Eq. (5.18) from the differences in the above quantities, and the function to be minimized may be regulated via the input data. The program gives a possibility for the simultaneous evaluation of different types of measurements, even if the numbers of components are not the same in the various samples. For example, through simultaneous minimization of the titration curves measured in the systems proton–ligand A, proton–ligand B, proton–ligand A–metal ion, proton–ligand B–metal ion, and proton–ligand A–ligand–B–metal ion (via orthogonal regression too), it is possible to calculate the pK values of the ligands and the formation constants of all of the metal complexes (including those of the mixed ligand complexes). At the same time, if these pH-metric measurements are supplemented with photometric measurements on the same or different solutions, the square sum of the differences between the measured and calculated absorbance values can be incorporated into the function to be minimized. This and other similar possibilities are expressed by the equation $F = \sum_{q=1}^{n_d} F_q$, where n_d is the number of measurement series of different types. It must be noted that, in spite of the fact that the possibilities for selecting the function-combination to be minimized are practically optional, the data calculated with the PSEQUAD program do not correspond perfectly with the strict laws of statistics. It is obvious that each step of an equilibrium measurement series (the weighing of the starting materials, the preparation of the stock solutions, the determination of their concentrations, the mixing of the samples to be studied, the calibration of the instrumentation, etc.) involves experimental errors, and the statistical methods, strictly speaking, should take the errors of these operations too into consideration. Only Cumming *et al.* [5] have employed such strictly interpreted statistics, but their programs can be used merely to evaluate the data on the simplest systems.

5.2.4.2 Checking and evaluation of the goodness of fitting

This is the most important step in the calculation of the constants, and requires great circumspection. There is no generally valid recipe for the satisfactory solution of this task; accordingly, we shall treat those aspects only that we consider to be of greatest importance. Above all, it must be borne in mind that the starting point in the use of the least squares principle to fit any function is that the experimental data to be fitted are subject only to chance experimental error. At the same time, it is clear that the errors in the similarly experimentally obtained, fixed data used in the calculations (total concentrations, auxiliary constants, etc.) are also present in the experimental data to be fitted, but as systematic errors.

In the more complicated equilibrium systems, a very great variety of complexes may be formed and, as we have already seen, the purpose of numerical analysis can only be the determination of the compositions and constants of the species having a considerable influence on the experimental data. Thus, besides the identified species, numerous further complexes may be formed in very low mole fractions, but still with slight effects on the experimental data. Neglect of these leads to a model error, which likewise appears as a systematic error in the experimental data.

As a consequence of the joint effects of these factors, the difference between the measured and the calculated data corresponds to the normal distribution characteristic of chance errors only extremely rarely. In the event of such a practically unavoidable systematic error, the question that arises is the fixing of some limit to the scatter of the data in the given series of experiments, differences larger than this limit then justifying the assumption that additional complexes are formed. It is very difficult to establish this limit; much reliance must be placed on the research worker's own personal experience. When some new minimization procedure or a full program is introduced, therefore, it is very helpful to re-investigate a few well-known equilibrium systems; the scatters obtained for these may be regarded as limiting scatters.

The literature contains abundant material exemplifying the choice of model on the basis of comparisons of scatters calculated via various assumptions [138–147]. Only one of these will be mentioned here for purposes of illustration.

Pettersson [138] made an investigation of the very involved equilibrium processes

$$p\mathrm{H}^+ + q\mathrm{MoO}_4^{2-} + r\mathrm{HAsO}_4^{2-} \rightleftharpoons (\mathrm{H}^+)_p(\mathrm{MoO}_4^{2-})_q(\mathrm{HAsO}_4^{2-})_r$$

through the pH-metric titration of 92 solutions with different compositions. The total concentration of the hydrogen ion was fitted during data evaluation.

Figure 5.19 presents the differences between the measured and the calculated data as a function of pH for three titration curves, under three different sets of conditions. The points denoted by o were calculated by taking into consideration only the data obtained in a preliminary independent study of the systems H^+–MoO_4^{2-} and H^+–HAsO_4^{2-}. The systematic large difference clearly points to the formation of heteropoly acids.

The heteropoly acids with p, q, r values (8, 5, 2), (10, 6, 2), (11, 6, 2) and (12, 6, 2) were identified in a total concentration interval much lower than that indicated here; the points denoted by ▲ were obtained when these species too were taken into account. It may be seen that the difference is now much smaller, but it remains considerable, especially at relatively high molybdate–arsenate concentration ratios.

Finally, the points denoted by ● demonstrate the best fitting; these were attained by considering not only the above species, but also those with p, q, r

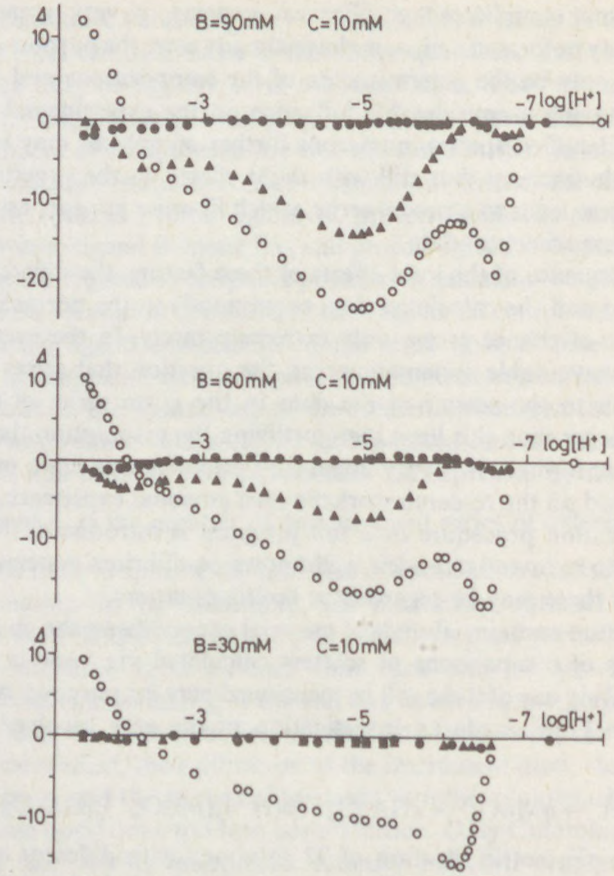

Fig. 5.19. $\Delta T_H = T_H^{\text{calcd.}} - T_H^{\text{measd.}}$ values calculated under different conditions in the H^+–MoO_4^{2-}–$HAsO_4^{2-}$ system [138]
○ — equilibrium data determined separately in the two-component systems H^+–MoO_4^{2-} and H^+–$HAsO_4^{2-}$; △ — assuming formation of the species (8, 5, 2), (10, 6, 2), (11, 6, 2) and (12, 6, 2), besides the data for the two-component systems; ● — additionally assuming formation of the species (14, 9, 1), (15, 9, 1) and (16, 9, 1).
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values (14, 9, 1), (15, 9, 1) and (16, 9, 1). In this latter case the difference fluctuates around zero, i.e. very slight systematic differences are still observable. However, the magnitude of the differences is not sufficient to justify the assumption that even more species are formed; the small systematic differences almost certainly stem from the error possibilities mentioned above.

The question of the goodness of the fitting was dealt with in detail by Vacca *et al.* [139], who proposed the introduction of a factor, which can be calculated from the laws of error propagation via a 'pessimistic estimation' of the possible experimental errors. They also pointed out that in some cases the experimental data may be described within the resulting limiting values by a number of models, and the choice of model then reflects the personal judgement of the research worker.

In a study of the Cu^{2+}–glycylglycine system, Gergely and Nagypál [140] demonstrated that the formation constant of the complex CuL_2 could not be calculated directly: when the formation constant of the complex was regarded as a parameter to be calculated, the equation system obtained in the Gauss–Newton iteration became poorly conditioned.

At the same time, when the formation constants of the other complexes were calculated at various fixed values of β_{CuL_2}, the fitting improved slightly; the 'best fitting' was found at a β_{CuL_2} value corresponding to roughly 15% CuL_2 formation at pH ~ 5. This means that the complex CuL_2 can not be detected even when it is formed to an extent of about 15%. The probable cause of this is that it can not be formed at a ligand–metal ion concentration ratio of 1 : 1, even if the constant is comparatively large, while at a ligand excess its effect appears in the pH range where the predominant complex is $CuLH_{-1}$, which similarly leads to the release of two protons.

These examples, and the numerous others to be found in the literature, confirm the truth of the statement made in the introduction: the checking and the acceptance or rejection of the goodness of the fit is the step demanding the greatest circumspection in the calculation of the constants, and assistance towards the correct solution of this task is primarily provided by experience.

5.2.4.3 Estimation of errors in constants

We shall deal with this question only in order to discuss the real meaning and significance of the errors of only ± 0.001–0.002 log unit reported for the equilibrium constants in the literature in some cases. Naturally, this topic has already been treated by a number of authors, but it appears that the misunderstandings have not yet been completely dispelled.

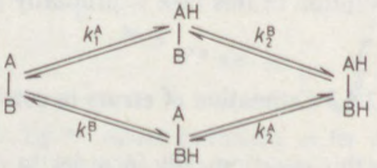
In an interpretation of the meaning of the errors, the starting point must be that, as mentioned at the end of Section 5.2.4.1, not a single general program satisfies the strictly taken rules of statistical evaluation. Further, in the sense of the considerations outlined in the previous section, the model error (no matter how small, but unavoidable) finally appears as the error in the constants. Accordingly, the calculated errors in the stability constants characterize the reproducibility of the determination of the constants under the given experimental conditions.

The true errors in the stability constants can be estimated with a high degree of certainty only through the comparison of constants obtained with methods differing in basic principle, or of constants obtained in independent laboratories. These considerations explain why, in the publications of the Commission on Equilibrium Data of the Analytical Chemistry Section of the IUPAC dealing with critical evaluations of stability constants in various systems, agreement within ±0.05 log unit is classified as very good agreement, even in systems that can be studied experimentally without difficulty [148–152].

5.2.5 Determination of microconstants

We have so far surveyed the methods serving for the determination and calculation of the compositions and formation constants of complexes, but without considering the structures of the complexes. It is obvious, however, that a species of given stoichiometry, that can be described thermodynamically by a single formation constant, may occur in various structural forms; the microconstants mentioned in the title to this section are the constants of the equilibrium processes between given species with different structural forms.

Let us consider, for example, a ligand capable of taking up two protons, the protonation sites not being equivalent chemically (e.g. aminocarboxylates or aminophenolates), and let us denote the protonation sites by A and B. The uptake of the protons in this case can proceed in accordance with the following scheme



$$L \xrightarrow{K_1^p} HL \xrightarrow{K_2^p} H_2L.$$

The constants describing the processes L→HL→H_2L are often termed macroconstants, but this nomenclature is justified only in work involving microconstants, in the interest of differentiating between the two types of constants. It can readily be seen that the following correlations hold between the micro- and the macroconstants

$$K_1^p = \frac{[HL]}{[H][L]} = \frac{[(AH)B + A(BH)]}{[H][L]} = k_1^A + k_1^B$$

$$\frac{1}{K_2^p} = \frac{[HL][H]}{H_2L]} = \frac{[(AH)B + A(BH)][H]}{[H_2L]} = \frac{1}{k_2^A} + \frac{1}{k_2^B}.$$

It can readily be shown that, as the number of donor groups able to undergo protonation increases, the number of microconstants is 2^n. It must also be borne in mind that a hydrogen-bond may be formed between adjacent donor groups, the number of microconstants then naturally decreasing, for by this means the structures (AH)B and A(BH) become indistinguishable, as (A ... H ... B).

The introduction of the concept of microconstants was necessitated by the consideration of the structural differences; hence, it is obvious that, for their determination, primarily those equilibrium study methods are suitable which, besides changes in the equilibrium state, provide information on the structural changes (spectrophotometry, NMR, CD). There is no difference in principle between the experimental methods for the determination of micro- and macroconstants; only the means of evaluating the experimental results differ. In connection with the evaluation methods, it is necessary to stress one circumstance (this is frequently not sufficiently emphasized, and it appears at times that it is not sufficiently well understood): the calculation of the microconstants is always based on some obvious assumption, but this assumption cannot be proved in a strict thermodynamic sense.

The assumption most frequently utilized in the chemical modification [153–157] is that the electronic structure of the molecule does not change if the hydrogen of the carboxyl group is replaced by a methyl group, e.g. the protonation constant of the amino group in glycine methyl ester is the same as the microconstant for the process

$$\mathrm{HOOC{-}CH_2{-}NH_2 + H^+ \rightleftharpoons HOOC{-}CH_2{-}NH_3^+}.$$

The starting point in the use of visible-UV spectrophotometry is the assumption that a spectral change relating to some chromophoric group of the molecule (e.g. a phenolic OH) is independent of the state of protonation of groups more distant from the chromophoric group [158–160].

The most direct method, and the most promising one from the aspect of determination of the microconstants, is NMR spectroscopy. When this is used, it can similarly be assumed that the chemical shift of some NMR-active nucleus close to the group undergoing protonation is not influenced by the state of protonation of the more distant groups [161–163]; in the refined variant, the effects of the neighbouring groups may be taken into account on the basis of measurements on model compounds [164, 165].

The references reveal that there is already an extensive literature on the determination of the microconstants. However, the great majority of the publications discuss the methods and results of studies on the protonation processes. Different structural forms corresponding to the same stoichiometric composition can naturally also occur among the metal complexes. In a wide-ranging equilibrium study of the DOPA (3,4-dihydroxyphenylalanine) complexes of transition metal ions, Kiss and Gergely [166] determined the microconstants of a number of metal complexes, while Kiss and Tóth [167] took the first steps towards separating the microconstants into the microenthalpy and microentropy changes.

Noszál and Burger [168] introduced the concept of the group constant to characterize the overlapping protonation equilibria of polyfunctional ligands. The essence of this is that, in the case of identical groups that do not mutually influence the respective protonation processes (when the macroconstants differ only because of the statistical effects), the protonation processes are described by means of the group constants freed from the statistical effects.

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Chapter 6

Factors determining the compositions and stabilities of metal complexes

A number of reviews have already appeared on the complex-forming properties of the individual metal ions and on the complexes of the various ligands with the different metal ions. Here, therefore, we shall devote our attention mainly to those phenomena which hold in general for a wide range of complexes. In the broadest sense, the compositions and stabilities of the complexes formed are determined by the chemical properties of the metal ion(s) and the ligand(s) as internal factors, and by the characteristics of the solvent, the temperature and the ionic strength as external factors. Complex formation in solution is always accompanied by the release of solvent molecules bound to the ligand, and by the solvation of the resulting complex. Accordingly, we shall deal first with the role of the solvent, with phenomenon of solvation (and in more detail with that of hydration), and then with attempts to determine the stabilities of aqua complexes and to eliminate the role of the solvent. Subsequently, we shall examine how the compositions of the resulting complexes are influenced by the chemical properties of the metal ions, the structures of the ligands and the nature of the donor atoms and donor groups, and finally we shall discuss the factors determining and influencing the values of the stability constants and the various derived equilibrium constants.

Since the bonding in outer sphere complexes and in mixed metal complexes generally differs in nature from that in complexes of other types, such complexes will be treated separately at the end of this chapter. The present aims and the nature of this book do not allow us to provide a detailed discussion of every question; we shall merely emphasize the main correlations and try to assist the reader in his orientation with as many useful literature references as possible.

6.1 Solvation and complex formation

Complex formation is accompanied by the displacement of solvent molecules from the coordination sphere of the metal ion, i.e. it can be described by the following general equations

$$\mathrm{MeS}_Q + \mathrm{L} = \mathrm{MeS}_{Q-i}\mathrm{L} + i\mathrm{S}$$

$$\vdots$$

$$\mathrm{MeS}_j\mathrm{L}_{N-1} + \mathrm{L} = \mathrm{MeL}_N + j\mathrm{S}$$

where Q = number of solvent molecules coordinated to the metal ion; N = maximum number of ligands; i = number of solvent molecules displaced by the first ligand; j = number of solvent molecules displaced by the Nth ligand.

Accordingly, instead of the expression

$$K_1 = \frac{[\mathrm{MeL}]}{[\mathrm{Me}][\mathrm{L}]} \tag{6.1}$$

the processes actually taking place are reflected by the equilibrium constant defined by the expression

$$K_1^* = \frac{[\mathrm{MeS}_{Q-i}\mathrm{L}][\mathrm{S}]^i}{[\mathrm{MeS}_Q][\mathrm{L}]}. \tag{6.2}$$

In dilute solutions, however, the concentration of the solvent is practically constant, and the quantities denoted by K_1 and K_1^* therefore differ only by a constant multiplication factor

$$K_1^* = K_1[\mathrm{S}]^i. \tag{6.3}$$

Thus, the constants defined by Eq. (6.1) are also suitable for characterization of the concentration distribution and thermodynamic stabilities of the various complexes. Equation (6.2), however, draws attention to the fact that, during the interpretation of the values of the constants, special attention must be paid to the phenomenon of solvation (in aqueous solutions hydration) and the manner in which this influences the values of the stability constants.

For the sake of completeness, it must be noted that there may be a specific interaction between the ligand and the solvent molecules too, which ceases as a consequence of complex formation. At the same time, new, likewise specific interactions may develop between the complex formed and the solvent molecules. These features further complicate the equilibrium conditions, and hence the equilibrium constant defined by Eq. (6.2) can not be regarded as complete either.

The role of the solvent in the energy conditions of complex-formation processes is strikingly illustrated, as an example, by the fact that the enthalpy of hydration of the Cu^{2+} ion is -2100 kJ mol^{-1}, whereas the enthalpy change accompanying the process

$$Cu(H_2O)_6^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4(H_2O)_2^{2+} + 4H_2O$$

is -92 kJ mol^{-1} [1], i.e. merely a few per cent of the hydration heat. If the energy conditions of solvation and of complex formation in solution are compared, it generally holds that the enthalpy change accompanying the complex formation is of a lower order of magnitude than the solvation heat. It is understandable, therefore, that change of the solvent may have an extremely great influence on the compositions and stabilities of the complexes formed. The solvents may be classified from numerous aspects. From the aspect of the analysis of the connection of solvation and complex formation, however, the most convenient classification is based on the nature of the interaction between the solvent molecules. On this basis, protic and aprotic solvents are distinguished.

The molecules of protic solvents are capable of forming hydrogen-bonds, i.e. they contain protons linked to O, N or F atoms; examples include water, methanol, ethanol and formamide. It is characteristic of these solvents that, due to the relatively strong, directed hydrogen-bonds, their molecules are situated in a more or less ordered way, and their melting and boiling points are therefore substantially higher than might be expected from their molecular masses alone.

Between the molecules of aprotic solvents, there are merely dipole–dipole or induced dipole–induced dipole interactions. In the former case we speak of polar aprotic solvents (e.g. dimethylformamide, dimethylsulphoxide, acetone or pyridine) and in the latter case of apolar aprotic solvents e.g. benzene, cyclohexane, hydrocarbons or carbon tetrachloride. In general, neither the metal ions nor the ligands dissolve in apolar aprotic solvents; thus, from the aspect of the equilibrium conditions of metal complexes it is only necessary to consider the solvation conditions prevailing in protic and polar aprotic solvents. The most typical protic solvent is water. In aqueous solutions, the metal ions are to be found in hydrated form or as aqua complexes. We speak of hydration in aqueous solutions of alkali metal and alkaline earth metal ions, for instance, where only ion–dipole interactions occur between the metal ions and the water molecules. For metal ions with unfilled *p*, *d* or *f* subshells (Be^{2+}, Al^{3+}, transition metal ions, rare earth metal ions), however, it is more correct to speak of aqua complex formation, for in this case the water is coordinated via one of the non-bonding electron pairs of its oxygen atom to an empty orbital of the metal ion. Naturally, a sharp dividing line can not be drawn between these two phenomena. In practice, the two phenomena may be distinguished by heating the aqueous solutions of metal chlorides. If, when the aqueous solution of the metal chloride in question is evaporated down, an anhydrous salt is formed, we may speak of hydration; if the evaporation gives rise to partial hydrolysis, i.e. hydrogen chloride is evolved, we may speak of aqua complex formation. No matter whether hydration or aqua complex formation is involved, the dissolution of metal ions is always accompanied by the breaking of hydrogen-bonds between the water molecules and by the formation of ion–dipole or coordinate bonds, i.e. by the rearrangement of the water molecules. However, the water molecules bound directly to the metal ions form further hydrogen-bonds through their hydrogen atoms, so that a second, more or less similarly ordered coordination sphere results. This is followed by the third sphere, a transition between the second coordination sphere and the bulk of the solvent.

In the case of cations dissolved in polar aprotic solvents, there is no second coordination sphere. The molecules bound in the first coordination sphere are no longer able for further interaction to form a definite shell with a different degree of ordering from that of the bulk of the solvent. The solvation conditions for cations in solvents of the above two types are illustrated in Fig. 6.1 [2].

Although the degree of ordering is lower in Case (b) than in Case (a) in Fig. 6.1, nevertheless (since there are only weak dipole–dipole interactions compared to hydrogen-bonds between the solvent molecules) solvation of Type (b) generally involves a larger solvation enthalpy change than does that of Type (a). Accordingly, the enthalpy change accompanying the transfer of a metal ion from aqueous solution into a polar aprotic solvent is negative. At the same time, solvation of Type (a) entails a considerable increase in the degree of disorder (relative to the bulk of the solvent), i.e. an entropy increase, which is in contrast with the effect of solvation of Type (b). To generalize, it may be stated that water and protic solvents in general are good solvents for the various

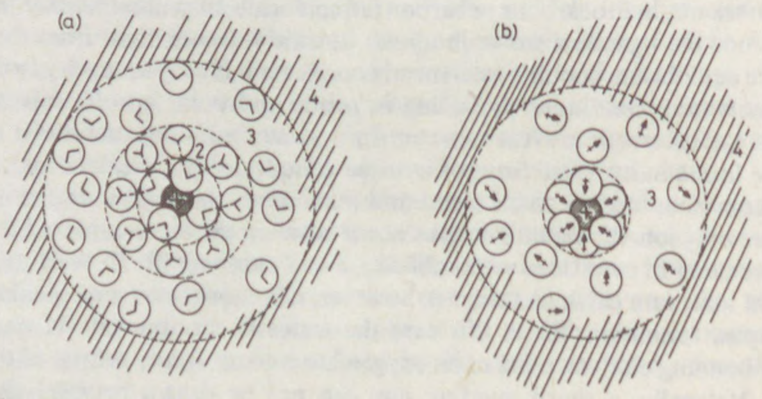


Fig. 6.1. Solvation of cations in (a) protic, and (b) polar aprotic solvents [2] (Reproduced with permission from *Aust. J. Chem.*, **27**, 477 (1974))

Table 6.1 Free energy, enthalpy and entropy changes of transfer of some ions from water to dimethylsulphoxide and to N, N′-dimethylformamide at 25 C° [2]

	Dimethylsulphoxide			N, N′-dimethylformamide		
	ΔG_{trans}	ΔH_{trans}	$-T\Delta S_{trans}$	ΔG_{trans}	ΔH_{trans}	$-T\Delta S_{trans}$
	kJ mole^{-1}					
Li^+	−14.6	−26.4	11.8	−9.6	−32.2	22.6
Na^+	−13.8	−27.6	13.8	−10.5	−33.1	22.6
K^+	−12.1	−34.7	22.6	−9.6	−39.3	29.7
Ag^+	−33.5	−54.8	21.3	−17.2	−38.5	21.3
NEt_4^+	−12.6	4.2	−16.8	−8.4	−0.8	−7.6
Cl^-	38.5	18.8	19.6	46.0	21.3	24.7
Br^-	25.5	3.3	22.2	30.1	3.3	26.8
I^-	9.2	−13.4	22.6	18.8	−13.8	32.6
ClO_4^-	−1.3	−19.2	17.9	0.4	−22.6	23.0

metal salts because of the positive solvation entropy, while the polar aprotic solvents are good solvents because of the negative solvation enthalpy.

As an illustration of the above considerations, Table 6.1 (based on the data of Cox *et al.* [2]) lists the free enthalpy, enthalpy and entropy changes for the transfer of some ions between water and two typically polar aprotic solvents. Table 6.1 also lists the halide ions serving as ligand.

The solvation conditions of the ligands are in general much less well clarified; quantitative data are available only for a few simple anion–ligands.

As concerns the halides as ligands, one of the most important points is that the fluoride ion forms very strong hydrogen-bonds with protic solvents, the chloride ion forms moderately strong ones, and the bromide ion forms weak ones, while the iodide ion is practically not incorporated into the system of hydrogen-bonds. One of the consequences of this is that the enthalpy change accompanying the transfer of the halide ions from water into polar aprotic solvents decreases in the sequence $Cl^- > Br^- > I^-$. For this reason, the chloride ion forms essentially more stable complexes in polar aprotic solvents than in water, whereas the stabilities of iodo complexes are almost the same in the two types of solvent. The data of Ahrland [3] are utilized in Table 6.2 to illustrate this phenomenon; Table 6.2 contains the stability constants of the halogeno complexes of Zn^{2+}, Cd^{2+} and Hg^{2+} in water and in dimethylsulphoxide. The tabulated data reveal that the stabilities of the chloro complexes in the two solvents differ by several orders of magnitude, whereas those of the iodo complexes differ by only a few tenths of a log unit. It is interesting to observe that in aqueous solution the halocomplexes of Cd^{2+} are characterized by the sequence $\log K_1^{Cl^-} < \log K_1^{Br^-} < \log K_1^{I^-}$, while in dimethylsulphoxide the opposite sequence holds.

Table 6.2 Stepwise stability constants of the halogeno complexes of Zn^{2+}, Cd^{2+} and Hg^{2+} [3]

Metal ion		Water, 3 *M* $NaClO_4$			DMSO, 1 *M* NH_4ClO_4		
		Cl^-	Br^-	I^-	Cl^-	Br^-	I^-
Zn^{2+}	log K_1	−0.19	−0.57	−1.50	1.94	0.84	−0.70
	log K_2	−0.40	−0.8	—	0.89	2.89	1.41
	log K_3	0.75	0.5	—	2.26	1.34	0.15
Cd^{2+}	log K_1	1.49	1.76	2.08	3.23	2.92	2.18
	log K_2	0.64	0.59	0.70	1.91	1.40	
	log K_3	0.18	0.98	2.14	2.57	2.75	2.93
	log K_4	—	0.38	1.60	1.75	1.68	1.17
Hg^{2+}	log K_1	6.74	9.05	12.87	10.87	12.14	13.52
	log K_2	6.48	8.28	10.95	7.10	8.06	9.76
	log K_3	0.85	2.41	3.78	3.99	5.14	6.01
	log K_4	1.00	1.26	2.23	2.08	2.54	2.62

It is well known that one basis for the classification of the metal ions with respect to their complex-forming tendencies is the sequence of stability of their halogeno complexes. However, the above data on the halogeno complexes of Cd^{2+} reveal that not only the properties of the metal ions, but also the tendencies of the halide ions to form hydrogen-bonds play important roles in the establishment of the stability sequence, which can therefore not be ascribed merely to the differences in the properties of the metal ions.

Information relating to the solvation conditions, to the geometry of the complexes formed and to variations in the geometry can also be obtained by comparing the enthalpy and entropy changes for the individual complex

Table 6.3 Stepwise formation enthalpy and entropy of cadmium halogeno complexes in water (25 C°, 3 *M* $NaClO_4$) and in DMSO (25 C°, 1 *M* NH_4ClO_4) (kJ $mole^{-1}$) [3]

	Water			DMSO		
	Cl^-	Br^-	I^-	Cl^-	Br^-	I^-
$-\Delta H_1$	0.4	4.1	9.5	6.3	3.9	−2.4
$-\Delta H_2$	−0.1	2.4	0.8	−15.0	−17.0	−27.0
$-\Delta H_3$	−7.7	−7.2	3.1	−1.0	−2.0	5.0
$-\Delta H_4$	—	−1.3	15.9	12.2	13.0	9.5
$T\Delta S_1$	8.6	5.9	2.4	12.2	12.8	14.9
$T\Delta S_2$	3.8	0.9	3.1	26.2	28.0	34.9
$T\Delta S_3$	8.6	12.8	9.2	15.8	17.6	11.9
$T\Delta S_4$	—	3.3	−6.8	−2.1	−3.6	−3.0

formation steps [3]. Table 6.3 likewise presents data of Ahrland [3] on the halogeno complexes of Cd^{2+}.

It may be observed from the Table that ΔH_2 and ΔS_2 in dimethylsulphoxide, and ΔH_3 and ΔS_3 in water, are abnormally positive, which points to a change in the geometry in the corresponding steps. In the absence of any other ligand, cadmium is known to form octahedral solvates in both solvents [4–6]. In both solvents, the saturated CdI_4^{2-} has a tetrahedral structure [7, 8], and there is no doubt that $CdCl_4^{2-}$ and $CdBr_4^{2-}$ are also tetrahedral. In some step of the complex formation, therefore, a change in structure occurs, i.e. the coordination of a single ligand is accompanied by the release of three solvent molecules. It is obvious that this process entails a very considerable entropy increase. At the same time, because of the breaking of the bonds, this step is endothermic, or only slightly exothermic. The tabulated data clearly show that the octahedral↔tetrahedral rearrangement takes place in the third step of complex formation in water, and in the second step in dimethylsulphoxide. It appears probable, however, that the whole series of complexes is characterized by the equilibrium of the octahedral and tetrahedral structures; at the beginning of the series, this equilibrium is shifted completely in favour of the octahedral configuration, whereas the tetrahedral structure becomes predominant at the step in question.

It is interesting to observe that in the initial steps, where the role of the change in geometry is not yet significant, the $-\Delta H$ values increase in the ligand sequence Cl^-, Br^-, I^- in water, whereas they decrease in the same sequence in dimethylsulphoxide. The role of the term $T\Delta S$ in the determination of the stability varies in exactly the opposite way. At the same time, it is obvious that the ionic or covalent nature of the Cd^{2+}—X^- bonds is practically unchanged in the two solvents. This tendency draws attention to the fact that conclusions as to the covalent or ionic nature of the coordinate bonds can not be drawn by resolving the $-\Delta H$ and $T\Delta S$ data into separate terms; the relative values of the $-\Delta H$ and $T\Delta S$ data are basically determined by the properties of the solvent. This was pointed out by Prue [9] in 1969; by means of detailed theoretical considerations, he demonstrated that the proportions of the $-\Delta H$ and the $T\Delta S$ data are governed not by the nature of the coordinate bond, but by the physicochemical parameters of the solvent [9].

The main regularities of the connection between solvation and the formation of metal complexes have become known only as a result of work during the past 10–15 years, and only for the simplest systems. It is clear that the connection between the two phenomena may be discovered primarily through comparative investigations in the pure solvents. An analysis of the conditions prevailing in mixed solvents would require the consideration of the interactions between the molecules of the two solvents too, which naturally makes evaluation of the results much more difficult.

In spite of this, during the past 10 years substantially more equilibrium studies have been carried out in mixed solvents containing water than in pure solvents. One of the reasons for this is undoubtedly that it is technically far easier to perform equilibrium investigations in water-containing mixed solvents than in absolute solvents. As the starting-point for the results obtained in water-containing mixed solvents is virtually always the purely aqueous medium, a consideration of these results will be delayed until the questions of hydration and the formation of aqua complexes have been discussed.

It must additionally be noted that, in the large majority of the cases, the formation of ion pairs and the formation of molecular complexes are studied in absolute solvents, and such work has given rise to many results leading to a deeper understanding of the phenomenon of solvation. A discussion of this topic falls outside the scope of the present book, however, and we therefore merely refer the reader to some reviews and monographs [10–15].

6.2 The hydration numbers of ions and the stabilities of aqua complexes

In the course of the comparison of the solvation conditions in protic and in polar aprotic solvents, we have already touched upon the phenomena of hydration and the formation of aqua complexes. A characteristic datum of the process in both cases is the hydration number. A number of methods are known for the determination of the hydration number. It can be calculated, for example, from the solvent transport data relating to the migration of ions in an electric field [16], from the effects of electrolytes on the dissolution of non-electrolytes [17], from water activity data [18], from the densities of salt solutions [19, 20], from the quantity of water extracted together with salts during their extraction with organic solvents [21, 22], etc.

There are often very large differences between the data obtained with the various methods. In the case of aqua complexes, the number of water molecules coordinated directly to the metal ion can be determined by means of an NMR method, isotope exchange or density measurement, and the result accords with the characteristic coordination number of the ion in question with small ligands. However, the results obtained with other methods may differ considerably from this. Such differences can be understood by reference to Fig. 6.1: in the course of the migration of ions, for instance, the metal ion in question may be accompanied by the water molecules attached by hydrogen-bonds to the directly coordinated water molecules.

Further, even the 'characteristic' coordination number is questionable within the series of rare earth metal ions. Numerous data indicate that the characteristic coordination number decreases by one in the middle of the series [23]. Many investigations have recently been carried out to determine the coordination number and to establish the exact position of the decrease in the series [24–26]. Even without providing the detailed results, it appears highly likely that the reason why the coordination number is uncertain is that the methods applied for its determination are not equally sensitive to the presence of water molecules bound with different strengths. At the same time, it is also probable that the change in the coordination number does not occur as a sharp break in the series; it is more likely that there is a progressive shift in the equilibrium of the various structures throughout the series of rare earth metal ions [27].

In connection with the aqua complexes, the question arises of the necessity to know the stabilities and the stability constants: these data might serve as the bases of comparison for all of the stability constants measured in aqueous solution. It is quite obvious that, in the case of the aqua complexes, there is no sense in speaking of stepwise complex formation: the coordination spheres of the metal ions in aqueous solutions are always saturated. The stabilities of aqua complexes with the maximum coordination number can be calculated from data determined in the gas phase, on the basis of the corresponding thermodynamic cycles. Calculations of this nature were made by Yatsimirskii [28], whose results are presented in Table 6.4.

Table 6.4 Thermodynamic constants of $Me^{2+}_{(g)} + 6\,H_2O_{(g)} = Me(H_2O)_{6(g)}$ reactions [28]

Cation	$-\Delta H$ kJ mole^{-1}	$T\Delta S$ kJ mole^{-1}	$-\Delta G$ kJ mole^{-1}	$\log \beta_6$
Ca^{2+}	1217	−172	1045	184
Mn^{2+}	1289	−172	1117	196
Co^{2+}	1527	−172	1355	238
Ni^{2+}	1560	−172	1388	244
Cu^{2+}	1565	−172	1393	245
Zn^{2+}	1502	−172	1330	234

In mixed solvents, the concentration of water can be regulated so that the coordination sphere is only partially saturated with water molecules. However, if the counter-ion is not coordinated, the remaining coordination sites will be occupied by molecules of the organic solvent. If the concentration of water is then increased, the organic solvent molecules will be progressively displaced from the coordination sphere. Accordingly, in mixed solvents there is a possibility to examine substitution reactions of this type. Such equilibria were first studied by Bjerrum and Jørgensen [29]. They followed the variation in absorbance accompanying increase of the concentration of water in methanolic solutions of a number of metal ions. By using the method of corresponding solutions, they calculated the values of the stepwise constants

$$K_i = \frac{[\mathrm{MeS}_{N-i}(\mathrm{H_2O})_i]\,[\mathrm{S}]}{[\mathrm{MeS}_{N-i+1}(\mathrm{H_2O})_{i-1}]\,[\mathrm{H_2O}]}\,. \tag{6.4}$$

Jørgensen later extended these investigations to other solvents [30].

The results were subsequently questioned by Katzin and Gebert [31]; they attributed the change in absorbance to the interaction between the metal ions and the counter-ions, in their opinion this interaction being influenced by variation of the water concentration. Finally, Jørgensen [32] came to the conclusion that the visible–ultraviolet spectra of salts in solvents of this type can not be interpreted by means of simple equilibrium considerations. The phenomenon that the anions are very strongly bound to the metal ions if the solvent is not capable of a sufficiently strong coordination is termed the Katzin effect [32]. With regard to the considerations and results discussed in Section 6.1, it is probable that a deeper interpretation of the phenomenon would also require that the interaction between the molecules of the two different solvents be taken into account, so that in effect the question remains open.

The data obtained by Bjerrum and Jørgensen [29] and by Jørgensen [30] are average constants. Later, the values of the stepwise constants too were determined; such values are given in Table 6.5. It should be mentioned that these tabulated data were calculated from the originally reported results, by taking into account the concentration of the organic solvent, via Eq. (6.4).

The values of the stepwise formation constants for the various systems may be plotted as a function of the ligand number and extrapolated to zero; such values were interpreted by Swinarski [33] as the stability constants of the aqua complexes. There is obviously no basis whatsoever for this assumption: the formation constants have chemical meaning only in the interval $1 \leqq i \leqq N$, the values of the formation constants being one by definition when $i = 0$.

It has already been mentioned that the equilibrium relations in dilute or moderately concentrated solutions are characterized unambiguously by the constants calculated via Eq. (6.1), the solvent concentration being neglected. However, if the concentration of water differs substantially in the different systems, the values of the constants can no longer be compared directly. During the past 15 years, a number of attempts have been made to take into account the concentration of water, or the changes in its concentration, and to eliminate the role of water.

The results of these considerations will be surveyed in the next section.

The stepwise coordination of the solvent molecules must naturally be taken into consideration in all solvent mixtures, regardless of whether water is one of the components or not. As an example, mention may be made of the stepwise coordination of dimethylformamide to the central copper(II) ion in a solvent mixture of acetonitrile and dimethylformamide, studied by Ishiguro and Ohtaki

Table 6.5 Stepwise stability constants defined by Eq. (6.4)

Metal ion	Solvent	$\log K_1^*$	$\log K_2^*$	$\log K_3^*$	$\log K_4^*$	$\log K_5^*$	$\log K_6^*$	Method	Remark	Reference
Cu^{2+}	Nitromethane	4.12	3.23	2.41	2.29	1.79	1.77	Polarography	0.1 *M* Et_4NClO_4	[34]
Cu^{2+}	Nitromethane	4.21	3.16	2.58	2.12	1.79	—	Spectrophot.	K_6^* K_5^*	[34]
Cu^{2+}	Ethanol	0.98	0.70	0.35	0.28	0.07	0.04	Spectrophot.	From ref. [38]	[35]
Cu^{2+}	Ethanol	—	—	—	—	1.41	−0.26	Spectrophot.	—	[35]
Cu^{2+}	Acetone	2.88	2.63	2.13	1.88	—	—	Polarography	0.1 *M* $LiClO_4$	[36]
Cu^{2+}	Acetone	2.88	2.38	1.93	1.78	—	—	Polarography	0.1 *M* Et_4NClO_4	[36]
Cu^{2+}	Acetone	—	—	—	—	2.51	−0.57	Spectrophot.	—	[35]
Co^{2+}	Ethanol	—	—	—	—	2.22	−0.46	Spectrophot.	—	[37]
Co^{2+}	Acetone	—	—	—	—	1.82	−0.56	Spectrophot.	—	[37]
Ni^{2+}	Ethanol	—	—	—	—	2.31	0.24	Spectrophot.	—	[37]
Ni^{2+}	Acetone	—	—	—	—	1.68	−0.79	Spectrophot.	—	[37]

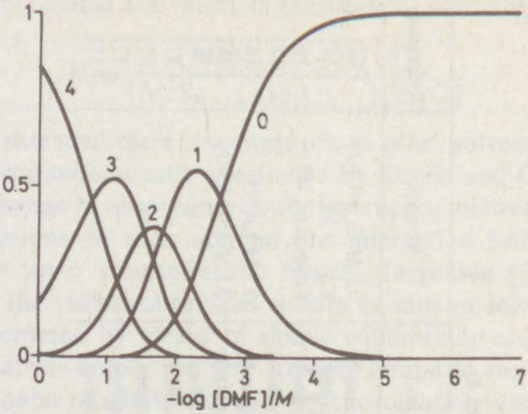


Fig. 6.2. Distribution curves of the $[Cu(DMF)_n]^{2+}$ ($n=1$–4) solvate complexes in the 0.1 *M* $(C_2H_5)_4NClO_4$ acetonitrile solution. Numbers represent *n*, the number of DMF molecules within the complexes [302]
(Reproduced with permission from S-I., Ishiguro, and H., Ohtaki, *Thermodynamics and Structure of Metal Complexes in Various Solvents*, Dept. Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta, 1985, p. 46.)

[302]. The stability constants were determined calorimetrically in $Cu(ClO_4)_2$ solutions, 0.1 *M* $(C_2H_5)_4NClO_4$ being applied to ensure a constant ionic medium. The stepwise coordination of dimethylformamide is described by the curves in Fig. 6.2. In fact, these complex formation processes are also substitution reactions, in the course of which the more weakly bound acetonitrile molecules are progressively replaced by dimethylformamide molecules.

6.3 Water as a component of complex formation equilibria

The vast majority of the complex equilibrium investigations during the past decades were carried out in aqueous medium. It became widely recognized that water as a solvent plays a fundamentally important role in the determination of the stability constants of metal ion complexes, and even in the sequence of their stabilities. It is understandable, therefore, that the attention of researchers turned towards the clarification of the role of water and the discovery of the quantitative correlations relating to its equilibrium chemical effects. For these purposes, many studies have been performed in water-containing solvent mixtures.

In water-containing solvent mixtures, the dielectric permittivity varies with the composition of the solvent, which therefore obviously influences the constants of complex formation equilibria that involve a change in charge or in the charge distribution. The electrostatic considerations of Born and Bjerrum [48] suggested that the logarithms of the equilibrium constants should vary linearly as a function of the reciprocal of the permittivity. The experimental results, however, reveal that linearity is observed only in exceptional cases [49–51]; in a large majority of the more complicated systems, the variation is not linear [52–60]. In the interpretation of the causes of this, and in the establishment of the quantitative correlations concerning the role of water, work of outstanding importance was carried out by Marshall and Quist [39–45]. They determined the equilibrium constants of numerous relatively simple systems as a function of the concentration of water. The water concentration was changed by varying the pressure in the interval above the critical temperature, or by applying a water–dioxane solvent mixture. The results of

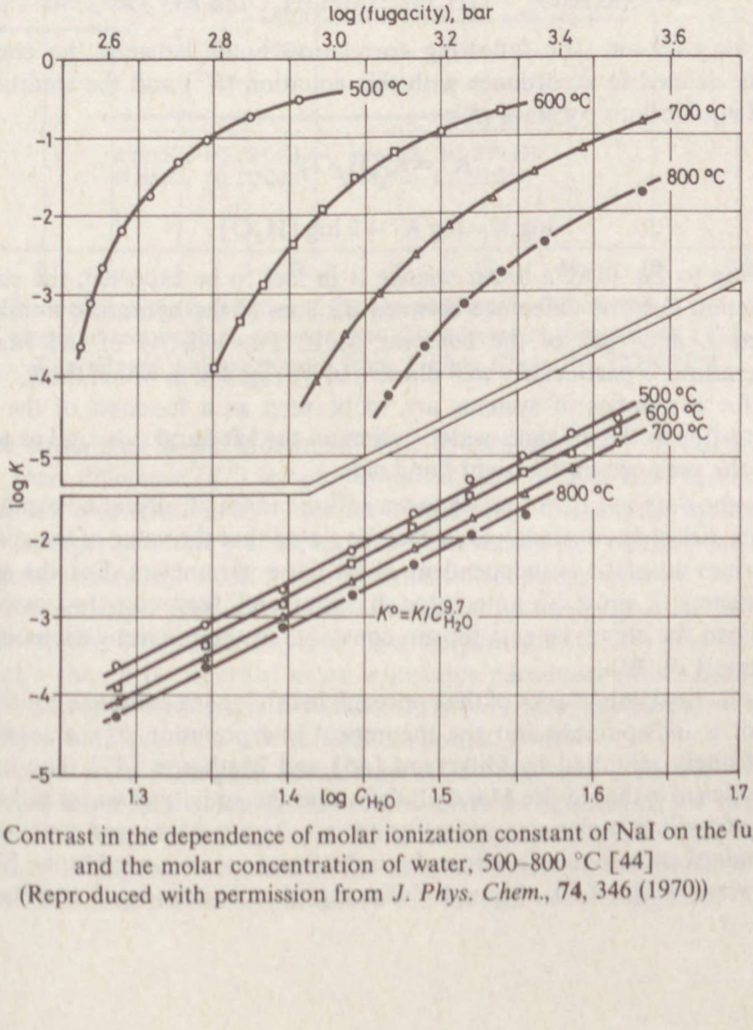


Fig. 6.3. Contrast in the dependence of molar ionization constant of NaI on the fugacity and the molar concentration of water, 500–800 °C [44]
(Reproduced with permission from *J. Phys. Chem.*, 74, 346 (1970))

their own studies and of their calculations utilizing the data of other authors indicated that the logarithm of the ion-pair formation constant varies strictly linearly as a function of the logarithm of the water concentration.

As an example, Fig. 6.3 depicts the logarithm of the dissociation constant of the ion pair NaI as a function of $\log C_{H_2O}$. These data were measured in the temperature interval 500–800 °C and the pressure interval 1000–4000 bar. The upper part of the Figure depicts the dependence of the logarithm of the equilibrium constant on the fugacity of water in the same system. The Figure clearly demonstrates that the variation is much more difficult to interpret as a function of the fugacity than as a function of the water concentration. To explain their results, they proposed the introduction of the concept of the complete equilibrium constant. The essence of this is that the role of water is also taken into consideration in the equilibrium process

$$\mathrm{Me(H_2O)}_x + \mathrm{L(H_2O)}_y \rightleftharpoons \mathrm{MeL(H_2O)}_w + k\,\mathrm{H_2O} \qquad (6.5)$$

where $k = x + y - w$. The following correlation holds between the complete constant defined in accordance with this equation (K°) and the traditionally defined equilibrium constant (K)

$$K^\circ = K/[\mathrm{H_2O}]^k$$

i.e.

$$\log K = \log K^\circ + k \log [\mathrm{H_2O}]\,. \qquad (6.6)$$

According to Eq. (6.6), a linear change is in fact to be expected; the slope of the function is k, the difference between the sum of the hydration numbers of Me and L and that of the complex MeL. The validity of the Marshall considerations is particularly well illustrated by Fig. 6.4, in which the K° values found for a number of systems are to be seen as a function of the water concentration in the dioxane–water system on the left-hand side, and as a function of the pressure on the right-hand side.

Since the data in Fig. 6.4 relate to very wide ranges of solvent concentration, pressure, dielectric constant, etc., it may be stated that the value of the complete equilibrium constant is independent of all these parameters. For the sake of completeness, it must be noted that Bjerrum and Jørgensen too essentially determined the complete equilibrium constants in their investigations of aqua complexes [29, 30].

The practical importance of the approach involving the complete equilibrium constant is indisputable, but the theoretical interpretation of the results has been strongly criticized by Gilkerson [46] and Matheson [47]. The basis of their criticism is that in the Marshall definition the activity of water is the same as the prevailing molar concentration (at any temperature and pressure), i.e. the standard state too varies throughout the functions presented in the Figures. In the view of Marshall, although the standard state does vary, and therefore

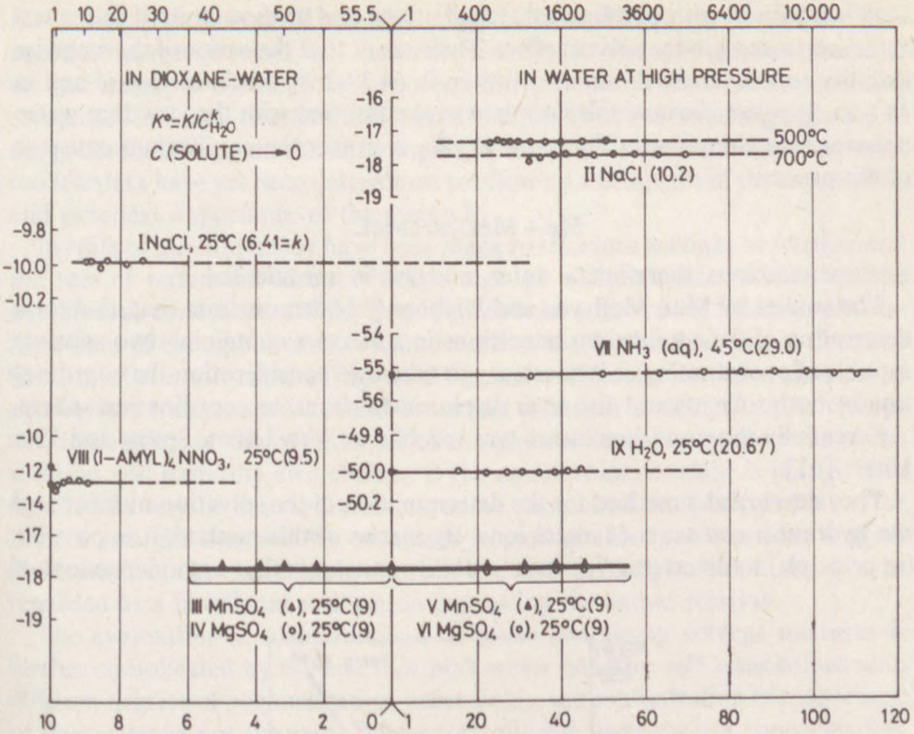


Fig. 6.4. Examples of the invariance of the complete equilibrium constant over extreme ranges of temperature, pressure, and dioxane–water composition [45] (Reproduced with permission from *J. Phys. Chem.*, **76**, 720 (1972))

the free enthalpies of the individual ionic species also vary throughout the curves, their difference ($K°$) remains constant. The data in the Figures attest that this latter conclusion does hold for a wide range of examined systems, but it must be regarded merely as a practical observation; this relation can not be the general theoretical basis of thermodynamic considerations.

It is evident from the dispute that Marshall's treatment, just like any other description of a complicated system, is a simplification of the real situation, and that n should be regarded as an adjustable parameter rather than as the effective change in hydration. Nevertheless, it may be expected that it will be of use from both practical and theoretical points of view.

Setting out from Marshall's considerations, a number of other authors have interpreted the results of studies in solvent mixtures in terms of the change in water concentration. However, in 1970 the investigations by Faraglia, Rossotti and Rossotti [56] drew attention to the fact that, although the change in water concentration does play an important role in the case of the complexes of Ni^{2+},

Cu^{2+} and Zn^{2+} with pyridine, ethylenediamine and glycine, in itself this is not sufficient to explain the solvent effect. Their result that the ratios of the stepwise stability constants are the same in water, in 54.3 wt. % water–methanol and in 48.1 wt. % water–dioxane solvent mixtures is consistent with the view that water behaves as a component. The ratio K_1/K_2 is in fact the equilibrium constant of the process

$$\mathrm{Me} + \mathrm{MeL_2} \rightleftharpoons 2\mathrm{MeL}\,.$$

In these reactions, therefore, a water molecule is not released.

The studies by Mui, McBryde and Nieboer [55] demonstrate that, in a total description of the equilibrium conditions in a mixture containing two solvents capable of coordinating, it is necessary to take into consideration the coordination by both solvents and also their displacement from the coordination sphere.

Essentially the same conclusion was reached by Van Uitert, Spicer and Van Uitert [61].

They developed a method for the determination of the solvation number and the hydration constants of metal ions. By means of this method, it is possible (in principle) to determine 'intrinsic' stability constants that are independent of

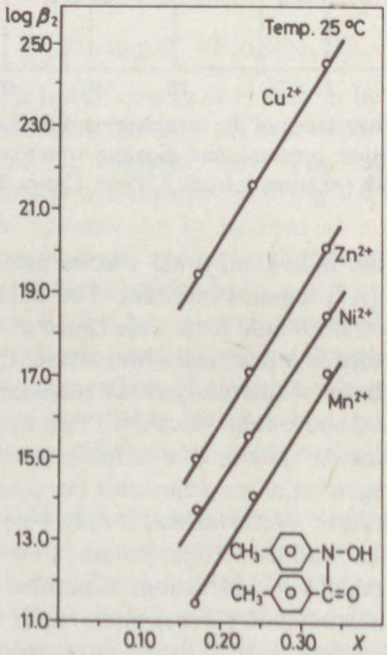


Fig. 6.5. Variation of the stability constant of transition metal complexes of N-*p*-tolyl-*p*-methylbenzohydroxamic acid with mole fraction of dioxane (*x*) [62]. (Reproduced with permission from *J. Inorg. Nucl. Chem.*, **38**, 1663 (1976))

the nature of the solvent. Their aim in this case, therefore, was not to take into account the role of water, but rather to eliminate it. The method was discussed on the example of the pH-metric equilibrium study of ethyl acetoacetate complexes in water — ethanol solvent mixtures. The theoretical significance of the procedure based on the fairly involved considerations is obvious; however, too few data have yet been determined to allow an assessment of the capabilities and practical importance of the method.

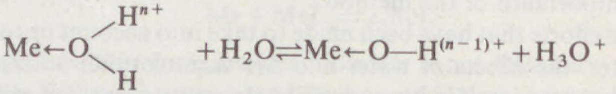
In spite of the efforts that have been made to take into account or to eliminate the role of water, the effects of water and the various other solvents on the equilibrium conditions are far from clarified. In some cases, for example, the logarithm of the equilibrium constant varies linearly as a function of the mole fraction of the solvent (see Fig. 6.5). The main difficulty in the evaluation of equilibrium measurements made in solvent mixtures is that, with the change in composition of the mixture, all of the physico-chemical parameters of the solution will naturally also change. If the equilibrium constant is plotted as a function of any of these parameters, some characteristically shaped curve or even a straight line will be obtained. A plot of this type provides a good illustration of the correlation between the two quantities, but it can not be regarded as a functional connection expressing the causal relation.

The evaluation of data obtained in water-containing solvent mixtures is further complicated by the fact that pure water contains self-associations with different degrees of polymerization; accordingly, the concentration of monomeric or free water is not the same as the formally calculated water concentration. When the solution composition changes, or even when the salt concentration changes in more concentrated electrolyte solutions, the concentration of the monomeric, non-associated water will vary in an unknown manner.

6.4 Classification of metal complexes on the basis of composition

In the previous sections, we have seen that the metal ions are to be found in the form of aqua or solvo complexes in solution, and that the interaction with ligands is accompanied by the displacement of solvent molecules from the coordination sphere. In solvents with a tendency to undergo autoprotolysis, however, not only the neutral molecules, but also the products of autoprotolysis are present. The anionic product of the autoprotolysis is coordinated to metal ions substantially more strongly than the neutral solvent is. As concerns the equilibria between metal ions and solvent anions as ligands, investigations have been performed to date practically only on the hydrolysis of metal ions in aqueous solutions or in water-containing solvent mixtures. On the basis of their composition, therefore, the hydroxo complexes are to be regarded as the simplest complexes.

The mechanism of formation of hydroxo complexes differs fundamentally from that for other complexes: the OH^- does not displace a water molecule from the coordination sphere, but is produced by the dissociation of one of the protons of a coordinated water molecule



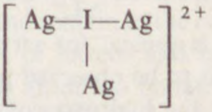
$$\mathrm{Me}\leftarrow\mathrm{O}\begin{array}{l}\diagup\mathrm{H}^{n+}\\ \diagdown\mathrm{H}\end{array}+\mathrm{H_2O}\rightleftharpoons\mathrm{Me}\leftarrow\mathrm{O}\text{—}\mathrm{H}^{(n-1)+}+\mathrm{H_3O}^+$$

Accordingly, this equilibrium indicates that metal ions in their solutions can be characterized by their acidic dissociation constants, in the same way as for simple weak acids. This analogy is not a total one, however, for the hydroxo complexes generally display a very strong tendency to polymerization, i.e. to the formation of complexes with the general formula $\mathrm{Me}_x(\mathrm{OH})_y$. In the case of simple weak acids, di- and polymerization processes occur to only very slight extents. It is a further general characteristic feature of hydroxo complexes that the process of formation of the parent complexes $\mathrm{Me(OH)}, \ldots, \mathrm{Me(OH)}_i, \ldots, \mathrm{Me(OH)}_N$ is very fast, whereas polymerization is otherwise a slow process. Thus, metal ions are very prone to form solutions that are supersaturated with respect to metal hydroxides, and in these solutions it is necessary to take into account metastable equilibria.

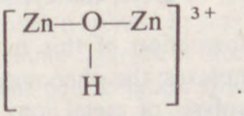
Apart from the series $\mathrm{Me(OH)}, \ldots, \mathrm{Me(OH)}_i, \ldots, \mathrm{Me(OH)}_N$, all those complexes are termed parent complexes that can be characterized by the general formula $\mathrm{MeL}, \ldots, \mathrm{MeL}_i, \ldots, \mathrm{MeL}_N$. In the sense of the previous sections, in these complexes too effectively two ligands, L and the solvent, are to be found in the coordination sphere, but as regards classification on the basis of composition the solvent is disregarded. A datum characteristic of the parent complexes is the maximum ligand number; for monodentate ligands this is the same as the maximum coordination number, while for multidentate ligands it naturally decreases as the number of functional groups in the ligand increases. The exclusive formation of parent complexes may be assumed only for ligands that are monodentate and contain only one electron pair capable of coordination (ammonia, amines). In all other cases, there is (in principle) a possibility for the formation of complexes with other compositions too; in practice, however, the formation of parent complexes is typical for the halides and for chelating ligands with relatively simple structures (glycine, ethylenediamine, glycollic acid). It must be mentioned that complexes with different compositions can also be formed in appreciable concentrations in solutions of ligands generally forming parent complexes, if the concentration conditions are extreme (see Figs 3.26 (a)–(d)).

Complexes containing more than one metal ion are termed polynuclear complexes. The simplest group of these consists of the polynuclear hydroxo complexes. In the Sillén school, the correlations, laws and calculation methods (already discussed in detail in Chapters 3 and 5) relating to the processes of formation of polynuclear complexes were elaborated with a view to interpreting the results obtained essentially from studies of metal ion hydrolysis. In the polynuclear hydroxo complexes, the OH^- ion acts as a bridging ligand; with the exception of the Hg_2^{2+} ion, direct metal ion–metal ion bonding occurs only exceptionally in solution. The Hg_2^{2+} ion does not dissociate in aqueous solution, and its complexes can therefore be treated as mononuclear complexes.

There is a possibility for the formation of polynuclear complexes if a donor atom coordinated to a metal ion has an additional pair of electrons capable of coordination, or if the situation of the donor atoms does not allow all of them to coordinate to one metal ion. The group acting as the bridge may therefore be a monoatomic, an oligoatomic or a polyatomic, polyfunctional ligand. In complexes containing monoatomic bridges, the bridging atom may be coordinated to two or more metal ions, e.g.



$$\left[\begin{array}{c}\mathrm{Ag{-}I{-}Ag}\\ | \\ \mathrm{Ag}\end{array}\right]^{2+}$$



$$\left[\begin{array}{c}\mathrm{Zn{-}O{-}Zn}\\ | \\ \mathrm{H}\end{array}\right]^{3+}.$$

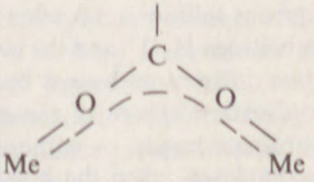
It is obvious that only atoms containing more than one non-bonding electron pair can behave as bridging ligands, though this in itself is not a sufficient, only a necessary condition. It has not yet been demonstrated that water can act as a bridging ligand, though this possibility can not be ruled out in a water-containing solvent mixture with appropriate composition. The following ions may act as monoatomic bridging ligands: F^-, Cl^-, Br^-, I^-, O^{2-}, OH^-, RO^-, S^{2-}, HS^-, RS^-, Se^{2-}, HSe^-, RSe^-, Te^{2-}, HTe^-, and RTe^-, where R is an organic group.

The characteristic feature of the oligoatomic bridging ligands is that the different donor atoms are either bonded directly to one another, or are separated by at most one other atom, e.g.

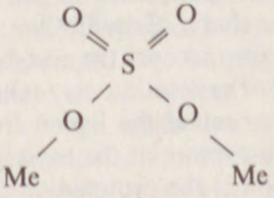
Me—CN—Me
Cyanide
bridge

Me—O—O—Me
Peroxo
bridge

M—SCN—Me
Thiocyanate
bridge

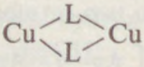


Carboxylate
bridge



Sulphate
bridge

There are extremely varied types of polyatomic bridging ligands. However, an essential difference may and must be made between the complexes formed with monoatomic or oligoatomic bridging ligands and those formed with polyatomic bridging ligands. The mono- and oligoatomic ligands form polynuclear complexes only with a well-defined group of metal ions, the properties of the metal ions governing whether or not the structure in question is stabilized.

The donor groups of the polyatomic ligands, however, are situated at greater distances from one another, and they are practically capable of mutually independent coordination; thus, if a metal ion forms a complex at all, then it will automatically form mono- and polynuclear complexes. This latter phenomenon may be illustrated on the example of the equilibrium constants of the copper(II) complexes of 2,7-diaminosuberic acid, HCOO—CH(NH$_2$)—CH$_2$—CH$_2$—CH$_2$—CH$_2$—CH(NH$_2$)—COOH. In agreement with statistical considerations, in this system the logarithm of the formation constant of the complex Cu—L—Cu is exactly twice the logarithm of the formation constant of the complex Cu(LH) [63]. Other polynuclear complexes too are formed in this system, of course; of these, the cyclic complex  $\mathrm{Cu}\begin{smallmatrix}\diagup \mathrm{L} \diagdown \\ \diagdown \mathrm{L} \diagup\end{smallmatrix}\mathrm{Cu}$ is of outstanding stability. Ring formation of this nature is typical for virtually all types of polynuclear complexes; the phenomenon is to be observed particularly clearly during the hydrolysis of metal ions, and the hydroxo complexes MOH are stabilized in the form  $\mathrm{HO}\begin{smallmatrix}\diagup \mathrm{M} \diagdown \\ \diagdown \mathrm{M} \diagup\end{smallmatrix}\mathrm{OH}$.

The energetic background of the tendency to ring formation has been studied quite comprehensively in the cases of chelate and macrocyclic complexes, and we shall deal with this question in some detail later. Ring formation in polynuclear complexes can in all probability be interpreted in terms of the entropy effect accepted as a simplified explanation of the chelate effect; nevertheless, the deeper correlations remain unclarified.

The metal ions coordinated to a given ligand in polynuclear complexes may be identical or different. In the event of the coordination of different metal ions, we speak of the formation of mixed metal complexes. A special type of mixed metal complexes comprises those complexes in which the ligand is coordinated to ions of one metal, but in different oxidation states. Such complexes are known as mixed valent metal complexes.

In the course of equilibrium studies in aqueous solutions, it is often necessary to take into account the acid–base reaction between H_3O^+ and the complex(es) formed. The reaction may take place by two different pathways: by complete displacement of the ligand from the coordination sphere of the metal ion, through rupture of the corresponding coordinate bonds, or without this. An exception is the protonation of hydroxo complexes, when the bond between the metal ion and the O donor atom does not break; however, the composition of the ligand is changed, and hence this process too can be regarded as total displacement.

The general equation of the process involving total displacement of the ligand is

$$\mathrm{MeL} + \mathrm{H} \rightleftharpoons \mathrm{Me} + \mathrm{HL}\,.$$

The equilibrium constant of this reaction is not independent of the constants for the processes $\mathrm{Me} + \mathrm{L} \rightleftharpoons \mathrm{MeL}$ and $\mathrm{H} + \mathrm{L} \rightleftharpoons \mathrm{HL}$; it can be calculated directly from them.

In processes in which the ligand is not displaced completely, protonated complexes are formed. In this case, the equilibrium constant of the reaction

$$\mathrm{MeL} + \mathrm{H} \rightleftharpoons \mathrm{MeLH}$$

is independent of the constants for the other equilibria, and is a characteristic datum for the protonation of the complex.

In the appropriate concentration and pH ranges, ligands containing several functional groups practically always form protonated complexes. The protonated donor group is generally not coordinated to the metal ion, but the other donor groups of the ligand remain in the coordination sphere. Exceptionally, however, even in the cases of mono- and oligoatomic ligands, it does occur that the protonated donor atom too remains in the coordination sphere. The complex acid of composition $\mathrm{FeCl_3HCl}$, for example, can be regarded as the protonated complex $\mathrm{FeCl_4H}$. The extensive solubilities of $\mathrm{Ag_2SO_4}$ or $\mathrm{PbSO_4}$ in concentrated sulphuric acid may similarly be interpreted in terms of the formation of protonated sulphato complexes. The changes induced by perchloric acid in the NMR relaxation properties and the visible spectrum of an aqueous solution of the vanadyl ion have been explained by the protonation of one of the equatorially coordinated water molecules, and by the continued presence of the $\mathrm{H_3O^+}$ ion in the coordination sphere [64]. A similar protonation without the rupture of the bond between the metal ion and the donor atom can naturally also occur in the case of the more complicated chelating ligands. It should be noted, however, that structural questions of this nature can not be decided from the results of equilibrium investigations. Findings as to the structures of protonated complexes can be made only from the simultaneous application of equilibrium methods and structural examination procedures.

The schemes for the protonation of complexes may be particularly complicated if the ligands contain a number of donor groups, each of which is independently capable of forming a coordinate bond. As an example, Fig. 6.6 presents the scheme of protonation and complex formation in the system $\mathrm{Ni^{2+}}$–2,5-diaminopentanoic acid (ornithine); the ligand here is a relatively simple one, containing donor groups corresponding to one α-amino acid and one aliphatic amine. By means of careful pH-metric examinations in a wide range of

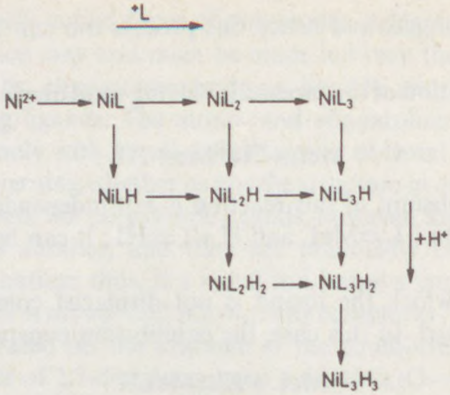


Fig. 6.6. Formation and protonation scheme of the complexes detected in the Ni^{2+}–ornithine system

concentrations, Brookes and Pettit [65] succeeded in demonstrating the formation of all of the complexes indicated in Fig. 6.6.

In the system presented in the Figure, practically only the chelating coordination of the amino acid group need be considered; coordination by the chain terminal amino group may be disregarded.

The situation is more complicated if the ligand in question contains two different donor groups, both of which are able to take part in chelate formation, and which are of comparable strengths from the aspect of complex formation. In such cases (as we have already mentioned), the formation occurs of both binuclear (or possibly polynuclear complexes, linked together in a chain-like manner) and protonated complexes. A possibility also exists for the formation of a new type of complex, mixed bonding mode complexes. The most typical and the most generally investigated ligand of this nature is 3,4-dihydroxy-L-β-phenylalanine DOPA. In the DOPA–metal ion systems, the complexes containing two ligands can occur in different structural arrangements, with one ligand being coordinated to the metal ion in a pyrocatechol-like manner, and the other in an α-amino acid-like manner. In systems of this type, of course, equilibrium chemical analysis is suitable only for establishment of the composition of the complex formed; conclusions as to the bonding mode can be drawn only from the results of structural studies.

Naturally, a complex of this type can also be formed if the solution in question contains pyrocatechol and α-alanine as independent ligands. In this case we speak of the formation of mixed ligand complexes. If we consider the findings in the earlier subsections dealing with solvation, with the exceptions of the coordinately saturated and the solvated metal ion, all of the members of the series MeL, ..., MeL_i, ..., MeL_N can in effect be regarded as mixed ligand complexes; however, from the aspect of the classification based on the composition, the solvent is disregarded. We generally speak of mixed ligand complex formation only if two different ligands (not identical with the solvent) are coordinated in the inner coordination sphere of the same metal ion. Two different ligands may also be associated with one metal ion in a different way: one of these ligands reacts with the metal ion to form a coordinately saturated complex, which is generally an ionic complex; the second ligand is then coordinated to this through electrostatic bonds, in the second coordination sphere. Such complexes are termed outer sphere complexes.

6.5 The chelate effect and the macrocyclic effect

The chelate effect, first defined by Schwarzenbach [66], is one of the oldest known phenomena in the chemistry of complex equilibria; even today, it remains a dispute topic. Its essence is that ligands containing two or more donor groups in such an arrangement that they are able to form five- or six-membered rings on coordinating to the metal ion yield complexes with substantially larger stability constants than those of the analogous complexes of the corresponding monodentate ligands. As an example, the formation constants of the zinc(II) complexes of ethylenediamine are $\log \beta_1 = 5.92$ and $\log \beta_2 = 11.07$. The formation constant of the complex of the tetrafunctional triethylenetetramine, which contains the same number of Zn—N bonds, is one order of magnitude higher: $\log \beta_1 = 12.1$. Likewise, the formation constants of the diamino and tetraamino complexes, which do not produce a chelate ring are more than one order of magnitude lower: $\log \beta_2 = 4.81$ and $\log \beta_4 = 9.46$.

The simplest explanation for the increased stability of chelate complexes is the entropy increase accompanying their formation [67, 68]. Let us compare the formation of the zinc(II) complexes of ammonia and ethylenediamine in aqueous solution:

$$\mathrm{Zn(H_2O)_6^{2+} + 2NH_3 \rightleftharpoons Zn(NH_3)_2(H_2O)_4^{2+} + 2H_2O}$$

$$\mathrm{Zn(H_2O)_6^{2+} + en \rightleftharpoons Zn(en)(H_2O)_4^{2+} + 2H_2O}\,.$$

In the ammonia reaction, the number of mutually independent species in solution does not vary, whereas in the ethylenediamine reaction three species are formed from two. By this means, the degree of order of the system decreases, and the entropy increases, which is reflected in a higher stability.

The chelate effect can also be interpreted on the basis of considerations relating to probability calculations and kinetics. It may be presumed that, when behaving as a monodentate ligand, ethylenediamine forms a complex with almost the same stability as that of ammonia. The other donor group of ethylenediamine is situated in the vicinity of the metal ion. This can be conceived as a situation in which the concentration of the donor group is essentially higher in the vicinity of the reaction partner; accordingly, it is much more probable that ring closure will occur than that a second ammonia molecule (to be found at a much greater distance in the solution) will be coordinated [66].

To confirm the correctness of this interpretation, instead of giving the numerical values of the formation constants let us examine the extent to which the concentration of metal ion not bonded in the complex decreases as a function of the free ligand concentration.

Figure 6.7 depicts the $\log \alpha_{\mathrm{Zn}^{2+}} = \log\left(1/\sum_{0}^{N} \beta_i [\mathrm{L}]^i\right)$ functions for the ammonia, ethylenediamine and triethylenetetramine complexes of Zn(II) as functions of the logarithm of the equilibrium ligand concentration. Figure 6.7 clearly shows that, with the increase of the concentration, there is a steady decrease in the difference in ability to complex the metal ion; indeed, at certain extremely high concentrations, ammonia diminishes the concentration of free zinc(II) ions to a better extent than do the other two ligands.

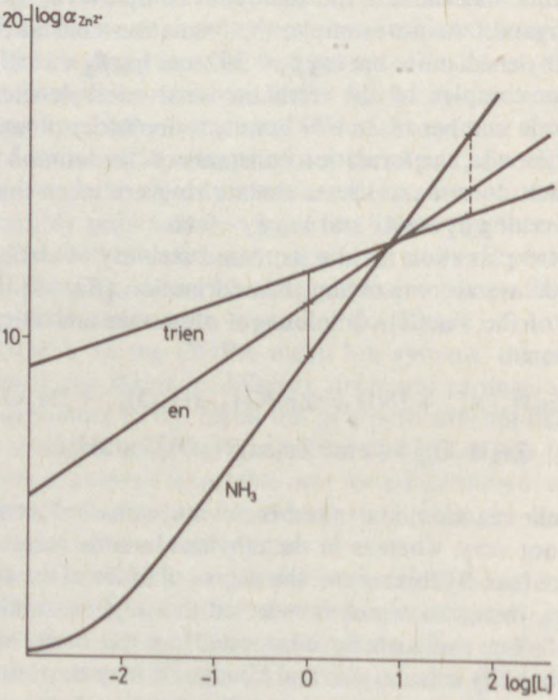


Fig. 6.7. $-\log \alpha_{\mathrm{Zn}^{2+}}$ functions, representing the complex forming ability of ammonia, ethylenediamine and trimethylenetetramine, as a function of the free ligand concentration

The vertical section in the Figure (full line) relates to a ligand concentration of 1 *M*. At this concentration there is still a considerable difference in metal ion-binding capacity: the difference in the $\log \alpha_{Zn^{2+}}$ values is practically equal to the difference in the $\log \beta_1^{trien}$, $\log \beta_2^{en}$ and $\log \beta_4^{NH_3}$ data. The concentration of 1 *M* indicated in the Figure effectively corresponds in the standard state used to express equilibrium constants. Thus, the given concentration-dependence too suggests the justification of the interpretation put forward by Adamson in 1954 [69]: the chelate effect is a consequence of the asymmetry of the standard states. The asymmetry of the standard states means that the concentrations of the reacting species are expressed in *M*, while the concentration of the solvent (water) playing important role in the process is expressed by convention in mole fraction, i.e. the concentration of the solvent does not feature in the equations defining the equilibrium constants. Comparative calculations on numerous systems have demonstrated that in many cases the chelate effect disappears; indeed, for complexes of Zn^{2+} and Cd^{2+} it changes sign if the concentrations of all the reacting ionic species are expressed uniformly in mole fractions, i.e. the pure forms of the reacting substances are regarded as the reference or standard states. Figure 6.7 reveals that, in the concentration interval 10–50 *M*, corresponding to ligands with unit mole fraction, ammonia is the strongest complex former in the systems in question. The same conclusion is reached if the constants expressed in the concentration units *M* are calculated in terms of mole fractions. In such calculations, it must be considered that the concentration of water in dilute solutions is ca. 55.5 *M*, and relative to this the amounts of all other ionic species are negligible. Accordingly*

$$\log \overset{x}{\beta}{}_4^{NH_3} = 9.46 + 4 \log 55.5 = 16.44 > \log \overset{x}{\beta}{}_2^{en} = 11.07 + 2 \log 55.5 = 14.56 >$$

$$> \log \overset{x}{\beta}{}_1^{trien} = 12.1 + \log 55.5 = 13.84$$

The vertical dashed line in Fig. 6.7 denotes the conditions prevailing in dilute aqueous solutions, but relating to unit mole fraction as standard state. It is readily observed and confirmed that the difference in the $\log \alpha_{Zn^{2+}}$ values for the individual ligands at this point is equal to the difference in the constants expressed in terms of mole fractions.

For the sake of completeness, it should be noted that, as shown in Fig. 6.7, the chelate effect disappears only for some metal ions; for the widely studied Cu^{2+}, Ni^{2+} and Co^{2+} complexes, the $\log \alpha_{Me}$ curves intersect one another only in chemically meaningless concentration ranges, i.e. the equilibrium constants

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* The symbol x above the β indicates that the formation constants are expressed in terms of mole fractions.

expressed in terms of mole fractions likewise display a considerable difference in favour of the polyfunctional ligands. As an example, for Cu^{2+}

$$\log \beta_4^{NH_3} = 12.67 + 4 \log 55.5 = 19.65 < \log \beta_2^{en} = 20.03 + 2 \log 55.5 = 23.52$$

For the constants expressed in terms of mole fractions too, the aqueous ethylenediamine complex is nearly four orders of magnitude more stable than the tetrammine complex.

From a comparison of the ring-closure of paraffins and chelate-formation processes, Westheimer and Ingraham [70] drew attention to the fact that, although the number of species with independent states of motion increases as a consequence of chelate formation, the closure of the chelate ring is accompanied by a loss in the possibilities of the ligand to rotate, i.e. by an entropy decrease, and hence the stability decreases. In the sections dealing with solvation, we have seen that the entropy change accompanying complex formation is influenced fundamentally by whether the solvent molecules leaving the coordination sphere become 'free', or take part in the relatively strong hydrogen-bonding system of the solvent. Another factor impeding the comparison of the stabilities of complexes formed from mono- or from polydentate ligands is that the values of the constants are also influenced by the different basicities of the donor groups of the ligand.

The outlined problems explain why the interpretation and quantitative description of the chelate effect remain at the centre of interest. The results and considerations published up to 1966 were reviewed by Martell [71]. The subsequent period has not led to comprehensive discoveries valid for a wide range of systems; the recent work has concentrated primarily on the laws relating to the various types of systems.

By taking into account the steric hindrance and the difference in the basicities of the ligands, Hancock and Marsicano [72] introduced the equation

$$\log K_1^{\text{polyamine}} = 1.152 \log \beta_n^{NH_3} + (n-1) \log 55.5 \qquad (6.7)$$

between the formation constants of the corresponding complexes of ammonia and the polyfunctional amines $H(NHCH_2CH_2)_yNH_2$ ($y = 1$–4). Figure 6.8 confirms the validity of this equation [73].

The full lines in this Figure are not the best-fitting lines, but those with slope 1.152 and intercept $(n-1) \log 55.5$ calculated from Eq. (6.7). The enthalpy and entropy changes accompanying complex formation by polyamines forming five- and six-membered chelate rings were interpreted with satisfactory accuracy on the basis of calculations designed to minimize the conformational energy [73, 74].

As a result of calculations involving cyclic processes of Born–Haber type, Myers [75] demonstrated that the difference in dissolution heats of the

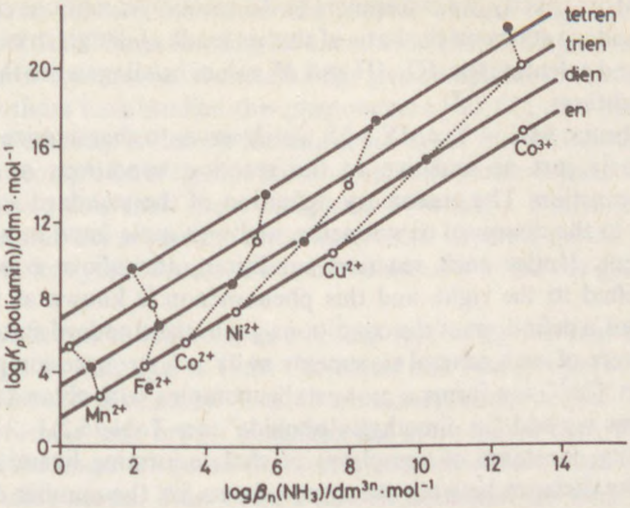


Fig. 6.8. Plot of log K_1(polyamine) vs. log $\beta_n(NH_3)$ for complexes of various metal ions with n-dentate polyamine ligands forming five-membered rings on complex formation Dotted lines connect points for the same metal ion with different polyamines [73] (Reproduced with permission from *Inorg. Chem.* **18**, 2847 (1979))

mono- and the polyfunctional ligands plays a part in the stability of chelate complexes; in some cases, however, it must be taken into consideration as a stability-decreasing factor. The enthalpy change accompanying the reaction

$$Cd(NH_2CH_3)_4^{2+} + 2en \rightleftharpoons Cd(en)_2^{2+} + 4CH_3NH_2$$

in aqueous solution is $+2.9$ kJ mol^{-1}, for instance. Myers assumed that the enthalpy change accompanying formation of the Cd–N bond is the same in the hypothetical gas phase; since the difference in the corresponding dissolution heats of the ligands, $2\Delta H_s^{en} - 4\Delta H_s^{CH_3NH_2}$, is $+34.9$ kJ mol^{-1}, it turns out that each Cd–N bond in the complex $Cd(en)_2^{2+}$ in aqueous solution is 8 kJ mol^{-1} weaker than those in the complex $Cd(CH_3NH_2)_4^{2+}$.

Rosseinsky regarded the solvent as a featureless continuum, and on this basis carried out comparative calculations to interpret the complex-forming properties of ligands containing sterically near and sterically distant donor atoms [76].

The authors of publications with the aim of explaining the chelate effect often pose the question of whether the effect is a real phenomenon in equilibrium chemistry, or whether it arises from the contradictions in the choice of standard state. In our view, this is not the essence of the question. It must be borne in mind that, by defining the standard state, we effectively define the reaction conditions. More exactly, we extrapolate to the reaction conditions corresponding to the standard states on the basis of studies made under given experimental conditions, and calculate the ΔG, ΔH and ΔS values holding under these defined reaction conditions.

The equilibrium $MX_2 + Y \rightleftharpoons MY + 2X$ which serves to characterize the chelate effect is clearly just as sensitive to the reaction conditions as any other equilibrium reaction. The customary definition of the standard state is 1 *M* with respect to the dissolved components, and unit mole fraction with respect to the solvent. Under such reaction conditions, the above equilibrium is generally shifted to the right, and this phenomenon is known as the chelate effect. Without a definition of the conditions, i.e. of the standard state, however, we must beware of such general statements as "Y is a stronger complex former than X". (Or "Cd^{2+} ion forms a more stable complex with chloride than with iodide", unless we add "in dimethylsulphoxide" (see Table 6.2).)

The stability constants of complexes of chelate-forming ligands obviously depend on the distance between the donor atoms, i.e. the number of atoms in the chelate ring, and also on the size of the metal ion and the geometry of the complex formed. For bidentate ligands it is a general rule that ligands containing donor atoms in an arrangement suitable for the formation of a five-membered ring yield more stable complexes than ligands containing the same donor atoms, but able to form only a six-membered chelate ring. For example, the stability constants of ethylenediamine, oxalate and glycinate complexes are larger than those of the corresponding complexes of 1,3-diaminopropane, malonate and β-alanine. Metals which tend to form complexes with linear geometry (e.g. Ag^+, Cu^+ and Hg^{2+}) are exceptions: for these, the complexes containing the higher number of ring atoms may be more stable.

The connection between the number of ring atoms and the stability is particularly interesting in the complexes of ligands that are able to form coupled chelate rings, or when the chelate rings form macrocyclic complexes. The complex-forming properties of ligands yielding coupled chelate rings, and the connection between the number of ring atoms and the stability, have been investigated by a number of authors. For the linear polyamine complexes, for instance, Margerum *et al.* [77] found that the Ni^{2+} complexes of polyamines forming 5,5 or 5,6-membered chelate rings are of roughly the same stability, whereas the Cu^{2+}, Ni^{2+} and Zn^{2+} complexes of a polyamine forming 5,6,5-membered chelate rings are more stable than those of a polyamine forming 5,5,5-membered chelate rings. The difference in stability depends to a large extent on the metal ion: the difference between the constants is 3.8 for the Cu^{2+} complexes, 2.0 for the Ni^{2+} complexes, and merely 0.7 log unit for the Zn^{2+} complexes.

The difference in stability is naturally also dependent on the structure of the ligand. For example, Nakahara *et al.* [78, 79] reported that the Cu^{2+} complexes of Schiff bases forming 5,6-membered coupled chelate rings are more stable than those of Schiff bases forming 5,5-membered chelate rings, while dipeptides forming 5,5 or 5,6-membered chelate rings give complexes of the same stability.

Many authors have studied this phenomenon [80–88], and accordingly the sequence of stability is known for numerous types of systems. It is a general rule that the complexes of ligands able to form only 5-membered coupled chelate rings are less stable than those complexes in which a 6-membered ring too occurs. The stability sequence varies, however; it depends on the nature of the donor atom, its hybrid state, the size of the metal ion and the geometry of the complex.

Macrocycles can be regarded as a special type of ligands that form coupled chelate rings. As long ago as 1969, Cabbiness and Margerum [89] established that 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane forms a Cu^{2+} complex which is four orders of magnitude more stable than the analogous complex of the linear tetramine that forms coupled chelate rings with the same number of ring atoms. They named this phenomenon the macrocyclic effect and, similarly to the chelate effect, interpreted it as an entropy effect. Following this, wide-ranging research work began with a view to determining and explaining the equilibrium, thermodynamic and structural data on the metal complexes of macrocycles [90–96]. The results to date reveal that the maximum macrocyclic effect is to be observed for 1,4,8,11-tetraazacyclotetradecane (cyclam) and its derivatives, which yield 5,6,5,6-membered chelate rings, and that the more favourable enthalpy and entropy changes also play a part in the stability increase relative to the linear amines.

6.6 Factors determining the ratios of the equilibrium constants

As a result of application of the experimental methods and evaluation procedures discussed in Chapters 4 and 5, we obtain the β values characteristic of the formation of the various associations from the components. In themselves, these data are generally not suitable for a comparative analysis of the equilibrium conditions in the system in question. The interpretation of the data requires the derived equilibrium constants, which are typical of the equilibrium state of each part-process, of the relative stabilities of the various complexes, of the stabilities of the metal complexes relative to those of the proton complexes, etc. These data may be given as an appropriate combination of the β values, generally as their quotients.

For some types of complexes, the expected values of the derived constants may also be calculated on the basis of statistical considerations. The starting-point in the statistical considerations is the assumption that the same interactions must be considered in each of the part-processes of complex formation; thus, the values of the constants, or their ratios, are determined by the number of possibilities of formation of the complex of given composition. From a chemical aspect, this starting assumption is clearly incorrect. Nevertheless, there is a need for the data calculated on the statistical basis, for the differences from these provide an indication of the specific interactions. Accordingly, we shall deal first with the statistical procedures that have been developed for the various types of equilibrium systems, and then with the considerations designed to interpret the differences from the expected values.

6.6.1 Statistical considerations

In Section 3.5 we have seen that, as concerns the formation of the parent complexes, the values of the stepwise stability constants must decrease for statistical reasons. Table 3.13 showed the expected values of the ratios of the constants for various maximum numbers of ligands, assuming the coordination of monodentate ligands. The Bjerrum considerations were extended by Sen [97], who took into account the coordination of polydentate ligands in a definite geometry. We shall deal here in any detail only with the octahedral coordination of a ligand containing two identical donor atoms. In the first step, the ligand may coordinate along any of the 12 edges of the octahedron, while its dissociation can occur in only one way. The second ligand can coordinate only along 5 edges, but dissociation can now take place in 2 ways. Finally, the third ligand can coordinate only along one edge, whereas there are now 3 possibilities for dissociation. This ratio must be modified, for one of the five possible complexes with composition MeA_2 (in which the ligands are to be found in one plane) is not capable of accepting a third ligand. For the expected ratios of the constants, therefore, we have

$$\left(\frac{K_1}{K_2}\right)_{\text{stat}} = \frac{12}{1} \times \frac{2}{5} = 4.8 \tag{6.8}$$

i.e. $\log (K_1/K_2)_{\text{stat}} = 0.68$, and

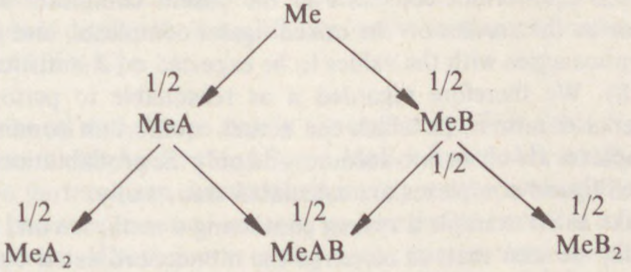
$$\left(\frac{K_2}{K_3}\right)_{\text{stat}} = \frac{5}{2} \times \frac{3}{1} \times \frac{5}{4} = 9.375 \tag{6.9}$$

i.e. $\log (K_2/K_3)_{\text{stat}} = 0.97$.

From an analysis of the possibilities of formation, it is also possible to calculate the statistical value of the equilibrium constant for the formation of the mixed ligand complex from the parent complexes,

$$MeA_2 + MeB_2 \rightleftharpoons 2MeAB.$$

Let us take a system containing a metal ion and two ligands, in which the possibilities of coordination of ligands A and B are the same. The probabilities of occurrence of the various reactions are shown by Scheme 1:



Scheme 1

The scheme reveals that the probabilities of formation of the complexes MeA_2 and MeB_2 are each $\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$, while that for MeAB is $2 \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{2}$. Thus, the value expected for the equilibrium constant of the process on a statistical basis is $(1/2)^2/(1/4)^2 = 4$. The statistical value of the equilibrium constant for the process $Me + A + B \rightleftharpoons MeAB$ also follows from this

$$\beta_{MeAB}^{stat} = 2\sqrt{\beta_{MeA_2}\beta_{MeB_2}} \tag{6.10}$$

$$\log \beta_{MeAB}^{stat} = \frac{1}{2}(\log \beta_{MeA_2} + \log \beta_{MeB_2}) + \log 2$$

The values to be expected on a statistical basis for the formation constants of the complexes with compositions MeA_2B, MeB_2A and MeABC can be calculated in a similar way:

$$\log \beta_{MeA_2B}^{stat} = \frac{2}{3}\log \beta_{MeA_3} + \frac{1}{3}\log \beta_{MeB_3} + \log 3 \tag{6.11}$$

$$\log \beta_{MeAB_2}^{stat} = \frac{1}{3}\log \beta_{MeA_3} + \frac{2}{3}\log \beta_{MeB_3} + \log 3 \tag{6.12}$$

$$\log \beta_{MeABC}^{stat} = \frac{1}{3}\log \beta_{MeA_3} + \log \beta_{MeB_3} + \log \beta_{MeC_3} + \log 6 \tag{6.13}$$

The same results can naturally also be reached by other means too [98].

In the earlier statistical considerations relating to the formation of mixed ligand complexes, the starting-point was always that the statistical laws hold for the entire equilibrium system, and within this for the parent complexes too. However, the equilibrium constants of the parent complexes are generally known prior to the studies on the mixed ligand complexes, and it was found that their ratios agree with the values to be expected on a statistical basis only exceptionally. We therefore regarded it as reasonable to perform partially statistical considerations, in which the actual equilibrium conditions for the parent complexes are taken into account, and only the probabilities of formation of the mixed ligand complexes are calculated statistically.

Let us take as an example a system containing a metal ion and two ligands. It can readily be seen that, as concerns the monocoordinated complexes, the probability of formation of the complex MeA is $K_1^A[A]/(K_1^A[A]+K_1^B[B])$, while that of the complex MeB is $K_1^B[B]/(K_1^A[A]+K_1^B[B])$. (The sum of the two probabilities is 1, of course.) If we consider the reactions of the complexes MeA and MeB with further ligands in terms of the analogous probability data, we obtain Scheme 2:

$$\begin{tikzcd}
 & & \mathrm{MeA_2} \\
 & \mathrm{MeA} \arrow[ur, "\frac{K_2^A[A]}{K_2^A[A]+X[B]}"] \arrow[dr, "\frac{X[B]}{K_2^A[A]+X[B]}"] & \\
\mathrm{Me} \arrow[ur, "\frac{K_1^A[A]}{K_1^A[A]+K_1^B[B]}"] \arrow[dr, "\frac{K_1^B[B]}{K_1^A[A]+K_1^B[B]}"'] & & \mathrm{MeAB} \\
 & \mathrm{MeB} \arrow[ur, "\frac{Y[A]}{K_2^B[B]+Y[A]}"'] \arrow[dr, "\frac{K_2^B[B]}{K_2^B[B]+Y[A]}"'] & \\
 & & \mathrm{MeB_2}
\end{tikzcd}$$

Scheme 2

As regards the values of X and Y, we may make use of the following assumptions:

(a) The monocoordinated complexes display the same affinity towards both ligands. The affinity of MeA for ligand A is characterized by K_2^A, and the assumption of the identical affinities therefore leads to $X = K_2^A$ and $Y = K_2^B$.

(b) The ligands display the same affinity for the monocoordinated complexes, i.e. $X = K_2^B$ and $Y = K_2^A$.

Assumptions (a) and (b) are clearly contradictory. This arises from the fact that the processes $MeA + B \rightleftharpoons MeAB$ and $MeB + A \rightleftharpoons MeAB$, which depend on both reaction partners, are characterized merely on the basis of the properties of one of the partners. In actual systems, on a statistical basis it is to be expected that the properties of both partners play equal roles in the determination of X and Y, i.e. we have $X = Y = (K_2^A K_2^B)^{1/2}$. Setting out from this latter relation

$$K_{\text{stat}} = \frac{[\text{MAB}]^2}{[\text{MA}_2][\text{MB}_2]} =$$

$$= \frac{\left(\dfrac{K_1^A[\text{A}]}{K_1^A[\text{A}] + K_1^B[\text{B}]} \cdot \dfrac{\sqrt{K_2^A K_2^B}[\text{B}]}{K_2^A[\text{A}] + \sqrt{K_2^A K_2^B}[\text{B}]} + \dfrac{K_1^B[\text{B}]}{K_1^A[\text{A}] + K_1^B[\text{B}]} \cdot \dfrac{\sqrt{K_2^A K_2^B}[\text{A}]}{K_2^B[\text{B}] + \sqrt{K_2^A K_2^B}[\text{A}]}\right)^2}{\dfrac{K_1^A K_2^A K_1^B K_2^B [\text{A}]^2[\text{B}]^2}{(K_1^A[\text{A}] + K_1^B[\text{B}])^2 (K_2^A[\text{A}] + \sqrt{K_2^A K_2^B}[\text{B}])(K_2^B[\text{B}] + \sqrt{K_2^A K_2^B}[\text{A}])}}. \tag{6.14}$$

Equation (6.14) may be rearranged and simplified in a series of simple elementary steps, so as to give the following relation

$$K_{\text{stat}} = 2 + \frac{K_1^A}{K_1^B}\sqrt{\frac{K_2^B}{K_2^A}} + \sqrt{\frac{K_2^A}{K_2^B}}\frac{K_1^B}{K_1^A}. \tag{6.15}$$

Equation (6.15) means that the equilibrium constant of the process $MeA_2 + MeB_2 \rightleftharpoons 2MeAB$ is 4 only if it holds that $K_1^A/\sqrt{K_2^A} = K_1^B/\sqrt{K_2^B}$. In cases where this is not so, a value larger than 4 is to be expected on a statistical basis. Figure 6.9 shows a plot of the value of $\log K_{\text{stat}}$ calculated via Eq. (6.15), as a function of $\log(K_1^A/\sqrt{K_2^A})(\sqrt{K_2^B}/K_1^B)$. In those systems in which the values of the constants agree with the data calculated via (6.15), the mixed ligand complex reflects the equilibrium conditions prevailing in the parent complexes. Differences from the calculated data are indicative of the specific effects characterizing formation of the mixed ligand complex. The interpretation here requires special chemical considerations.

For the sake of completeness, it should be noted that, if assumption (a) holds, i.e. $X = K_2^A$ and $Y = K_2^B$, we have

$$K_{\text{stat}} = 2 + K_1^A/K_1^B + K_1^B/K_1^A \tag{6.16}$$

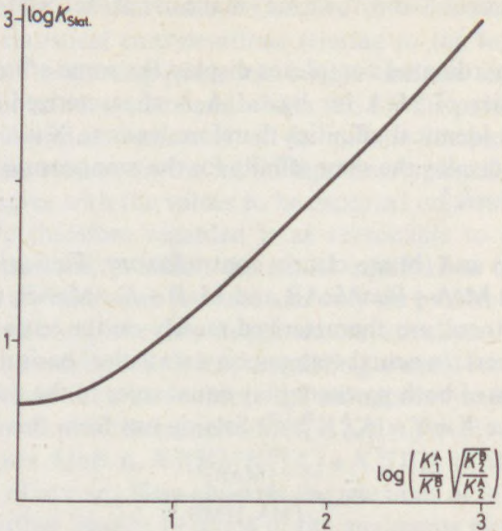


Fig. 6.9. The expected equilibrium constant for $MeA_2 + MeB_2 \rightleftharpoons 2MeAB$ reaction as a function of $\log((K_1^A/K_1^B)\cdot\sqrt{K_2^B/K_2^A})$, according to Eq. (6.13)

while if assumption (b) holds

$$K_{stat} = 2 + \frac{K_1^A/K_2^A}{K_1^B/K_2^B} + \frac{K_1^B/K_2^B}{K_1^A/K_2^A}. \tag{6.17}$$

In systems satisfying the above relations, however, a separate explanation must be given as to why the affinities of the monocoordinated metal complexes or of the ligands for the reaction partner are independent of the nature of the partner.

Strictly speaking, the considerations of Sigel [99] can not be regarded as statistical, but merely of a statistical nature. Sigel characterized the formation of the mixed ligand complexes by means of the equilibrium constant of the reaction

$$MeA + MeB \rightleftharpoons MeAB + Me$$

and denoted its logarithm as $\Delta \log K$. The numerical value of this can be calculated from the relation

$$\Delta \log K = \log \beta_{MeAB} - \log \beta_{MeA} - \log \beta_{MeB}. \tag{6.18}$$

However, the meaning of $\Delta \log K$ stands out more clearly if it is interpreted as the difference between the logarithms of the equilibrium constants of the processes

$$Me + B \rightleftharpoons MeB$$

and

$$\mathrm{MeA + B \rightleftharpoons MeAB.}$$

In this comparison, the value of $\Delta\log K$ expresses the extent to which the affinity of the metal ion for ligand B varies as a consequence of the coordination of ligand A. Since the overall system is 'symmetrical', this means at the same time the extent to which the affinity of the metal ion for ligand A varies as a consequence of the coordination of ligand B.

Processes analogous to these can also be written for the parent complexes

$$\mathrm{2MeA \rightleftharpoons MeA_2 + Me}$$

and

$$\mathrm{Me + A \rightleftharpoons MeA}$$

$$\mathrm{MeA + A \rightleftharpoons MeA_2.}$$

The difference between the logarithms of the equilibrium constants of the latter two processes is $\log(K_2/K_1)$. $\Delta\log K$ is therefore a quantity analogous to $\log(K_2/K_1)$. For copper(II) complexes of bidentate ligands in which there is no steric hindrance, $\log(K_2/K_1)$ is known to have a value of ~ -1.2. If it is considered that the number of possibilities for the formation of MeAB is twice the number for $\mathrm{MeA_2}$ or $\mathrm{MeB_2}$, the value should be increased by log 2, i.e. a value of $\Delta\log K \sim -0.9$ is to be expected for the mixed ligand copper(II) complexes. Differences from the found $\Delta\log K$ data are indicative of specific interactions that are characteristic not of the parent complexes, but merely of the mixed ligand complexes.

6.6.2 The statistical considerations in practice

The statistically calculated constant ratios are encountered only very rarely in practice for the various complexes. To illustrate this, Table 6.6 contains the differences from the $\log(K_1/K_2)$ and the $\log(K_2/K_3)$ values to be expected on a statistical basis for the copper(II), nickel(II) and zinc(II) complexes of some simple ligands. The tabulated data show that the ratios of the constants are larger than the statistically expected values. This is understandable if it is borne in mind that, with the formation of a coordinate bond between the ligand and the metal ion, the electron density on the metal ion generally increases, with the result that the affinity for the subsequent ligand decreases. It may also be observed that the difference from the statistical value is much smaller for the complexes of ligands forming a five-membered chelate ring than for those of ligands forming a six-membered chelate ring (cf. the data on the complexes of the ligand pairs glycine and β-alanine, oxalate and malonate, and ethylenediamine and 1,3-diaminopropane). The partial shielding of the donor group

Table 6.6 The deviation of $\log(K_i/K_{i+1})$ data* from the statistically expected** values in case of Cu(II), Ni(II) and Zn(II) complexes with some simple ligands

System	$\Delta \log(K_1/K_2)$	$\Delta \log(K_2/K_3)$
Cu^{2+}–ethylenediamine	0.48	—
Ni^{2+}–ethylenediamine	0.44	1.07
Zn^{2+}–ethylenediamine	0.09	2.07
Cu^{2+}–1,3-diaminopropane	1.80	—
Zn^{2+}–1,3-diaminopropane	1.36	2.36
Cu^{2+}–N-methyl-ethylenediamine	0.88	—
Ni^{2+}–N-methyl-ethylenediamine	0.89	2.78
Zn^{2+}–N-methyl-ethylenediamine	0.29	—
Cu^{2+}–glycine	0.41	—
Ni^{2+}–glycine	0.10	0.39
Zn^{2+}–glycine	0.02	0.67
Cu^{2+}–N-methyl-alanine	0.64	—
Ni^{2+}–N-methyl-alanine	0.40	0.70
Cu^{2+}–N-methyl-glycine	0.44	—
Ni^{2+}–N-methyl-glycine	0.26	0.54
Cu^{2+}–oxalate	0.34	—
Zn^{2+}–oxalate	0.68	—
Cu^{2+}–malonate	1.65	—
Zn^{2+}–malonate	0.90	—

* Data from Martell, A. E. and Smith, R. M., *Critical Stability Constants*.

** Statistically expected ratios of the stability constants: $\log(K_1/K_2) = 0.9$ for copper(II) and $\log(K_1/K_2) = 0.68$, $\log(K_2/K_3) = 0.97$ for nickel(II) and for zinc(II) complexes.

similarly results in an increase in the ratio of the constants (cf. the data on the complexes of the ligand pairs ethylenediamine and N-methylethylenediamine, and glycine and N-methylglycine).

In the latter two cases, we have spoken of a steric hindrance factor, which means that the uptake of further ligand(s) is obstructed by the incorporation into the coordination sphere of ligands that are relatively large or contain partially shielded donor groups.

The extent of steric hindrance naturally also depends on the size of the metal ion: it decreases with increase in the size of the ion. This phenomenon can be observed clearly in the data in Table 6.7, i.e. the $\log(K_1/K_2)$ data on the complexes obtained between certain ligands and copper(II) and chromium(II) [109]; although these ions have different sizes (copper(II) 69 pm, chromium(II) 82 pm), their complexes have similar structures.

The tabulated data demonstrate that, in spite of the different ionic radii of the two metal ions, with ligands forming a five-membered chelate ring they give complexes with nearly the same values of K_1/K_2. In contrast, there are

Table 6.7 $\log(K_1/K_2)$ data for some complexes of Cu(II) and Cr(II) [108]

Ligand	$\log(K_1/K_2)$	
	Cu^{2+}	Cr^{2+}
Glycine	1.31	1.15
Ethylenediamine	1.38	1.34
Malonate	2.56	1.65
Iminodiacetate	4.58	1.83
Nitrilotriacetate	8.46	3.18

substantial differences between the K_1/K_2 values for the complexes of malonate, which forms a six-membered chelate ring, and for those of ligands containing more donor groups.

Analysis of the ratios of the constants permits other structural conclusions. Dellien [100], for example, compared the data on the complexes in the Sc^{3+}–thiodiacetate system with those on complexes of ligands with similar structures; from the low K_2 values and the high K_1/K_2 values, he concluded that the second ligand (at least in part) is bonded to the central metal ion through only one of its donor groups. Powell, Farrel and Kulprathipanja [101] studied the lanthanide complexes of 3,4-dihydroxy-2-methylbutanoate. The K_1 values did not vary monotonously, but exhibited a maximum at samarium and a minimum at dysprosium, whereas the K_1/K_2 values varied practically monotonously between 6.5 and 4.7. From this, they concluded that there is a decrease from three to two in the number of coordinated donor atoms between samarium and dysprosium.

Ohyoshi [102] investigated the possibilities of separating the nitrilotriacetate complexes of the lanthanide ions, and pointed out that the separation factor depends not only on the stepwise stability constants K_1 and K_2, but also on the difference in the quotients K_1/K_2.

The equilibrium systems with K_i/K_{i+1} data that are smaller than the statistically expected ones are particularly interesting. It is obvious that all such data reflect the special behaviour that the coordination of some ligand to the metal ion facilitates the coordination of the subsequent ligand. In spite of this, a number of cases are to be found in the literature where the authors report such unusual data, but do not call attention to them or even attempt to explain them [103–107]. As mentioned in Sections 3.5 and 6.1, such a constant ratio is to be expected if a structural rearrangement occurs in some step of the complex formation, or if, because of back-coordination, the incorporation of the first ligand does not increase, but decreases the electron density on the metal ion.

It is of interest to consider the ratios of the statistical constants relating to the formation of mixed ligand complexes. For illustrative purposes, Table 6.8

Table 6.8 The formation constants of some parent and mixed complexes of Cu(II), and the stabilization constants calculated in different ways

Ligand A	Ligand B	$\log K_1^A$	$\log K_2^A$	$\log K_1^B$	$\log K_2^B$	$\log \beta_{MeAB}$	$\Delta \log \beta_{MeAB}$	$\Delta \log \beta'_{MeAB}$	$\Delta \log K$
Oxalate	Ethylenediamine	4.84	3.6	10.44	9.16	14.49	0.17	−0.94	−0.79
Glycine	Ethylenediamine	8.27	6.92	10.44	9.16	17.91	0.21	−0.05	−0.80
Malonate	Ethylenediamine	5.10	2.55	10.44	9.16	14.78	0.85*	0.13	−0.76
β-Alanine	Ethylenediamine	7.07	5.61	10.44	9.16	16.58	0.14	−0.37*	−0.93
1,3-Diaminopropane	Ethylenediamine	9.82	7.22	10.44	9.16	18.71	0.09	0.05	−1.55*
Oxalate	1,3-Diaminopropane	4.84	3.6	9.82	7.22	14.31	1.27*	−0.01	−0.35*
Glycine	1,3-Diaminopropane	8.27	6.92	9.82	7.22	17.30	0.88*	0.47*	−0.79
Malonate	1,3-Diaminopropane	5.10	2.55	9.82	7.22	13.62	0.97*	0.08	−1.30*
β-Alanine	1,3-Diaminopropane	7.07	5.61	9.82	7.22	15.71	0.55*	−0.13	−1.18

$$\Delta \log \beta_{MeAB} = \log \beta_{MeAB} - 1/2\,(\log \beta_{MeA_2} + \log \beta_{MeB_2} + \log 4)$$

$$\Delta \log \beta'_{MeAB} = \log \beta_{MeAB} - 1/2\left(\log \beta_{MeA_2} + \log \beta_{MeB_2} + \log\left(2 + \frac{K_1^A}{K_1^B}\sqrt{\frac{K_2^B}{K_2^A}} + \frac{K_1^B}{K_1^A}\sqrt{\frac{K_2^A}{K_2^B}}\right)\right)$$

$$\Delta \log K = \log \beta_{MeAB} - \log \beta_{MeA} - \log \beta_{MeB}$$

contains data reported by Sigel *et al.* [108] on some simple systems. Quite deliberately, the Table involves only simple ligands, where a specific interaction is not expected for the mixed ligand complexes. Besides the experimental results, the Table contains three 'stabilization' data: the differences from the log $\beta^{\text{stat}}_{\text{MeAB}}$ values calculated by means of Eqs (6.8) and (6.13), and the Sigel $\Delta \log K$ data. It is observed that for every mixed ligand complex the equilibrium constant is larger than the statistical value interpreted uniformly for the overall system and characterized by $(\text{MeAB})^2/[\text{MeA}_2][\text{MeB}_2] = 4$. In five cases, the difference from the statistical value is so large that it definitely requires explanation. These data in the Table are denoted by*. According to the statistics employed in the derivation of Eq. (6.13), where the actual equilibrium conditions for the parent complexes were taken into account, in six cases the equilibrium conditions for the parent complexes are also reflected in the mixed ligand complexes, in two systems a considerable destabilization is observed, and in one case there is an appreciable stabilization [109].

Similarly, three of the $\Delta \log K$ data differ to a significant extent from the expected value of ~ -0.9. It is further clear that no correlation can be found between the differences from the values derived via the three approaches. There is no system which behaves in a special way in all three senses, and only two systems are characterized by mixed ligand complexes with stabilities that are special from two different aspects.

The initially surprising result becomes understandable if it is remembered that the value of log β_{MeAB} to be expected from Eq. (6.10) is calculated only from the log β_{MeA_2} and log β_{MeB_2} data, regardless of how the β_2 values can be broken down into the stepwise constants. At the same time, the $\Delta \log K$ values are calculated from log β_{MeAB} and the experimental log K_{MeA} and log K_{MeB} data, regardless of the constants for the second steps. It emerges from Eq. (6.15), however, that the expected stability of the mixed ligand complex is influenced by all of the data relating to the parent complexes, which is in accordance with the chemical considerations.

Finally, it must be emphasized that the statistical considerations do not serve for the interpretation of the values and ratios of the constants, but merely for the establishment of a basis of comparison, differences from which point to specific interactions. For this reason, it is more advantageous to carry out comparisons with the data calculated via Eq. (6.15) than simply to examine differences from the expected value $[\text{MeAB}]^2/[\text{MeA}_2][\text{MeB}_2] = 4$.

6.6.3 Specific factors influencing the ratios of the constants

We have seen that the majority of systems are characterized by K_i/K_{i+1} data that are larger than the ratio of these constants calculated on a statistical basis. There are two general reasons for this: the progressive increase in the electron density on the metal ion, and steric hindrance. In this section, we shall consider those specific effects occurring only in a definite group of equilibrium systems, which likewise exert a significant effect on the ratios of the constants.

6.6.3.1 Structural changes

Among the structural changes, the changes in the geometry of the coordination sphere are of particular importance. A deep analysis and interpretation of this phenomenon was given by Ahrland [110], on the basis of the hard-soft theory. From a large number of experimental data, he concluded that a change in the geometry of the coordination sphere is not to be expected for complexes of hard metal ions with ligands containing hard donor atoms; in these cases the constants display a regular tendency to decrease. Primarily the soft metal ions are prone to undergo a change in the geometry of the coordination sphere. Table 6.9 presents some $\log(K_i/K_{i+1})$ data to illustrate the equilibrium consequences of such changes in geometry.

The effect of the change in geometry is particularly interesting in the Hg^{2+}–Cl^- system. The Hg^{2+} aqua ion has an octahedral structure. The constant relating to the uptake of the first chloride ion is therefore governed by the affinity of the octahedral aqua ion for the chloride ion. With the formation of the monochloro complex, the structure becomes linear, whereby the affinity of the second coordination site for chloride ion increases. This increased affinity

Table 6.9 Some examples for extreme $\log(K_i/K_{i+1})$ explained by the change of the geometry of the coordination sphere

System	$\log(K_1/K_2)$	$\log(K_2/K_3)$	$\log(K_3/K_4)$	Reference
Hg^{2+}–Cl^-	0.26	5.63	−0.15	[116]
Hg^{2+}–I^-	1.92	7.17	1.55	[116]
Cd^{2+}–Br^-	1.16	−0.39	0.60	[117]
Cd^{2+}–I^-	1.38	−1.43	0.53	[117]
Zn^{2+}–Cl^-	−0.15	−0.79	—	[118]
Zn^{2+}–Br^-	0.26	−1.34	—	[118]
Zn^{2+}–SCN^-	0.38	0.20	−0.20	[119]
Zn^{2+}–CN^-	—	—	1.41	[120]*

* Only the $K_1K_2=\beta_2$ formation constant could be determined for Zn^{2+}–CN^- system, therefore the K_1/K_2 and K_2/K_3 can not be calculated.

explains why $\log (K_1/K_2)$ is smaller than the statistical value. The linear complex $HgCl_2$ resulting from the incorporation of the second ligand is stable in a broad chloride ion concentration range. The uptake of a third ligand is hampered by the fact that this necessitates a further change in the geometry: rearrangement of the linear structure to a tetrahedral one. However, if the tetrahedral structure is produced through the incorporation of a third ligand, the fourth chloride ion can coordinate to the metal ion more easily. This change explains why the actual value of $\log (K_3/K_4)$ is much smaller than the statistical one. Similar changes obviously occur during the stepwise complex formation in the Hg^{2+}–I^- system too, but (probably due to the steric hindrance resulting from the larger size of the iodide ion) a constant quotient smaller than the statistical one is not observed in this system.

If the data for the Cd^{2+} complexes are considered in a similar way, it may be stated that the change in geometry from octahedral to tetrahedral takes place in the second step. In the Zn^{2+}–Cl^- and the Zn^{2+}–Br^- systems, however, the structure is progressively shifted in the direction of tetrahedral geometry in the first and second steps, and only the halogen complexes ZnX_3^- are stabilized. In contrast, in the Zn^{2+}–CN^- system, the geometry change probably proceeds in the first step; this increases the affinity of the residual coordination sites for cyanide to such an extent that the second ligand is incorporated in the same step, i.e. only the value of $\log \beta_2$ can be determined. It is a very commonly observed phenomenon for cyano complexes that several ligands are incorporated simultaneously in the first step of complex formation, the intermediate complexes effectively not being observed in the process [111, 112]. This means in fact that $K_2 \gg K_1$.

The structural changes accompanying the equilibrium processes are sometimes also reflected in the ratios of the constants relating to the uptake or loss of protons by the ligands and the metal complexes. A case essentially belonging in this type is the relation $pK_1 > pK_2$ for the Hg^{2+} aqua complexes as dibasic weak acids. In this case, however, the loss of protons means the formation of hydroxo complexes, as discussed in connection with the chloro complexes of Hg^{2+}.

For the macrocyclic ligands too, it occurs that the difference between the logarithms of the successive protonation constants is smaller than the statistical value, or certain of the protonation steps cannot be observed. The protonation equilibria of $\alpha,\beta,\gamma,\delta$-tetra(4-N-methylpyridyl)porphyrin were studied by Hambright and Fischer [113], who found that only the constant of the process $H_2L + 2H \rightleftharpoons H_4L$ can be determined; the formation of H_3L can not even be detected. According to the investigation of this phenomenon by Stone and Fleischer [114], it can be explained by the fact that in the ionic species stabilized in the form H_4L the porphyrin ring is distorted, i.e. it is not planar. The loss of a single proton diminishes the stability of the distorted structure to such an extent that this eliminates a further proton and is stabilized in the planar form H_2L.

The unusual ratio of the constants relating to the third and fourth steps of protonation of 1,4,8,11-tetraazacyclotetradecane can be explained in a similar way [93]. As an example of protonation constants of complexes with an unusual ratio that can be explained by a change in structure, we may mention the copper(II)–glycylglycylhistidine system studied by Aiba, Yokoyama and Tanaka [115]. These authors reported that at low pH values glycylglycylhistidine behaves as a bidentate ligand: the terminal amino group remains in a protonated form. As the pH is raised, the peptide group adjacent to the imidazole also undergoes deprotonation and coordination, which would be a process involving loss of a proton. As a consequence of the rearrangement necessary for this, however, a structure results in which the following peptide group too comes into the environment of the metal ion. Accordingly, besides proton loss, this too is readily coordinated, and the coupled chelate ring system is closed through coordination of the terminal amino group. The structural rearrangement between bidentate and tetradentate coordination leads to the loss of 3 protons in one step, i.e. the complexes in intermediate states of protonation can not be detected (see Fig. 6.10).

A phenomenon similar to that presented in Fig. 6.10 frequently occurs with the complexes of other tri- and oligopeptides with copper(II) and other metal ions. Sigel and Martin [121] referred to this phenomenon as cooperative deprotonation.

We have so far concentrated primarily on constant ratios that are smaller than the statistical values and that can be explained in terms of changes in structure. However, a change in structure often gives rise to just the opposite effect: an extremely large ratio of the constants. In connection with the Hg^{2+}–Cl^- system discussed above, it was seen that an expansion of the coordination sphere, in this case the structural rearrangement from linear to tetrahedral, explains the extremely large value of $\log(K_2/K_3)$. A similar situation frequently arises for other metal ions too. For example, the pentammine effect in the copper(II)–ammonia system [122] can be explained in this way. The first four ammonia molecules are coordinated in the equatorial plane of the copper(II), and up to the fourth step the system is characterized by K_i/K_{i+1} values only slightly larger than statistical. The incorporation of the fifth ligand

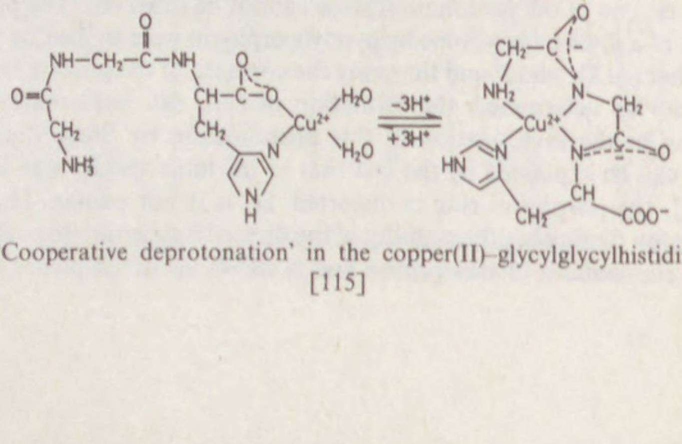


Fig. 6.10. 'Cooperative deprotonation' in the copper(II)–glycylglycylhistidine system [115]

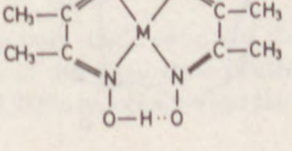
is accompanied by the transformation of the tetragonally strongly distorted octahedral structure into a tetragonal pyramid, i.e. by an expansion of the coordination sphere, which shows up in a very large value of $\log(K_4/K_5) = \sim 2.5$. An expansion of the coordination sphere and the resulting large ratio of the constants are primarily typical of square planar complexes, but the phenomenon also occurs for linear and tetrahedral complexes.

A change in structure similarly explains the relatively large difference in the pH values of ligands containing closely situated donor groups with a tendency to undergo protonation. The phenomenon was presented in another connection in Table 3.13. In these cases, the structural rearrangement merely means that a hydrogen-bond is formed between the two donor groups in the ionic species HL. Consequently, the dissociation of H_2L has a relatively small pK value, while that of HL has a large one, i.e. $pK_1 \ll pK_2$. As a result of the hydrogen-bond, the microconstants discussed in Section 5.2.5 cannot be determined, or (as pointed out by Kiss and Tóth [123]) the microconstants calculated by means of the usual assumption agree with one another.

6.6.3.2 Interaction between coordinated ligands

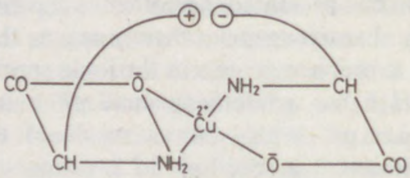
The interaction of the ligands or of the donor atoms of the ligands through the coordination sphere is one of the most general phenomena in the chemistry of complex equilibria; a full survey of this can naturally not be given. We shall discuss mainly those specific interactions which also appear between the non-coordinated ligands, but which become particularly marked when the ligands are coordinated to the same metal ion. This interaction is manifested quite characteristically in the ratio of the constants. As concerns the interactions occurring through the coordination sphere, we shall deal only with the Tanaka considerations relating to complexes of copper(II) and nickel(II) with ligands containing nitrogen and oxygen donor atoms, and with the specific interactions between ligands containing aromatic nitrogen and oxygen donor atoms.

Interactions outside the coordination sphere are responsible for the outstandingly high stability of the Ni(dimethylglyoxime)$_2$ complex, and for the observed value of $K_1/K_2 \sim 0$ in this system. The explanation of this phenomenon is the formation of hydrogen-bonds between the coordinated ligands; this makes formation of the bis complex especially favoured, and stabilizes the square planar arrangement

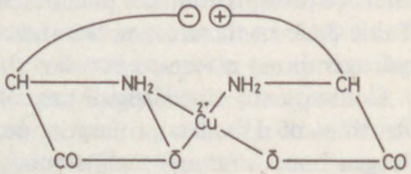


A similar phenomenon naturally occurs in the complexes of other metal ions and other dioxime ligands [124].

A stabilizing effect may likewise be exerted by the electrostatic interaction between non-coordinated, charged groups of the ligands. Sakurai *et al.* carried out extensive studies to establish the laws governing interactions of this nature [125–128]. As an example, the following formulae depict the assumed structures of the mixed ligand complexes formed between copper(II), aspartic acid and lysine, with coordination of the different optical isomers



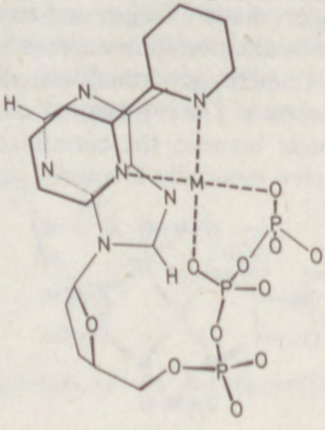
Cu(L-A)(L-B)



Cu(D-A)(L-B)

The diagrams indicate that the trans structure is stabilized when the two L ligands are coordinated, whereas the cis structure is stabilized when the D and L ligands are coordinated; this effect can be observed in the stability constants of the corresponding mixed ligand complexes.

Another considerable stabilizing factor is the stacking interaction in polar solvents between molecules containing aromatic rings. For instance, it was found by Naumann and Sigel [129] that an adduct with $\log K = 0.9 \pm 0.2$ is formed between ATP and bipyridyl. At the same time, the formation constant of the complex formed in the reaction between ATP and the monobipyridyl complex of copper(II) is $\log K = 6.96$. Naumann and Sigel interpreted this phenomenon in that the adduct is stabilized by coordination of a phosphate group of the ATP to the central copper(II) ion. From a coordination chemical aspect, however, it is more reasonable to state that the mixed ligand complex is stabilized by the two ligands interacting outside the coordination sphere.



Finally, Schiff base formation between the coordinated ligands also belongs formally in this category. The phenomenon was subjected to very wide-ranging investigations by Leussing *et al.* [130–134]. Water is formed in the reaction, but, since water is generally neglected as a component of equilibrium reactions in the definition of the equilibrium constants, the formation of these Schiff bases can be regarded as a consequence of the ligands in question forming particularly stable complexes.

In another type of interactions of the ligands or of the donor atoms, the characteristic feature is that the interactions occur only through the electron system of the metal ion; in the absence of the metal ion they cannot be observed. Tanaka set out from kinetic considerations, and derived a general formula for the formation constants both of the parent complexes (containing more than one ligand) and of the mixed ligand complexes of nickel(II) [135] and of copper(II) [136] with amines and aminocarboxylates; these general formulae also took into account the interaction of the donor atoms within the coordination sphere. The starting-points in his considerations were as follows: the Eigen mechanism of formation of metal complexes [137]; the special mechanism of formation of copper(II) complexes; and the assumptions that the rate of the dissociation $\mathrm{MeAL} \rightleftharpoons \mathrm{MeA} + \mathrm{L}$ is (1) inversely proportional to the Brønsted basicity and the electron-donating ability of the ligand L, and (2) directly proportional to the electron-donating ability of the residual ligand A. (Data relating to this latter point were reported by Edwards [138].) On this basis, the general equations for copper(II) complexes are

$$\begin{aligned}\log K_{\mathrm{CuAL}}^{\mathrm{CuA,L}} = \log K_{\mathrm{CuL}}^{\mathrm{Cu,L}} + \log K_{\mathrm{os(CuA,L)}} - (\log K_{\mathrm{os(Cu,L)}}) + \\ + \sum^{I} \sum^{J} \delta_{ij} \mathrm{X}_i(\mathrm{A}) \mathrm{Y}_j(\mathrm{L})\end{aligned} \tag{6.19}$$

$$\begin{aligned}\log K_{\mathrm{CuL}_n}^{\mathrm{CuL}_{n-1},\mathrm{L}} = \log K_{\mathrm{CuL}}^{\mathrm{Cu,L}} + (\log K_{\mathrm{os(CuL}_{n-1},\mathrm{L})} - \\ - \log K_{\mathrm{os(Cu,L)}} + \sum^{I} \sum^{J} \delta_{ij} \mathrm{X}_i(\mathrm{L}) \mathrm{Y}_j(\mathrm{L}) - \log n.\end{aligned} \tag{6.20}$$

The species featuring as the lower and upper indices of the constants define the equilibrium in question. K_{os} is the formation constant of the outer sphere complex relating to the ionic species following the lower index os. These values can be calculated from the Eigen–Fuoss equation [139–140]. Thus δ_{ij} is the effect of the donor atom X_i of ligand A (or L) on the donor atom Y_j of ligand L, while $\mathrm{X}_i(\mathrm{A})$ and $\mathrm{Y}_j(\mathrm{L})$ are the numbers of donor atoms X_i and Y_j in ligands A and L.

For nickel complexes, the only modification to the above equations is that the logarithms of the ratios of the numbers of water molecules bound to the complexes MeA or MeL and to the nickel aqua ion also feature on the right-hand side. Tanaka calculated the δ_{ij} values reflecting the interaction of the donor atoms from the experimental data on more than 150 systems, and obtained the following results. For the nickel(II) complexes

$$\delta_{\mathrm{N,N}} = -0.25; \quad \delta_{\mathrm{O,O}} = -0.16; \quad \delta_{\mathrm{O,N}} = \delta_{\mathrm{N,O}} = +0.11.$$

For the copper(II) complexes

$$\delta_{\mathrm{N(al),N(al)}} = -0.35; \quad \delta_{\mathrm{N(ar),N(ar)}} = -0.39;$$
$$\delta_{\mathrm{N(al),N(ar)}} = \delta_{\mathrm{N(ar),N(al)}} = -0.25;$$
$$\delta_{\mathrm{N(ar),O}} = +0.09; \quad \delta_{\mathrm{N(al),O}} = -0.26; \quad \delta_{\mathrm{O,O}} = -0.29$$

for ligands in which an aromatic π-system is not linked to the oxygen donor atom;

$\delta_{\mathrm{O,O}} = -0.10$ for ligands in which a π-system is linked directly to the oxygen donor atom (acetylacetone, salicylaldehyde, etc.).

N(al) and N(ar) in the indices of δ denote aliphatic and aromatic nitrogen donor atoms.

If the repulsion of the donor atoms through the coordination sphere is taken into consideration, negative values would be expected for δ_{ij} in every case. This expectation does not materialize in the case of nitrogen and oxygen donor atoms for nickel(II), or in the case of aromatic nitrogen and oxygen donor atoms for copper(II); accordingly, some explanation is required.

The positive $\delta_{\mathrm{N,O}}$ value for the nickel(II) complexes resulted from an analysis of the equilibrium constants for only a few systems, and thus it may be rather inexact. We are not aware of any attempts to interpret it.

In contrast, the positive $\delta_{\mathrm{N(ar),O}}$ value for the copper(II) complexes is well known; a comprehensive study of the phenomenon was carried out by Sigel *et al.* [141]. It is important that, besides the σ-donor coordination of the nitrogen atoms in the aromatic ring, the *d* electrons of the copper(II) ion interact with the aromatic π-system through back-coordination. This leads to a decrease in the electron density on the metal ion, which increases the possibility of coordination of the second ligand. This effect is particularly marked for ligands containing oxygen donor atoms, in all probability as a consequence of the non-bonding electron pairs of oxygen participating (through the mediation of the metal ion) in the development of a π-electron system extending to the entire molecule. In the absence of a non-bonding electron pair, there is no possibility of this with nitrogen donor atoms of amine type. The phenomenon has not been subjected to a deeper theoretical interpretation. One reason why this is necessary is that it would greatly promote an understanding of the role of

Table 6.10 The equilibrium constant for some MeA + MeB = MeAB + Me reactions for illustration of the interaction between the aromatic nitrogen and the oxygene donor atoms

Me	A	B	$\Delta \log K$	Reference
Cu^{2+}	Bipyridyl	Ethylenediamine	−1.29	[142]
Cu^{2+}	Bipyridyl	Glycine	−0.35	[142]
Cu^{2+}	Bipyridyl	Oxalate	+0.70	[145]
Cu^{2+}	Bipyridyl	Pyrocatechol	+0.43	[142]
Co^{2+}	Bipyridyl	Ethylenediamine	−0.27	[142]
Co^{2+}	Bipyridyl	Glycine	−0.14	[142]
Co^{2+}	Bipyridyl	Pyrocatechol	+0.76	[142]
Ni^{2+}	Bipyridyl	Ethylenediamine	−0.18	[142]
Ni^{2+}	Bipyridyl	Glycine	−0.21	[142]
Ni^{2+}	Bipyridyl	Pyrocatechol	+0.36	[142]
Cu^{2+}	Histamine	Ethylenediamine	−1.49	[144]
Cu^{2+}	Histamine	Glycine	−0.65	[144]

copper(II) in biological systems. A similar phenomenon has been demonstrated in cobalt(II) and nickel(II) complexes [142, 143].

Table 6.10 presents the equilibrium constants for a number of systems; these reflect the special affinity of aromatic nitrogen atoms, through the coordination sphere of the metal ion, for ligands containing oxygen donor atoms.

6.7 Factors determining the values of stability constants

The values of the stability constants are determined by the properties of the metal ions and the ligands, but also by external factors. In a strict sense, these latter can not be separated, for they mutually influence one another. Nevertheless, in the following sections we shall discuss separately the connections between the ionic strength, the pressure, the temperature, the parameters reflecting the chemical properties of the metal ions and the ligands, and the values of the stability constants.

Establishment of such correlations naturally requires a comparison of reliable stability constants. First of all, therefore, we shall deal with some questions of the critical evaluation of the stability constants to be found in the literature.

6.7.1 Critical evaluation of stability constants

An enormous number of stability constants have been reported, and the number of systems examined continues to grow rapidly. Orientation for those interested in complex stability data is greatly facilitated by the series *"Stability Constants"*, which started in 1957. The most recent volumes contain the literature data published on the complexes or organic ligands up to 1973, and on those of inorganic ligands up to 1974. The data are continuously processed by the IUPAC Commission on Equilibrium Data, and a data bank will shortly be created.

By the end of the 1960's, it became clear that an appreciable proportion of the published data are not reliable. For research workers who are not fully familiar with this subject, and for those who merely wish to make use of the values of the stability constants, the situation is made extremely difficult by the numerous contradictory data. For this reason, the above commission has decided that critical evaluations must be performed for the complexes of the most important ligands, and the *"Critical Evaluation of Equilibrium Constants"* volumes have already appeared for a number of ligand families [146–150]. However, a considerable time will elapse before truly critically evaluated data are available for all of the more important complexes. The "*Critical Stability Constants*" volumes by Martell and Smith [152] may conveniently be used (with certain reservations), but we feel that a really critical evaluation of all existing stability constants is beyond the power of a small number of chemists, no matter how outstanding and experienced they may be.

We shall not deal here with the aspects involved in the critical evaluation of stability constants; in the present book, in the course of the discussion of the various experimental procedures and evaluation methods, we have paid special attention to the sources of error in the determination and the evaluation, and these considerations were reported recently [151]. Here, we merely draw attention to the fact that the most recent data are not necessarily to be considered as the most reliable, and that even agreeing results by different authors do not always stand the test of thorough critical evaluation [152].

Even in spite of the extensive investigations, the situation often arises that data are not to be found in the literature for the complexes of some not very unusual ligand. In such a case, of course, the only reliable course of action is to determine the missing data by means of an adequate method. In many cases, however, there is a possibility for the sometimes surprisingly accurate estimation of the data through various interpolation procedures [153]. In a large number of systems, however, some characteristic behaviour is observed which prevents even an approximate estimation for analogous systems. As an example, molybdenum(V) forms a fairly stable complex with EDTA, whereas with DCTA complex formation can not even be detected [154].

6.7.2 Effects of external factors on the values of stability constants

6.7.2.1 Roles of the ionic strength and the ionic medium

The various salts applied to keep the ionic strength constant may influence the values of the various types of constants in different ways. They have the common feature, however, that, on variation of the nature and the concentration of such salts, changes occur in the values of the activity coefficients, and hence the equilibrium constants expressed in terms of concentrations are also modified. The effects of the ionic strength and the ionic medium on the values of the constants can to a first approximation be classified into two types: (a) the effects of changes in the activity coefficients, and (b) specific interactions.

The nature of an ionic strength-dependence that can be interpreted in terms of changes in the activity coefficients is related to the charges on the ionic species participating in the equilibrium. As an example of an ionic strength-dependence typical of processes not involving charge compensation, Figs 6.11 and 6.12 depict the protonation constants of ethylenediamine and the stepwise stability constants of its complexes with the copper(II) ion, as functions of the square root of the ionic strength, which was adjusted with sodium perchlorate; these data are based on the studies by Koskinen [153].

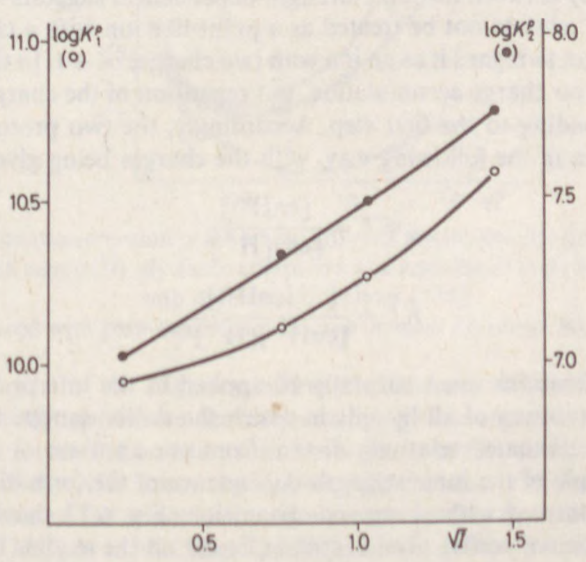


Fig. 6.11. The stepwise protonation constants of ethylenediamine as a function of ionic strength adjusted with $NaClO_4$

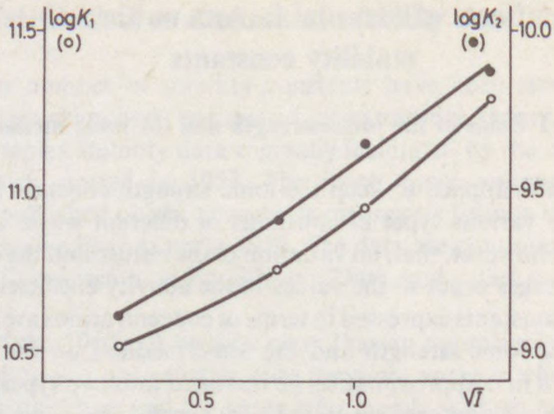


Fig. 6.12. The stepwise formation constants of copper(II)–ethylenediamine complexes as a function of ionic strength adjusted with $NaClO_4$

It may be seen that, although neither charge compensation nor charge accumulation occur in the process, the first protonation constant of ethylenediamine changes by ca. 0.7 log unit between ionic strengths of 0 and 2 *M*. Although the second step is theoretically accompanied by a charge accumulation, the value of the constant varies in nearly the same way as that for the first protonation process.

The similarity between the ionic strength-dependences suggests that the ionic species H_2en^{2+} should not be treated as a point-like ion with a charge of +2; it is more correct to regard it as an ion with two charges of +1. In this approach there is in fact no charge accumulation, but repetition of the charge rearrangement corresponding to the first step. Accordingly, the two protonation steps are best written in the following way, with the charges being given

$$K_1^p = \frac{[enH^+]}{[en][H^+]}$$

$$K_2^p = \frac{[^+HenH^+]}{[enH^+][H^+]}.$$

Similar considerations must naturally be applied in the interpretation of the protonation processes of all ligands in which the donor groups that undergo protonation are situated relatively distant from one another.

As an example of the ionic strength-dependence of the formation constants of complexes formed with charge compensation, Fig. 6.13 shows the results obtained for the copper(II)–glycine system, based on the studies by Gergely *et al.* [154]. In systems of this tpye, it is a general experience that the constants vary in accordance with minimum curves.

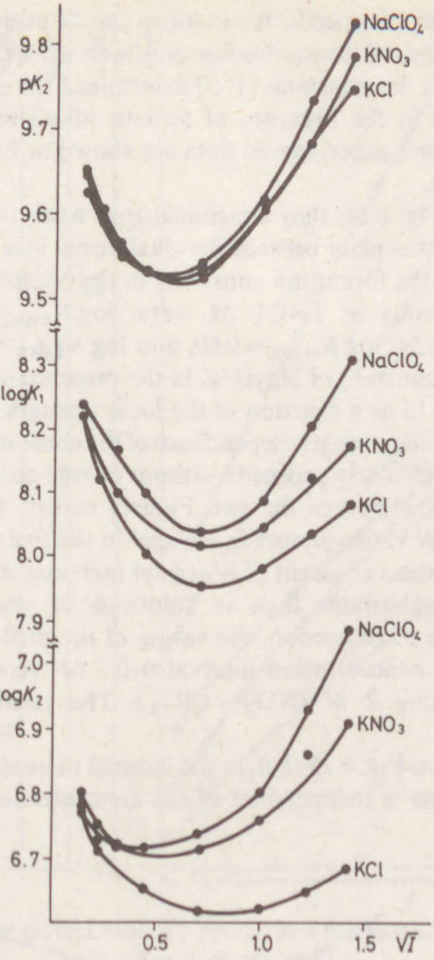


Fig. 6.13. Protonation constant of the amino group of glycine and the stepwise formation constants of the copper(II)–glycinato complexes as a function of ionic strength adjusted with different electrolytes [154]
(Reproduced with permission from *Magyar Kémiai Folyóirat*, **80**, 25 (1974))

The upper part of the Figure confirms that the activity coefficients do not differ significantly in the three electrolytes employed to adjust the ionic strength. The complex formation constants, however, vary in essentially different ways as functions of the KCl concentration, though the nature of the change is the same: the values of the constants decrease considerably compared to the data obtained in KNO_3 or in $NaClO_4$. This difference is indicative of the occurrence of specific interactions: in the given system the effect of the formation of chloro complexes, for instance.

In favourable cases, the specific interactions can be evaluated quantitatively; this permits calculations of the equilibrium constants involved in the interactions. Danielle, Rigano and Sammartano [155] determined the protonation constant of the sulphate ion in the presence of various alkali metal and tetraethylammonium salts. Their experimental data are shown in Fig. 6.14 as a function of the ionic strength.

On the basis of Fig. 6.14, they concluded that weak (but not insignificant) complex formation takes place between the alkali metal ions and the sulphate ion, and they calculated the formation constants of the complexes at various ionic strengths. Their results at I=0.1 *M* were: $\log K_{\mathrm{LiSO_4^-}}=0.77$, $\log K_{\mathrm{NaSO_4^-}}=$ $=0.40$, $\log K_{\mathrm{KSO_4^-}}=0.54$, $\log K_{\mathrm{RbSO_4^-}}=0.60$, and $\log K_{\mathrm{CsSO_4^-}}=0.70$.

The protonation constant of bipyridyl in the presence of various electrolytes is depicted in Fig. 6.15 as a function of the ionic strength [151]. For purposes of comparison, the ionic strength-dependence of the constant for the protonation of ammonia, which similarly proceeds without charge compensation, is shown in Fig. 6.16. A comparison of the two Figures reveals that the protonation constant of ammonia varies almost in parallel in the five different electrolytes, whereas the protonation constant of bipyridyl increases much more rapidly in the presence of perchlorates than in solutions of nitrates. For a deeper interpretation of the phenomenon, the values of the protonation constants in the perchlorate ion concentration interval 0–0.5 *M* were also determined in electrolytes containing 2 *M* ($NO_3^- + ClO_4^-$). The results are presented in Fig. 6.17.

It may be seen from Fig. 6.15 that, in the interval in question, the protonation constant of ammonia is independent of the concentration of the perchlorate

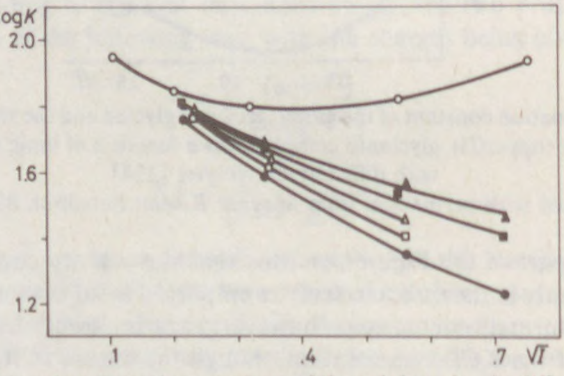


Fig. 6.14. Conditional protonation constant of the sulphate ion in different background electrolytes [155]
○ — Et_4N^+, ▲ — Na^+, ■ — K^+, △ — Rb^+, □ — Cs^+, ● — Li^+
(Reproduced with permission from *Inorg. Chim. Acta*, **63**, 267 (1982))

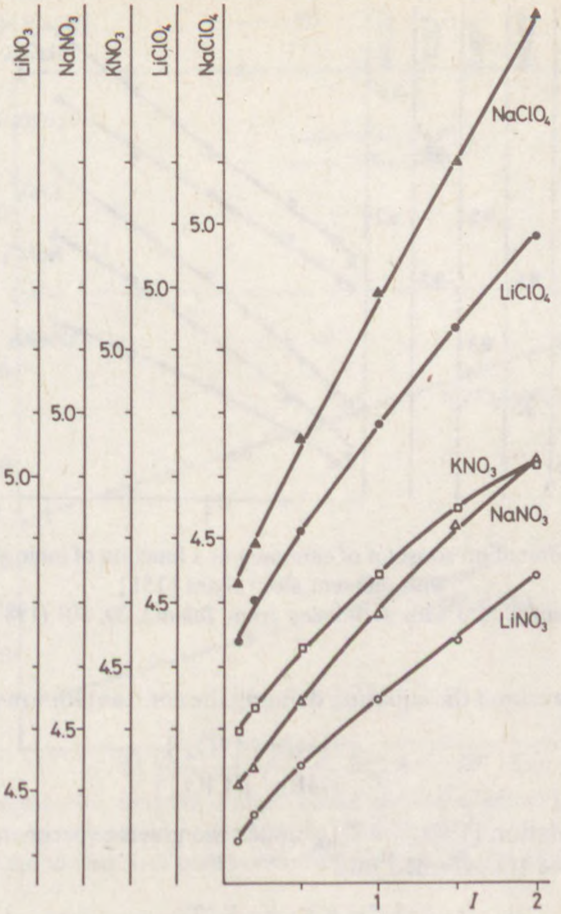


Fig. 6.15. The protonation constant of bipyridyl as a function of ionic strength adjusted with different electrolytes [151]
(Reproduced with permission from *Talanta*, **30**, 801 (1983))

ion, whereas the protonation constant of bipyridyl increases linearly. The change can be interpreted in terms of a specific interaction between the protonated bipyridyl and the perchlorate ion: ion-pair formation. This indicates that the measured value is in fact an apparent protonation constant, defined by the equation

$$K_p^m = \frac{[\mathrm{HBp}^+] + [\mathrm{HBp}^+\mathrm{ClO}_4^-]}{[\mathrm{H}^+][\mathrm{Bp}]}. \qquad (6.21)$$

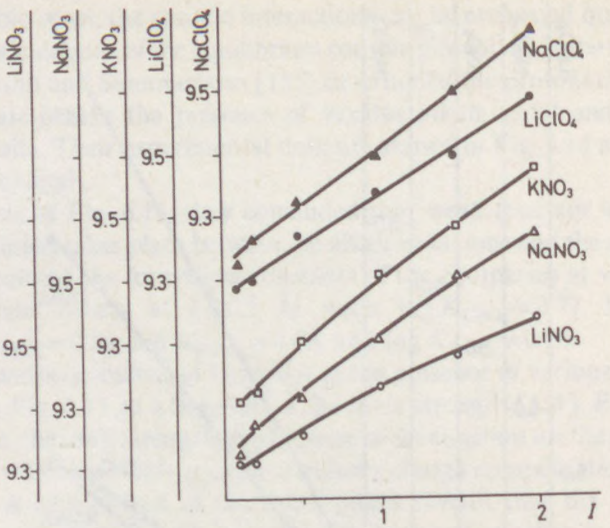


Fig. 6.16. The protonation constant of ammonia as a function of ionic strength adjusted with different electrolytes [151]
(Reproduced with permission from *Talanta*, **30**, 801 (1983))

If we take into account the equation defining the constant for ion-pair formation

$$K_{ip}=\frac{[\mathrm{HBp^+ClO_4^-}]}{[\mathrm{HBp^+}][\mathrm{ClO_4^-}]} \tag{6.22}$$

and also the relation $[\mathrm{ClO_4^-}] \sim T_{\mathrm{ClO_4^-}}$ under the given experimental conditions, Eq. (6.21) can be transformed into

$$K_p^m = K_p^\circ + K_{ip} K_p^\circ T_{\mathrm{ClO_4^-}} \tag{6.23}$$

where

$$K_p^\circ = \frac{[\mathrm{HBp^+}]}{[\mathrm{H^+}][\mathrm{Bp}]}\,. \tag{6.24}$$

Equation (6.23) indicates, in accordance with Fig. 6.16, that a linear variation is to be expected; the constant for ion-pair formation can be calculated from the slope of the straight line: $K_{ip}=0.54$ in 2 *M* NaNO$_3$, and $K_{ip}=0.45$ in 2 *M* LiNO$_3$.

In spite of the presented examples and the abundant literature relating to the ionic strength-dependence of the equilibrium constants, the laws governing the changes are still not known. There is as yet no comprehensive theory that can answer the fundamental questions concerning the dependence of the constants on the ionic strength. The situation is complicated by the fact that

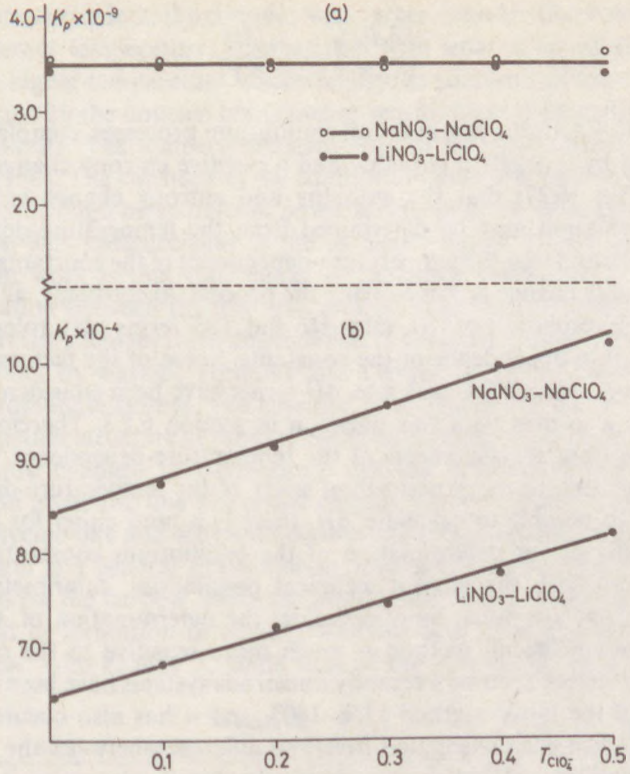


Fig. 6.17. The protonation constant of ammonia (a) and that of bipyridyl (b) at $I = 2.0\ M$, as a function of perchlorate concentration [151]
(Reproduced with permission from *Talanta*, **30**, 801 (1983))

the concentration of water also varies in relatively concentrated electrolyte solutions; hence, the effects arising from the role of water as a component of the equilibrium reactions appear as an ionic strength-dependence. Consequently, it may even occur that the effects resulting from variation in the water concentration are attributed to a fictive equilibrium process, and constants are calculated for equilibria which do not exist.

6.7.2.2 Effect of temperature

The thermodynamic correlations describing the effects of variation of the temperature are well known

$$\Delta G = -RT \ln K \tag{6.25}$$

$$\Delta G = \Delta H - T\Delta S \tag{6.26}$$

$$\left(\frac{\delta \Delta G}{\delta T}\right)_p = -\frac{\Delta H}{RT^2}. \tag{6.27}$$

According to Eq. (6.26), just as for all equilibrium processes, complex formation is promoted by a negative enthalpy and a positive entropy change. It may be seen from Eq. (6.27) that the enthalpy and entropy change accompanying complex formation may be determined from the temperature-dependence of the constants, and that the temperature-dependence of the constants is governed by the enthalpy change accompanying the process. Accordingly, all factors that influence the resolution of ΔG, into ΔH and $T\Delta$S terms play roles in shaping the temperature-dependence of the constants. Some of the factors influencing the resolution of the ΔG values into ΔH terms have been considered in section 6.1, and we also deal with this question in section 6.7.3. Therefore, we shall discuss here only specific effects of the temperature-dependence, and certain questions relating to the experimental study of the temperature-dependence.

In order to be able to calculate ΔH, there is a need either for calorimetric measurements or for determination of the equilibrium constants at various temperatures. With the present technical possibilities, calorimetry generally yields data that are much more accurate; the determination of ΔH with the 'temperature coefficient' method is much more sensitive to the experimental error. Nevertheless, even very recently numerous systems have been investigated by means of the latter method [156–160], and it has also occurred that the value of ΔH has been calculated from the difference between the equilibrium constants measured at merely two, relatively close-lying temperatures [161].

The method of temperature coefficients has the virtually unavoidable error that the concentration expressed in terms of molarity is temperature-dependent, and thus the coefficient of thermal expansion of the solvent is also transformed into ΔH values. This obvious circumstance is neglected in the vast majority of studies.

However, the high-accuracy measurement of the equilibrium constants defined in molality concentration units, in a wide range of temperature, yields deeper information even than that obtained by calorimetry, as it also provides a possibility for the determination of the temperature-dependence of ΔH, and hence the value of ΔC_p [162]. The same aim can naturally be attained through the calorimetric determination of ΔH at various temperatures [163]. The $\log K = f(1/T)$ data may similarly be required if the aim is the separation of the components of the thermodynamic quantities that are dependent on temperature and on the dielectric constant [164].

Certain nickel(II) and cobalt(II) complexes provide a dramatic example of the temperature-dependence of the equilibrium state [165–172]. The essence of the phenomenon is that the configuration of the complex is strongly temperature-dependent: the complex with larger coordination number predominates at lower temperature, whereas that with smaller coordination number does so at higher temperature. Accordingly, the solutions of the complexes are characterized by the unusual temperature-sensitivity of their visible spectra, i.e. of their colours. The temperature-sensitivity of the spectrum is illustrated in Fig. 6.18 [166]. The constant of the equilibrium between the two forms may be determined through measurement of the spectrum or of the magnetic moment. The reason why measurement of the magnetic moment finds applications in equilibrium work is that the change in geometry means at the same time a transformation between the low-spin and the high-spin structures.

An interesting temperature-dependence, in contrast with the general change, was observed by Farkas, Homoki and Gergely [173] in the nickel(II)–2,3-diaminopropionate system. The complex NiL_2 formed in this system is yellow and has a planar structure at room temperature; on elevation of the temperature, the structure changes to octahedral, and the complex becomes blue. The explanation given for this abnormal change was that there is an equilibrium between glycine-like and ethylenediamine-like structures in this system. Planar coordination is a general phenomenon among complexes of ethylenediamine substituted on the carbon, while the amino acids form octahedral complexes.

The heat of formation of nickel(II)–amino acid complexes of composition MeL_2 is ca. $-20\ \text{kJ mol}^{-1}$, while that of the ethylenediamine complexes of

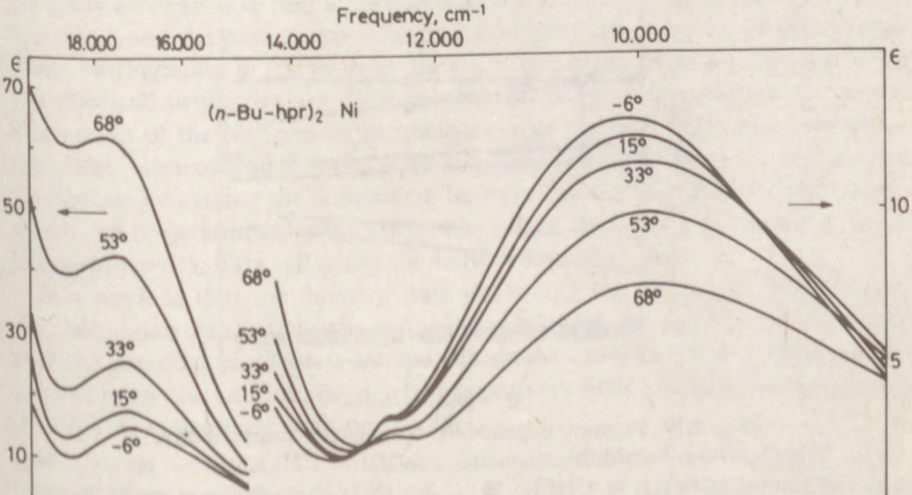


Fig. 6.18. Variable-temperature electronic spectral data for *n*-butyl-2-hydroxypropiophenimin in pyridine. Solute concentration is $\sim 7 \times 10^{-3}\ M$ [166]
(Reproduced with permission from *Inorg. Chem.*, **9**, 1153 (1970))

analogous composition is ca. $-40\ \mathrm{kJ\ mol^{-1}}$. In the sense of Eq. (6.27), it follows from this that, on the elevation of the temperature, the stability of the ethylenediamine-like complex decreases to a greater extent than that of the glycine-like complex, i.e. as the temperature rises, the glycine-like, octahedral structure assumes predominance.

6.7.2.3 Effect of pressure

The effect of pressure on the equilibrium constants is described by the well-known thermodynamic correlation

$$\left(\frac{\delta \ln K}{\delta P}\right)_T = -\frac{\Delta V}{RT} \tag{6.28}$$

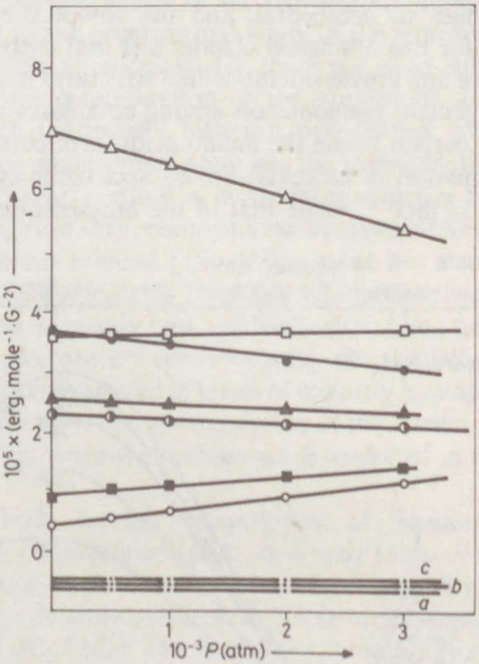


Fig. 6.19. Pressure dependence of magnetic susceptibility.
△ — Tris (N,N-di-n-butyldithicarbamato iron(III) in $CHCl_3$; □ — bis (N-phenylsalicylaldimino) nickel(II) in $CHCl_3$; ● — bis (N,N′-diethylamino-troponeimineato) nickel(II) in $CHCl_3$; ▲ — tris (N-ethylxantoto) iron(III) in $CHCl_3$; ◑ — tris (N-methylxantato)iron(III) in $CHCl_3$; ■ — bis (N-n-heptylsalicylaldimino) nickel(II) in CH_2Cl_2; ○ — bis (N-n-propylsalicylaldimino) nickel(II) in $CHCl_3$.
a,b,c — Common solvents, $CHCl_3$, CH_2Cl_2, $(CH_2OH)_2$, respectively [174]
(Reproduced with permission from *Coord. Chem. Rev.*, **12**, 185 (1974))

where ΔV is the difference between the partial molar volumes of the species featuring on the right and on the left-hand side of the equilibrium process.

Study of the effects of pressure is not merely of theoretical significance: the equilibrium processes occurring in the sea, for instance, can be understood only through investigation of the pressure-dependence. The results of complex equilibrium studies carried out under pressure were reviewed by Sinn [174]. The temperature-dependent structural equilibria discussed in the previous section are also sensitive to pressure. The sign of the pressure dependence may vary with the system, as shown in Fig. 6.19, which depicts the pressure-dependence of the magnetic susceptibility.

It must be mentioned that there are essential differences between the pressure-dependences of the Fe^{3+}–Cl^- and the Fe^{3+}–NO_3^- equilibria [175]; this can be explained in that an outer sphere complex is formed in the Fe^{3+}–NO_3^- system, and an inner sphere complex in the Fe^{3+}–Cl^- system.

6.7.3 Connection between equilibrium constants and parameters describing the properties of the central ion and the ligand

The aim of comparative studies of the various equilibrium processes in virtually all cases is to find a correlation between the values of the equilibrium constants and the parameters reflecting the chemical properties of the components participating in the process. Basically two types of parameters reflecting the chemical properties are distinguished: (a) physical parameters due to the interaction of the component in question with physical fields (e.g. ionization potential, electroaffinity, ionic potential, polarizability); and (b) correlation coefficients expressing the connection between the various chemical properties, which can be determined from a large number of studies (e.g. Hammett σ value, electronegativity, data reflecting the hard-soft nature, etc.).

It is obvious that the different data describing the chemical properties are mutually interrelated; thus, the connections between the equilibrium constants and the physical parameters or the correlation coefficients can mutually be derived from one another, though at present very little quantitative knowledge is available concerning such possibilities.

6.7.3.1 Connection between metal ion properties and complex equilibrium constants

6.7.3.1.1 Effect of ionic radius

If the metal–ligand interaction were purely of an ionic nature, then the stabilities of complexes of a given ligand with central metal ions having the same charge would be proportional to the reciprocal of the ionic radius. For metal ions with similar electronic configurations, this correlation does hold by and large, but there is no such correlation between the stability constants of the complexes of metal ions from different groups of the periodic system.

In a comparison of the complexes of metal ions with different charges, in place of the ionic radius it is more reasonable to seek a correlation between the stability constants and the ionic potential (the ratio of the charge and the radius). If the condition concerning the given electronic structure is taken into account, however, in this way it is possible to find a connection between the complex-forming properties of only very few metal ions. A survey and a detailed analysis of the correlations between the ionic radius and the ratio of the charge and the ionic radius were given by Hefter [177] for the fluoro complexes.

The approach by Brown, Sylva and Ellis [176] appears to be promising; with this, at least for the hydroxo complexes, a linear correlation of almost completely general validity is found if the effective charges of the ions are considered.

6.7.3.1.2 Effect of ionization potential and electronegativity

The ionization potential is a direct measure of the electron-attracting ability of a metal ion. It is obvious, therefore, that there must be a connection between the ionization potentials and the complex stability constants. In some cases, a very good correlation has in fact been observed [178–180], or the deviations have been used to draw conclusions as to the change in electronic structure [181].

For the complexes of numerous metal ions, Van Panthaleon van Eck [182] found that the following correlation holds

$$\log K_1 = p(I - q) \tag{6.29}$$

where I is the ionization potential for the gas-phase process $\mathrm{Me} \rightarrow \mathrm{Me}^{n+} + ne$, while p and q are constants, the numerical values of which depend only on the ligand and the experimental conditions (temperature, ionic strength). p is characteristic of the number of donor groups and the polarizability of the ligand, while q is characteristic of the nature of the donor atoms. The complexes of

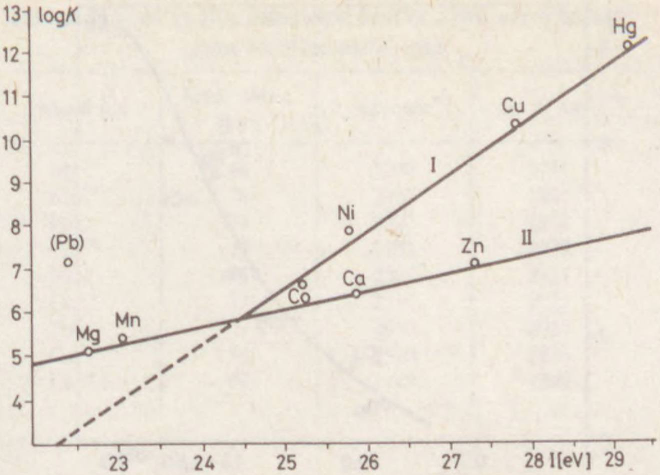


Fig. 6.20. Stability constants of different metal complexes of glycine as a function of the ionization potential of the central ion. The stability constants are dimensionless quantities, the concentrations being expressed in mole fractions [182] (Reproduced with permission from *Rec. Trav. Chim. Pays-Bas*, **72**, 50 (1953))

certain bidentate ligands can be divided into two groups, each group having its own characteristic *p* and *q* values. This is illustrated in Fig. 6.20.

From a comparison of the different systems, it was concluded [182] that in complexes of Type II the carboxylate group of the ligand is coordinated, while in complexes of Type I the amino group is coordinated or chelate formation occurs. Since the chelate effect is a general phenomenon (though its extent differs) and clearly exists in complexes of Type II too, it seems reasonable to explain the difference in that the carboxylate–metal ion bond is the stronger in the case of the metal ions in Group II, whereas the amine–metal ion coordinate bond is the stronger for those in Group I, while additionally the chelate effect is present as a stability-increasing factor in both types.

A number of authors have studied the connection between the electronegativity and the stability [183–187]. Similarly as in Fig. 6.20, Fig. 6.21 presents the stability constants of some complexes of glycine as a function of the electronegativity. It is an interesting phenomenon that, in spite of the correlation between the ionization potential and the electronegativity, the points lie on a single plot, in contrast with the two straight lines in Fig. 6.20.

The specific factors (discussed in detail in the previous section) determining the ratios of the constants will naturally also appear if the values of the stepwise stability constants are plotted as a function of the ionization potential or the electronegativity.

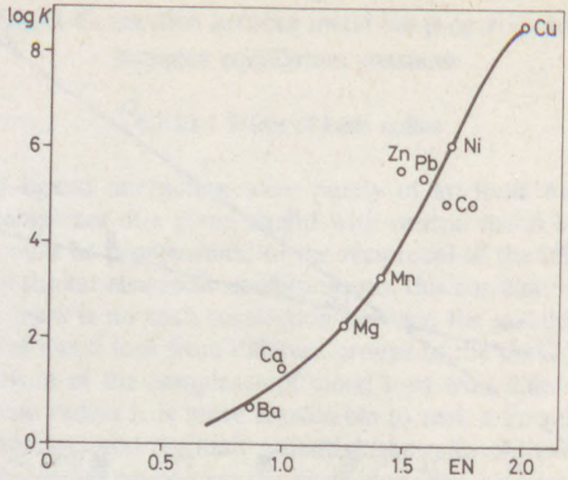


Fig. 6.21. Stability constants of different metal glycine complexes as a function of the electronegativities of the metal ions [185]
(Reproduced with permission from *Nature*, **174**, 887 (1954))

6.7.3.1.3 Effect of electronic configuration of metal ion

The complex-forming properties of the transition metal ions are often characterized by means of stability sequences. Of these, the Irving–Williams series is of outstanding importance [188, 189]; this holds for the complexes of the 3*d* transition metal ions with ligands containing nitrogen and oxygen donor atoms. Irving and Williams explained the well-known sequence of stability ($Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$) in terms of the ionic radius and the second ionization potential of the metals. The data are listed in Table 6.11, while the validity of the series is depicted in Fig. 6.22.

In principle, it is to be expected that a similar series holds for the complexes of the d^0–d^5 transition metal ions, i.e. $Ca^{2+} < Sc^{2+} < Ti^{2+} < V^{2+} < Cr^{2+} > Mn^{2+}$. However, several of these metal ions are such strong reductants that their complex-forming properties can not be studied in aqueous solution.

In the sense of the crystal-field theory, the Irving-Williams series is a consequence of crystal-field stabilization [190, 191]. This means that, with the exceptions of the d^0, d^5 and d^{10} configurations (Ca^{2+}, Mn^{2+} and Zn^{2+}), the splitting caused by the ligands in the energy levels of the *d* electrons diminishes the total energy of the system, i.e. it results in stabilization. The maximum in the stabilization occurs for complexes of Ni^{2+} and Cu^{2+}. The crystal-field stabilization energy can be calculated from the spectra, and it frequently agrees well with the energy calculated from the difference between the experimentally

Table 6.11 Ionic radius, ionization heat and hydration heat of some bivalent metal ions

Metal ion	Ionic radius (pm)	I_2 kJ mole^{-1}	$-\Delta H$ kJ mole^{-1}
Mg^{2+}	66	2200	1941
Mn^{2+}	78	2237	1861
Fe^{2+}	76	2337	1958
Co^{2+}	74	2452	2079
Ni^{2+}	73	2506	2121
Cu^{2+}	72	2714	2122
Zn^{2+}	72	2650	2056
Cd^{2+}	96	2510	1826
Ca^{2+}	99	1747	1598

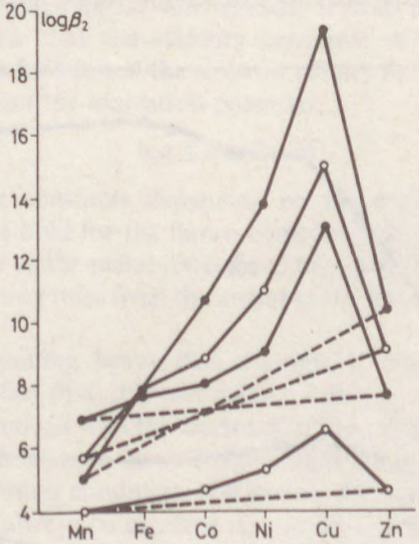


Fig. 6.22. log β_2 of complexes of several ligands as a function of the atomic number of bivalent transition metal ions.
○ — Salicylaldehide; ◑ — glycine; ● — ethylenediamine; ◓ — oxalate. Dashed lines are linear interpolations between Mn^{2+} and Zn^{2+}

measured stability constant and that resulting from interpolation between the stability constants for the Mn^{2+}–Zn^{2+} complexes.

It is worth noting that the analysis by Cannon [192] of the literature data, and also the results of Micskei *et al.* [109], indicated that the stabilization for Cr^{2+} complexes is about 0.55 times that for Cu^{2+} complexes, independently of the nature of the donor atoms. However, the Cr^{2+} complexes of polyfunctional ligands containing coupled five-membered chelate rings display destabilization [109], which may be explained by the much larger size of the metal ion.

These considerations hold only for high-spin complexes; deviations from the Irving-Williams stability series are common among low-spin complexes (of ligands with strong fields).

In principle, a similar crystal-field stabilization should be observed for the complexes of the lanthanide ions. In these systems, however, the splitting between the energy levels of the *f* electrons is of a much lower extent, and thus the stabilizing effect is not significant. The sequence of stability here is governed by the decrease in the ionic radius resulting from the change in the electronic configuration (lanthanide contraction) and by the accompanying change in the coordination number. For these and other, as yet not completely clarified reasons, the stability sequence varies, depending on the ligands, as demonstrated in Fig. 6.23.

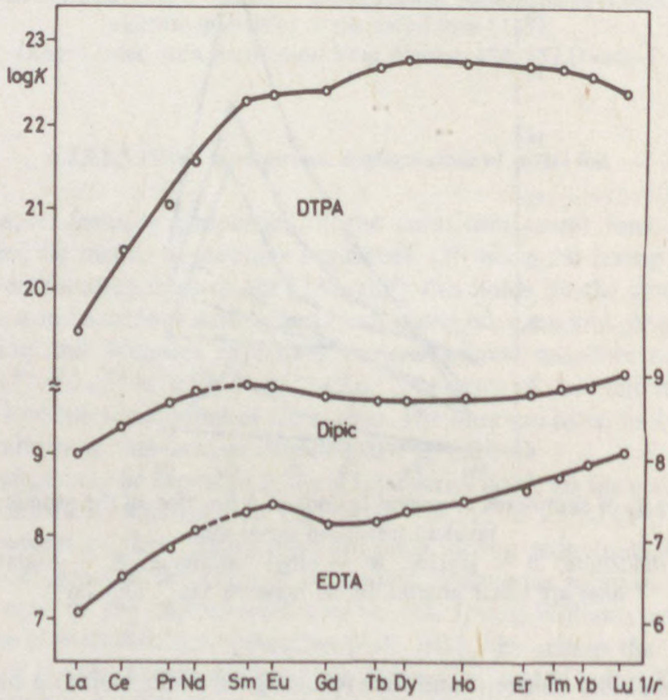


Fig. 6.23. Typical plots of stability constants of complexes of trivalent lanthanide ions against the reciprocal of the ionic radius of the corresponding metal ion.
EDTA — Ethylenediamine-N,N'-tetraacetic acid; Dipic — dipicolinic acid; DTPA — diethylenetriamine-N,N,N',N',N''-pentaacetic acid
(Reproduced with permission from *Chem. Rev.*, **65**, 1 (1965))

6.7.3.2 Connection between donor atom properties and complex equilibrium constants

In the overwhelming majority of ligands, the donor atoms exhibit a tendency to undergo protonation. Since both the protonation equilibria and the metal complex formation equilibria are influenced by the nature of the donor atom, it is understandable that the stabilities of the proton and metal complexes are interrelated. We shall deal in more detail with this question in Section 6.8, which discusses the correlations between the equilibrium constants. It was seen earlier that the stabilities of complexes of chelate-forming ligands are influenced fundamentally by the number of atoms in the chelate ring and by the number of such rings, i.e. by the structure of the ligand. Here, therefore, we shall consider only the connection between the stability and the nature of the donor atoms.

For the monoatomic halide ion ligands, it was demonstrated by Van Panthaleon van Eck that the stability constants of the Cd^{2+} and Hg^{2+} complexes vary as a function of the electron affinity in the same way as found for the dependence on the ionization potential:

$$\log K = a(E - b) \qquad (6.30)$$

where a and b are constants depending on the metal ion. However, this correlation does not hold for the fluoro complexes. It is obvious that, just as was seen in the case of the metal ions, the charge and the radius of the donor atoms play determining roles from the aspect of the strength of the electrostatic interaction.

For ligands containing heavy donor atoms (P and S), the situation is complicated by the fact that, besides forming σ-donor bonds, these atoms take part in $d\pi$–$p\pi$ interactions with the electrons in the d orbitals of the metal ions. This phenomenon is referred to as back-coordination; it has a fundamental effect on the equilibrium conditions. Of course, the significance of the dπ–pπ interaction can not always be ascribed to a given donor atom; it often results from the overall structure of the ligand (e.g. CO, CN^-, bipyridyl). A detailed discussion of this question leads us to the hard–soft theory; within this, it is convenient to examine jointly the connections between the formation constants and the properties of the metal ions and the ligands.

6.7.3.3 Interpretation of formation constants via the hard–soft theory

The hard–soft theory permits the interpretation of an enormous amount of experimental data and experience, chemical phenomena that can be explained in terms of donor–acceptor interactions. Following the pioneering work by

Sidgwick [193] and Grinberg [194], the basic organizing principles relating to the complex-forming properties of the metal ions were put forward independently by Ahrland and Larsson [195] and Carleson and Irving [196]. Pearson [197] extended the basic principles to the ligands, and introduced the hard–soft nomenclature. Hard acceptors (acids) are small ions with a large positive charge, and hence with a rigid electron shell structure, and compounds which do not contain readily excitable electrons. Hard bases similarly have rigid electronic structures and are difficult to polarize and oxidize; they are ligands containing donor atoms with high electronegativity. The acceptor atoms of soft acids (soft metal ions) are large, with a low charge and a loose electron shell structure, and they contain readily excitable outer electrons. The soft bases are similarly ligands containing donor atoms with a loose electron shell structure, that are easily polarized and oxidized, and are of low electronegativity.

Practically the same features are expressed by the classification system of Ahrland, Chatt and Davies [198], presented in Fig. 6.24. Acceptors of *a* type and *b* type correspond to hard and soft acids, respectively.

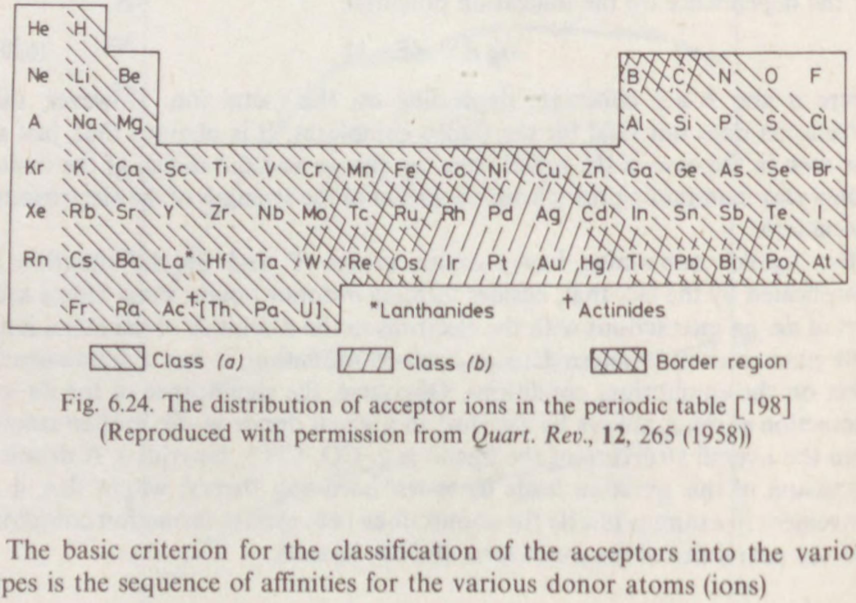


Fig. 6.24. The distribution of acceptor ions in the periodic table [198] (Reproduced with permission from *Quart. Rev.*, **12**, 265 (1958))

The basic criterion for the classification of the acceptors into the various types is the sequence of affinities for the various donor atoms (ions)

Metal ions of *a* type (hard)	Metal ions of *b* type (soft)
$F \gg Cl > Br > I$	$F \ll Cl < Br < I$
$O \gg S > Se > Te$	$O \ll S \simeq Se \simeq Te$
$N \gg P > As > Sb$	$N \ll P > As > Sb$.

The properties of the hard and the soft ligands and the above stability sequences clearly show that hard metal ions form stable complexes with hard ligands, as do soft metal ions with soft ligands; hard–soft and soft–hard interactions result in relatively weak complexes. Table 6.12 classifies the various donors and acceptors on the basis of the hard–soft theory.

The bonding-theory background of the classification into the various types involves the tendencies to form covalent and electrostatic bonds. Hard metal ions and hard ligands primarily participate in electrostatic interactions; their

Table 6.12 Hard–soft classification of acids and bases

Hard acids	Soft acids
H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}	Cu^+, Ag^+, Au^+, Ti^+, Hg_2^{2+}
Ca^{2+}, Sr^{2+}, Mn^{2+}	Pb^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, CH_3Hg^+
Al^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, La^{3+}	$Co(CN)_5^{2-}$, Pt^{4+}, Te^{4+}
N^{3+}, Cl^{3+}, Gd^{3+}, Lu^{3+}	Ti^{3+}, $Tl(CH_3)_3$, BH_3, $Ga(CH_3)_3$
Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, CH_3Sn^{3+}	$GaCl_3$, GaI_3, $InCl_3$
Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, U^{4+}	RS^+, RSe^+, RTe^+
Pu^{4+}, Ce^{3+}, Hf^{4+}, WO^{4+} MoO^{3+}	I^+, Br^-, HO^+, RO^-
UO_2^{2+} $(CH_3)_2Sn^{2+}$, VO^{2+}, Sn^{4+}	I_2, Br_2, ICN, etc.
$Be(CH_3)_2$, BF_3, $B(OR)_3$	Trinitrobenzene, etc.
$Al(CH_3)_3$, $AlCl_3$, AlH_3	Chloraniline, chinones, etc.
RPO_2^+, $ROPO_2^+$	Tetracyanoethylene, etc.
RSO_2^+, $ROSO_2^-$, SO_3	O, Cl, Br, I, N, RO, RO_2
I^{7+}, I^{5+}, Cl^{7+}, Cr^{6+}	Me^0
RCO^+, CO_2, NC^+	Metal surfaces
HX (hydrogene bonded molecules)	CH_2, carbenes

Borderline acids
Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Sn^{2+}, Sb^{3+}, Bi^{3+}, Rh^{3+}, Ir^{3+}
$B(CH_3)_3$, SO_2 NO^+, Ru^{2+}, Os^{2+}, R_3C^+, $C_6H_5^+$, GaH_3

Hard bases	Soft bases
H_2O, OH^-, F^-	R_2S, RSH, RS^-
$CH_3CO_2^-$, PO_4^{3-}, SO_4^{2-}	I^-, SCN^-, $S_2O_3^{2-}$
Cl^-, CO_3^{2-}, ClO_4^-, NO_3^-	R_3P, R_3As, $(RO)_3P$
ROH, RO^-, R_2O	CN^-, RNC, CO
NH_3, RNH_2, N_2H_4	C_2H_4, C_6H_6
	H^-, R^-

Borderline bases
$C_6H_5NH_2$, C_5H_5N, N_3^-, NO_2^-, SO_3^{2-}, N_2

reactions are accompanied by charge compensation and by the release of water molecules bound strongly to the ligand and to the metal ion. Accordingly, the thermodynamic driving force of complex formation is the large positive entropy change; in comparison, the stabilizing role of the enthalpy change is insignificant, and in fact the reaction may even be endothermic. In contrast, the interactions of soft metal ions and soft ligands lead to covalent bonds, to the accompaniment of a considerable enthalpy decrease. The role of the entropy change is negligible, for the soft metal ions and the soft ligands are not very hydrated in aqueous solution. It must be emphasized that these statements relate to aqueous solution. In solvents with lower dielectric permittivities than that of water, the electrostatic interactions may be stronger, and the outlined stability sequences and tendencies, and even the proportions of involvement of the terms ΔH and $T\Delta S$ in ΔG, may be reversed.

Ever since the emergence of the hard–soft theory, it has been the subject of scientific debate, which has at times been sharp [199, 200]. It is generally agreed only that the theory provides a very illustrative picture of the stability conditions; a number of questions remain open, however. For example, various authors have attempted to characterize the hard and soft natures by means of quantitative data. This has even led to such results as that some acceptor A is markedly harder, but also markedly softer in nature than another acceptor B. Some authors have even questioned the necessity of using the expressions hard and soft.

The reader is referred to some of the original publications for the details of the dispute [201–210]. In our own view, the importance of the hard–soft theory is unquestionable as concerns the systematization and qualitative interpretation of the phenomena connected with donor–acceptor reactions. Nevertheless, if it is remembered that a chemical reaction always involves an interaction, which means that the extent to which some property of one of the reaction partners is manifested automatically also depends on the nature of the second reaction partner, it is clear that, even in the best case, formulae derived from the hard–soft theory can provide only a semiquantitative description of the phenomena. Efforts to discover the quantitative correlations inherent in the theory may shed light on many part-questions, but overall success is not to be expected. The data expressing the hard–soft nature can promote only a semiquantitative orientation, in a very similar way as the electronegativity values, which became a chemical concept much earlier.

6.8 Correlations of equilibrium constants

One of the earliest aims of solution equilibrium studies was to discover correlations between the stability constants of the complexes of a given metal ion with different ligands, or of the complexes of a given ligand with different metal ions. Before a discussion of such correlations and of the principles of comparison of the constants, it must be stressed that equations describing the connections between the equilibrium constants merely express the correlations between the constants; they cannot be regarded as causality relations. The reason for the correlation is always some (frequently unknown) common structural feature which is reflected in both series of data, the correlation being a consequence of this.

6.8.1 Paradoxes in correlations

Since the basis of the correlation is always some structural similarity, it is very important that only the values of constants reflecting the same structural feature should be compared. It is not always simple for the obvious criterion to be achieved: as discussed earlier, the macroscopic equilibrium constants define only the composition, and various structures may develop at the same composition. The consequences of this may be illustrated via some concrete examples. In the course of our examples, we shall sometimes deliberately point out false conclusions; however, these will serve only to illustrate the contradiction, and they are not to be regarded as the conclusions drawn by the authors referred to.

The equilibrium conditions for the copper(II) complexes of *o*-tyrosine were studied by Letter and Baumann [211], who found that the complex $Cu(HL)_2$ is formed in this system; as a dibasic acid, this complex has the dissociation constants $pK_1 = 8.79$ and $pK_2 = 9.71$. Since the p*K* value for the phenolic OH group of *o*-tyrosine was found to be 10.66, it appears clear that the ligand is coordinated in an amino acid-like way to the metal ion, and that the basicity of the phenolic OH decreases because of the electron-attracting effect of the metal ion. This conclusion, however, is wrong for two reasons:

(1) As mentioned previously, the hydrogen-bonding between the adjacent donor groups in *o*-tyrosine means that the measured p*K* values can not be ascribed to the protonation of either of the donor groups.

(2) Proton loss from the phenolic OH is accompanied by an extensive structural rearrangement of the complex; as demonstrated by means of calorimetry and spectrophotometry [211], *o*-aminophenol-like coordination occurs instead of the amino acid-like coordination.

Gergely *et al.* [212] determined a p*K* value of 9.08 for the amino group of phenylalanine, and p*K* values of 9.05 and 10.14 for the amino and hydroxy groups of *p*-tyrosine. If the smaller p*K* value were assigned to the amino group, and the larger one to the hydroxy group, it could be stated that the phenolic OH attracts electrons, for it decreases the p*K* value of the amino group. This would be in contradiction with tendencies known from organic chemistry. The contradiction may similarly be solved by means of the microconstants. It was established by Kiss and Tóth [123] that both pK values to be ascribed to the amino group are larger than the pK value for phenylalanine, and the apparent contradiction arises merely because of the combination of the microconstants. The values of the microconstants must also be taken into consideration in the calculation of the formation constants of metal complexes. In their absence, for instance, the calculated stability constant for the copper(II) complex of tyrosine corresponds to the definition

$$K_1 = \frac{[\mathrm{Cu}(^-\mathrm{AH})]}{[\mathrm{Cu}^{2+}]([\mathrm{AH}^-]+[\mathrm{HA}^-])}$$

whereas, if a comparison is to be made with the stability constant of the similar complex of phenylalanine, for example, it is necessary to know

$$K_1^* = \frac{[\mathrm{Cu}(^-\mathrm{AH})]}{[\mathrm{Cu}^{2+}][^-\mathrm{AH}]}$$

where $^-$AH denotes the species containing the amino group in deprotonated form and the phenolic hydroxy group in protonated form.

Brookes and Pettit [65] found that the logarithm of the formation constant of the amino acid-like coordinated complex of Ni^{2+} with ornithine is 15.25, while glycine is well known to form a Ni^{2+} complex with $\log K_1 \sim 5.8$. There is no chemically explainable reason for the difference in stability of nearly ten orders of magnitude; because of the difference in dimensions, the two constants are not comparable. In fact, the formation constant for the ornithine complex refers to the process

$$\mathrm{Ni}^{2+} + \mathrm{L}^- + \mathrm{H}^+ \rightleftharpoons \mathrm{NiLH}^{2+}$$

while that for the glycine complex refers to the process

$$\mathrm{Ni}^{2+} + \mathrm{L}^- \rightleftharpoons \mathrm{NiL}^+ .$$

Data that can be compared are obtained if we take into account the equilibrium constant of the process

$$\mathrm{Ni} + \mathrm{HL} \rightleftharpoons \mathrm{Ni(HL)}$$

which expresses the coordinating ability of the protonated form of ornithine, HL. Even in this case, of course, it must be borne in mind that the form HL may have two different structures.

Similar difficulties may be encountered in any relatively involved equilibrium system. Such questions can be solved only through efforts to establish the microconstants of the protonation equilibria and the metal complex formation equilibria [213–217], and by widening our equilibrium chemical horizons.

6.8.2 Correlation between protonation constants of ligands with similar structures and the formation constants of their complexes

Since complex formation is in most cases a process involving competition between the metal ion and the proton, it is understandable that it is often possible to find a close correlation between the protonation and the complex formation of ligands with similar structures. The first such example was reported by Larsson in 1934 [218]; more recently, it has become quite general for the factors influencing the values of the constants to be discovered and interpreted on the basis of correlations of this nature [219–226]. As an example of the ample literature material available, in Fig. 6.25 we present merely the correlation relating to the Mg^{2+} and Cu^{2+} complexes of 8-hydroxyquinoline and its derivatives [227].

Figure 6.25 reveals that the points deviate from linearity if the carbon atoms adjacent to the donor atoms are substituted, i.e. if there is steric hindrance to metal complex formation. Such hindrance is not observed with the much smaller proton.

Naturally, a comparison of this nature is possible only if the donor atoms of the ligands are identical, and even then only if they are in the same hybrid

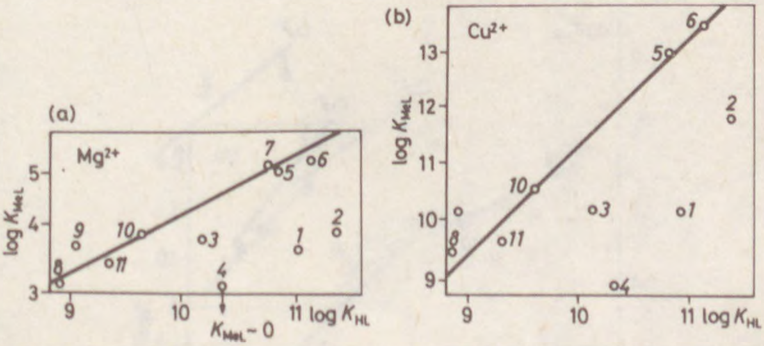


Fig. 6.25. log K_{MeL} as a function of log K_{HL} for Mg^{2+} (a) and Cu^{2+} (b) complexes of 8-hydroxyquinoline and its derivatives in 50% v/v aqueous dioxane (0.3 *M* $NaClO_4$) at 20 °C.

Open points refer to ligands with a substituent adjacent to the chelating nitrogen atom. *1* — 2-Methyl-8-hydroxyquinoline; *2* — 1,2,3,4-tetrahydro-10-hydroxyacridine; *3* — 8-hydroxy-2,4-dimethylquinazoline; *4* — 4,8-dihydroxy-4-methyl-2-phenylquinazoline. Full points refer to the following ligands: *5* — 8-Hydroxyquinoline; *6* — 5-methyl-8-hydroxyquinoline; *7* — 6-methyl-8-hydroxyquinoline; *8* — 8-hydroxycinnoline; *9* — 8-hydroxyquinoline and its derivatives in 50% v/v aqueaus dioxane (0.3 *M* $NaClO_4$) at [227]

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state. The —NH— group of peptide bonds, for example, can not be compared with amine nitrogen or with nitrogen in a heteroaromatic ring.

The basis of the correlation between pK_{HL} and $\log K_{MeL}$ is the identical nature of the proton–ligand and the metal ion–ligand bonds. If these bonds differ in nature, a linear correlation is not to be expected; indeed, an inverse correlation may even be observed. Such examples are to be found among the complexes of soft metal ions with soft ligands, where the natures of the H—L and Me—L bonds may differ fundamentally as a consequence of back-coordination. Instances of these latter cases are presented in Table 6.13 and Fig. 6.26.

The most convenient method of plotting and studying the correlation between the pK_{HL} and $\log K_{MeL}$ values depends, among other factors, on how many

Table 6.13 pK values and stability constant of copper(II) complexes of bipyridinium (H_2Bp^{2+}) ion and its reduction products

Ligand	pK_1	pK_2	$\log \beta_2$
2,2′-Bipyridyl	−0.20	4.37	13.66
2,2′-Pyridyl-pyperidyl	2.0	9.10	12.20
2,2′-Dipyperidyl	7.0	10.16	17.94

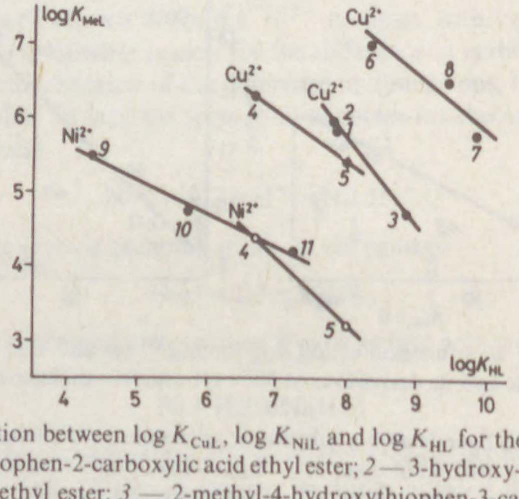

Fig. 6.26. Correlation between $\log K_{CuL}$, $\log K_{NiL}$ and $\log K_{HL}$ for the following ligands. *1* — 3-Hydroxythiophen-2-carboxylic acid ethyl ester; *2* — 3-hydroxy-5-methylthiophen-2-carboxylic acid ethyl ester; *3* — 2-methyl-4-hydroxythiophen-3-carboxylic acid ethyl ester; *4* — 2-acetyl-3-hydroxythiophen; *5* — 3-acetyl-4-hydroxythiophen; *6* — 2-hydroxynaphtaldehyde-1; *7* — 2-hydroxynaphtaldehyde-3; *8* — salicylaldehyde; *9* — 8-hydroxy-6-methyl-1,6-naphtyridinium iodide; *10* — 5-hydroxy-1-methylquinoxalinium iodide; *11* — 8-hydroxy-6-methylquinazolinium iodide
(Reproduced with permission from *Helv. Chim. Acta*, **49**, 1617 (1966))

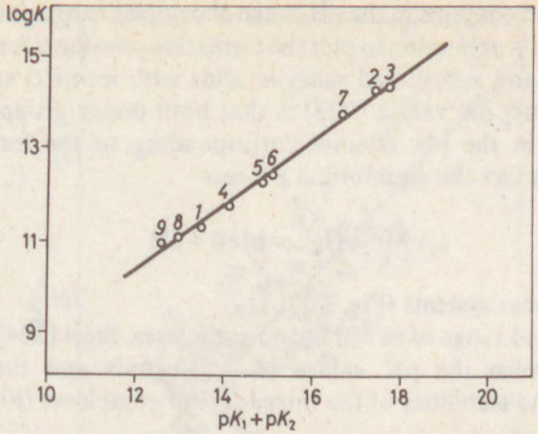

Fig. 6.27. Plot of log K, vs. $pK_1 + pK_2$ for the iron(III) complexes of some substituted salicylic acids.
1 — 3-Bromosalicylic acid; *2* — 4-hydroxysalicylic acid; *3* — 4-aminosalicylic acid; *4* — 5-sulfosalicylic acid; *5* — 5-chlorosalicylic acid; *6* — 5-iodosalicylic acid; *7* — 5-hydroxysalicylic acid; *8* — 3,5-dibromosalicylic acid; *9* — 3,5-dichlorosalicylic acid [223]
(Reproduced with permission from *J. Inorg. Nucl. Chem.*, **36**, 2388 (1974))

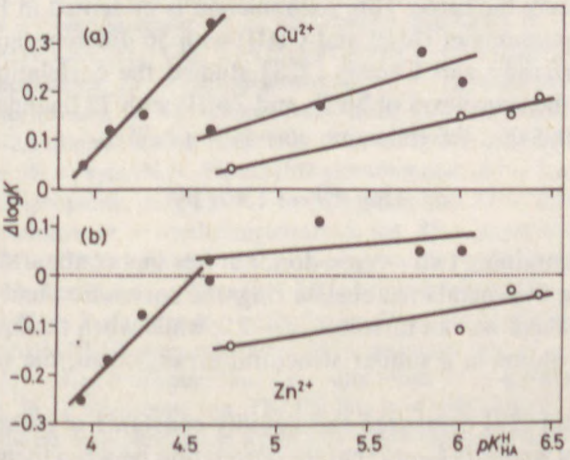

Fig. 6.28. Relation between $\Delta \log K$ and pK^{H}_{HA} for the mixed ligand complexes Cu(bipyridyl) (carboxylate) (a) and Zn (bipyridyl) (carboxylate) (b) [224]
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protons the ligand contains in the pH range of complex formation. For instance, the reason why it is preferable to plot the formation constants for the complexes of salicylic acid and substituted salicylic acids with iron(III) as a function of the sum of the two pK values [223] is that both donor groups of the ligand are protonated in the pH interval corresponding to the formation of the complexes, i.e. in fact the equilibrium process

$$\mathrm{Me} + \mathrm{H_2L} \rightleftharpoons \mathrm{MeL} + 2\mathrm{H}$$

takes place in these systems (Fig. 6.27).

In a fairly broad range of mixed ligand complexes, Sigel [224] found a linear correlation between the pK values of the ligands and the $\Delta \log K$ data characterizing the stabilities of the mixed ligand complexes (Fig. 6.28).

6.8.3 Correlation between stability constants of complexes of two metal ions with ligands with similar structures

In the above sense, it is obvious that a correlation must also be found between the formation constants of the complexes formed by two metal ions with ligands with similar structures. This correlation may be even closer than that between pK_{HL} and $\log K_{\mathrm{MeL}}$, for the probability is smaller (but not excluded) that the natures of the coordinate bonds will differ, and the effects of the steric factors too will be nearly the same. This phenomenon is presented in Fig. 6.29 on the example of complexes of Ni(II) and Cu(II) with 56 different ligands [227].

Freiser, Fernando and Cheney [228] studied the correlation between the constants for the complexes of Ni(II) and Zn(II) with 72 ligands. In 42 of these cases they found that the following correlation held

$$\log \beta_2^{\mathrm{Ni}} = 1.13 \log \beta_2^{\mathrm{Zn}}$$

For ligands containing two oxygen donor atoms in a configuration suitable for formation of a five-membered chelate ring, the correlation had the same slope as above, but there was an intercept of -2.0, while when the ligands contained two nitrogen atoms in a similar structural arrangement, the slope was found to be $+2.0$.

Yatsimirskii [229] compared the stability constants of complexes of Mg^{2+} and Zn^{2+}, and similarly found that the correlation between them was a function of the nature of the donor atoms.

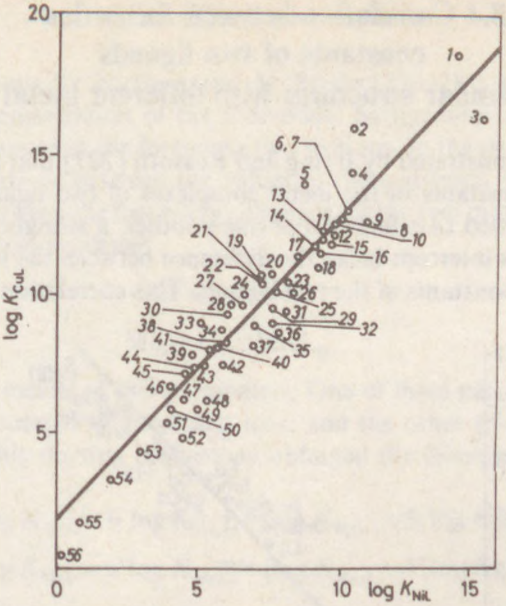

Fig. 6.29. log K_{CuL} as a function of log K_{NiL} for complexes of different ligands. *1* — Triaminotriethylamine; *2* — diethylenetriamine; *3* — ethylenediamine-N-diacetic-N′-dipropionic acid; *4* — tiron (pyrocatechol-3,5-disulphonic acid); *5* — 1,3-diamino-propane-2-ammonium ion; *6* — 8-hydroxyquinoline; *7* — dibenzoylmethane; *8* — thenoylbenzoylmethane; *9* — nitriloacetic acid; *10* — benzoylfuroylmethane; *11* — $CH_3CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot Si(CH_3)_3$; *12* — dithenoylmethane; *13* — acetylbenzoylmethane; *14* — acetylacetone; *15* — furoylthenoylmethane; *16* — acetylthenoylmethane; *17* — $(CH_3)_3SiC_2H_4 \cdot CO \cdot C_2H_4Si(CH_3)_3$; *18* — 1,2,3-triaminopropane; *19* — N-methylethylenediamine; *20* — ethylenediamine; *21* — 1,2-diamino-propane; *22* — iminopropionicacetic acid; *23* — iminodiacetic acid; *24* — N-ethylethylenediamine; *25* — 8-hydroxy-2,4-dimethylquinazoline; *26* — 8-hydroxy-2-methylquinoline; *27* — 1,3-diaminopropane; *28* — sym. N,N′-dimethylethylenediamine; *29* — 5-hydroxyquinoxaline; *30* — iminodipropionic acid; *31* — 8-hydroxycinnoline; *32* — folic acid; *33* — N-propylethylene-diamine; *34* — triethylenetetramine ion; *35* — aspartic acid; *36* — 1,10-phenantroline; *37* — 2,2′-dipyridyl; *38* — α-alanine; *39* — leucine; *40* — glycine; *41* — isonicotini hydrazide; *42* — 2-methyl-1,10-phenanthroline; *43* — salicylaldehyde; *44* — sarcosine; *45* — β-alanine; *46* — riboflavin; *47* — glycyl-glycine; *48* — oxalate ion; *49* — 2,9-dimethyl-1,10-phenanthroline; *50* — malonate ion; *51* — salicylaldehyde sulphonic acid; *52* — 4-hydroxypteridine; *53* — ammonia; *54* — pyridine; *55* — acetate ion; *56* — nitrocetate ion. The full line is of unit slope [227]

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6.8.4 Correlation between formation constants of two ligands with similar structures with different metal ions

It was first demonstrated by Irving and Rossotti [227] that if the logarithms of the stability constants of the metal complexes of two ligands with similar structures are plotted as a function of one another, a straight line is obtained with unit slope, its intercept being the difference between the logarithms of the first protonation constants of the two ligands. This correlation is shown in Fig. 6.30.

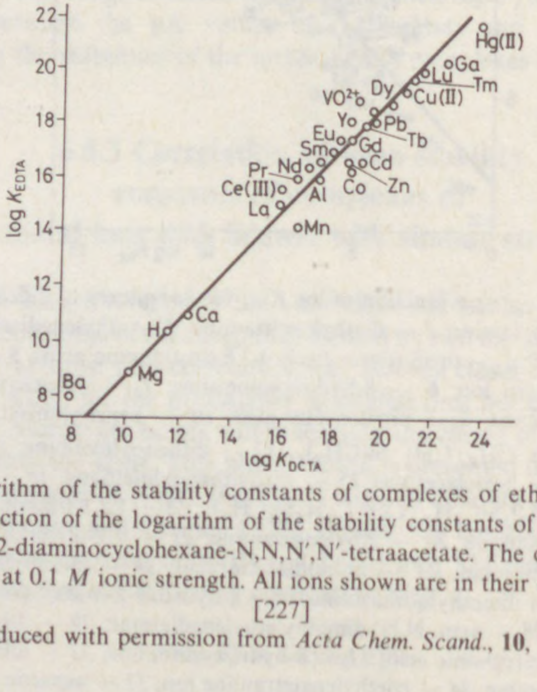

Fig. 6.30. Logarithm of the stability constants of complexes of ethylenediaminetetraacetate as a function of the logarithm of the stability constants of the corresponding complexes of 1,2-diaminocyclohexane-N,N,N′,N′-tetraacetate. The constants were obtained at 20 °C, at 0.1 *M* ionic strength. All ions shown are in their usual valency state [227]
(Reproduced with permission from *Acta Chem. Scand.*, **10**, 72 (1956))

Similar correlations have been observed for other equilibrium systems. For the complexes of polydentate ligands, the value of the intercept may be open to question; in the sense of the considerations in the previous section, the value of the intercept depends on how many of the donor groups of the ligand are to be found in protonated form in the pH range relating to the formation of the complexes.

6.8.5 Other correlations

The publications by Nieboer and McBryde [230–232] provide a detailed survey and systematization of the theoretical background of the correlations of the types discussed in the foregoing two sections. In the derivation of general correlation equations between the values of the constants, they assumed that the difference between the free energy changes for the two mutually independent complex formation processes

$$\mathrm{Me} + \mathrm{L} \rightleftharpoons \mathrm{MeL}$$

$$\mathrm{Me_s} + \mathrm{L_0} \rightleftharpoons \mathrm{Me_sL_0}$$

can be given by means of two parameters. One of these parameters reflects the difference in properties of the metal ions, and the other the difference for the ligands. From this starting point, they obtained the following equations

$$\log K_{\mathrm{MeL}} = \mathrm{B} \log K_{\mathrm{Me_sL}} + (\log K_{\mathrm{MeL_0}} - \mathrm{B} \log K_{\mathrm{Me_sL_0}})$$

$$\log K_{\mathrm{MeL}} = \mathrm{C} \log K_{\mathrm{MeL_0}} + (\log K_{\mathrm{Me_sL}} - \mathrm{C} \log K_{\mathrm{Me_sL_0}})$$

where $\mathrm{Me_s}$ and $\mathrm{L_0}$ are the metal ion and ligand taken as the basis of comparison.

During the comparison of the correlations with the experimental data, two types of behaviour were observed. In certain systems, the values of B and C depended on the properties of the examined metal ions and ligands; in other systems, both parameters had a value of one. By developing their considerations further, Nieboer and McBryde essentially arrived at the hard–soft theory, with data indicative of the positions of the metal ions on the hard–soft scale.

Numerous other correlations are known within limited groups of complexes. One such correlation exists for mixed ligand complexes where the coordination of some ligand A, which forms a very stable complex, is followed by the coordination of another ligand, B

$$\mathrm{MeA} + \mathrm{B} \rightleftharpoons \mathrm{MeAB}.$$

The equilibrium constant of this process is inversely proportional to the constant for the process

$$\mathrm{Me} + \mathrm{A} \rightleftharpoons \mathrm{MeA}.$$

To a first approximation, this can be interpreted in that the complex formation processes of the metal ion in question are characterized by a tendency to an almost constant free energy change (coordination force), and if ligand A 'consumes' more of this, less 'remains' for ligand B. The validity of this correlation, reported in the first edition of our book, has since been confirmed in many systems [285, 286, 303–305].

6.9 Equilibrium conditions of outer sphere complexes

In the condensed phase, the coordination sphere of the central metal ion is generally saturated, i.e. the number of donor atoms bound to the metal ion is the same as the maximum coordination number. As we have already seen, however, the maximum coordination number depends on the size and electronic structure of the ligands. It is well known, for example, that the square planar copper(II) complexes can coordinate a further two ligands, giving rise to a distorted octahedral structure. As proposed by Jørgensen [233], complexes in which some of the donor atoms are strongly coordinated, i.e. the bond distance is relatively short, while the other donor atoms are to be found at a much greater distance, i.e. they are coordinated to the metal ion much more weakly, are referred to as anisotropic complexes.

Even the expansion of the coordination sphere does not mean that the coordinately saturated complex no longer displays any specific affinity for the other ionic species to be found in the solution. Attention was drawn to interactions of this type by Werner [234], and abundant experimental evidence has subsequently been accumulated demonstrating the formation of outer sphere complexes. A general feature of these complexes is that there is no direct coordinate bond between the metal ion and the ligands to be found in the outer sphere. There is naturally a continuous transition between inner sphere complexes, anisotropic complexes and outer sphere complexes, and their definite distinction is rarely possible.

Distinction is relatively simple if a complex with a coordinately saturated inner sphere is inert, and does not vary during the time of the equilibrium investigation. The differentiation of outer sphere complexes formed simultaneously with labile inner sphere complexes, however, poses certain problems. In aqueous solution, for example, the outer and inner sphere complexes of some metal ion Me and ligand L differ merely in that a water molecule is wedged between the two components in the former case, whereas this water molecule is missing from the inner sphere complex, a direct coordinate bond existing between L and Me. In the equations defining the equilibrium constants, the role of water as a component of the reactions is disregarded, and thus the compositions of the two complexes are formally the same. Accordingly, the experimentally measured formation constant is the sum of the formation constants of the two types of complexes

$$\beta_1^{\text{exp}} = \frac{[\text{Me}(\text{H}_2\text{O})_5\text{L}] + [\text{Me}(\text{H}_2\text{O})_6\text{L}]}{[\text{Me}(\text{H}_2\text{O})_6]\,[\text{L}]} = \beta_1^{\text{inner sph.}} + \beta_1^{\text{outer sph.}}.$$

Analogous correlations naturally hold in the further steps of complex formation. For purposes of differentiation (similarly as for the determination of the microconstants), it is always necessary to utilize some assumption that can not be proved in a strict thermodynamic sense. In order for the assumptions to be well founded, it is important to carry out equilibrium studies on outer sphere complexes of inert inner sphere complexes.

The inner and outer sphere complexes can be investigated with practically the same experimental methods; in this respect, therefore, we merely provide some literature references relating to the possibilities of application of polarography [235–240], conductivity measurements [241–244], solubility measurements [245–248], liquid–liquid extraction [249], the study of ion-exchange equilibria [250, 251], pH measurements [252, 253], NMR [254–256], spectrometry [257–261], polarimetry and CD studies [262–271], and reaction kinetic measurements [259].

One of the greatest problems in the experimental study of outer sphere complexes is to ensure a suitable constant ionic strength. The vast majority of these complexes have low stabilities, and thus a high ligand concentration must be employed to attain a measurable equilibrium conversion. It follows from this that the experiments must be carried out at relatively high ionic strength. At the same time, the ions applied in the study of inner sphere complexes naturally tend to form outer sphere complexes.

A comprehensive analysis of the tendency of the perchlorate ion to undergo complex formation, and within this to form outer sphere complexes, was performed by Johansson [272]. The studies by Ilcheva and Beck [261] indicated that, in investigations of outer sphere complexes, it is advisable to apply fluoride ion to maintain the ionic strength at a constant level. It is also possible to encounter examples of equilibrium investigations performed with violation of the principle of a 'constant ionic medium' [262].

Basically, an electrostatic interaction is responsible for the stability of outer sphere complexes. This statement is supported by the fact that no outer sphere complex has yet been found which contains a neutral inner sphere complex. Accordingly, there is a very close connection between the theory of electrolyte solutions and the theory of ion association, ion-pair formation and outer sphere complex formation; Yokoyama and Yamatera [273] have in fact attempted to unify these theories completely. Because of the determining role of the electrostatic interaction, it is obvious that the stability of outer sphere complexes depends primarily on the charge conditions and the dielectric constant of the solvent. The stability may also be affected by other factors, however. For instance, the ligand in the outer sphere may be linked to the ligands in the inner sphere through hydrogen-bonding, while certain photometric investigations suggest an interaction that can be explained in terms of charge transfer.

In such charge transfer, the ligands of the inner sphere play the role of the 'bridge'.

Within the chemistry of complex equilibria as a whole, the proportion of publications dealing with studies of outer sphere complex formation is quite low, and it has displayed a tendency to decrease in the past 10 years. The cause of this is probably that the fundamental questions were solved by the end of the 1960's [274], while the theoretical knowledge required for a detailed analysis is still not available.

6.10 Equilibrium conditions in mixed metal complexes

The complexes belonging in this category on the basis of their compositions exhibit great differences in structure and bonding conditions. However, so few investigations have been performed in this field that the results can not be discussed from a uniform system of aspects. Here, therefore, we shall merely survey some of the main results of work of special importance.

Mixed metal complexes include those complexes in which ions of the same metal are to be found in different oxidation states. It is a general feature of such complexes that their colour is appreciably deeper than that corresponding to the average colour of their constituents. Werner [275] reported that the colour of complexes containing both Pt(II) and Pt(IV) ions is much deeper than the colours of the mononuclear complexes of the same ions. He called attention to the analogy of this phenomenon and the behaviour of the quinone–hydroquinone system. The best-known phenomenon in this field is the variation in colour of the iron hydroxides. Iron(II) hydroxide is white, iron(III) hydroxide is reddish-brown, and the mixed hydroxide is black. Wells [276] pointed out that even a similar electronic configuration is sufficient for development of the deep colour; it is not essential that the ions with different oxidation numbers be derived from the same element. As an example, $Cs_2Ag(I)Au(III)Cl_6$ is a complex with a much deeper colour than those of the mononuclear components.

Davidson [277–280] made a systematic study of interactions of this type. He found that interactions may be detected in hydrochloric acid solutions of the pairs Sb(III)–Sb(V), Sn(II)–Sn(IV), Cu(I)–Cu(II), and Fe(II)–Fe(III), but that the equilibrium conversion is not sufficient for the constants to be calculated. Figure 6.31 illustrates the interaction between the chloro complexes of iron(II) and iron(III).

The fact of interaction can also be detected in the iron(II)–iron(III)–citrate system [283], but the value of the constant cannot be calculated here, either. An interaction of this nature has not been experienced between the aqua ions, i.e. a chloride ion, or some other, appropriate bridging ligand appears necessary

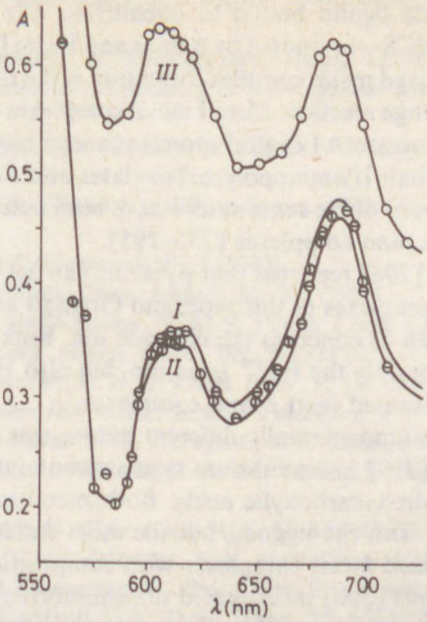

Fig. 6.31. Effect of different salts on the spectrum of iron(III) in 12 *M* HCl. Curve *I* — 0.88 *M* $FeCl_3$; Curve *II* — 0.88 *M* $FeCl_3 + 0.13$ *M* $MeCl_2$ (Me = Mn, Mg, Zn); Curve *III* — 0.88 *M* $FeCl_3 + 0.13$ *M* $FeCl_2$ [279]
(Reproduced with permission from *J. Am. Chem. Soc.*, **72**, 5557 (1950))

for the formation of metal complexes with mixed oxidation numbers. It was not possible either to detect an interaction between the coordinately saturated complexes $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ [281], or between tris(phenanthroline)iron(II) and tris(phenanthroline)iron(III) [282]. Complexes of this type are often formed in the redox reactions of certain ligands and metal ions. One of the best-known reactions is that between Cu^{2+} and penicillamine, the reaction depending on the molar ratio and on the nature and concentration of the background electrolyte; one of the products formed in this reaction is a red, water-soluble complex with composition $[Cu(II)_6Cu(I)_8(PA)_{12}X]^{5-}$ [284].

In most of the work designed to reveal the equilibrium conditions concerning mixed metal complexes, studies have been carried out on the interactions of metal ions and some coordinately saturated cyano, thiocyanato or isothiocyanato complex. A characteristic feature of all three ligands is that they can act as bridging ligands; the 'other end' of a ligand bound in the stable (often inert), coordinately saturated complex still possesses a significant ability to coordinate to certain metal ions.

Falk and Linck [287] demonstrated the formation of metal complexes with compositions of 1 : 1 and 1 : 2 between the mercury(II) aqua ion and complexes containing thiocyanate ligand bound to cobalt(III). The similar reaction of Hg^{2+} and $Cr(H_2O)_5NCS$ was studied by Armor and Haim [288]. In this system, however, binuclear mixed metal complex formation is the rapid pre-equilibrium of the metal ion exchange reaction. Mixed metal complexes are similarly formed in pre-equilibrium processes of central atom exchange reactions in the course of the reactions of cobalt(II)aminopolycarboxylates and $Fe(CN)_6^{3-}$ [289, 290]. A number of interactions of the same nature have been detected in the reactions of cyano and mixed cyano complexes [291–295].

Pereira and Malin [296] reported that pyrazine can act as a bridging ligand in the formation of complexes of this type, and Országh and Beck [297] came to the same conclusion as concerns the chloride ion. Beck and Porzsolt [298] demonstrated that not only the Hg^{2+} aqua ion, but also $Hg(CN)_2$ can interact with coordinately saturated inert cyano complexes.

An interaction of a fundamentally different nature was discovered by Adin, Klotz and Newman [299] in equilibrium systems containing In^{3+} and UO_2^{2+} ions and various hydroxycarboxylic acids. Both metal ions form dimeric or polymeric complexes with the ligands, but the most stable of the polynuclear complexes are the mixed metal complexes with composition $InUO_2L_2$.

Touche and Williams [300] investigated the equilibrium conditions relating to mixed metal complexes of glutathione, containing donor groups of different natures within one molecule; the metal ions were selected on the basis of the hard–soft theory, so as to exhibit preferred affinity for the various donor groups. Finally, mention must be made of the work of Galembeck *et al.* [301], who demonstrated the formation of 18 mixed metal complexes with different compositions in aqueous solution in the $Fe(CO)_4^{2-}$–Zn^{2+} system. This system displays the feature that, in the course of complex formation, metal–metal bonds undergo formation and dissociation even in aqueous medium.

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Chapter 7

Prospects

A few decades ago the formation of complexes was considered more as an exception than a rule. Owing to the very intensive researches from the early fifties, the ubiquitous nature of complex formation has become evident. Since equilibrium "constants" can in most cases be obtained with readily available instruments, many laboratories became engaged in investigations in this field. It was almost inevitable that besides papers offering reliable data obtained by careful experimental work and using well-chosen methods, a great number of papers were published whose data are either not accurate or even wrong. As discussed in the previous chapters, we now have reliable experimental methods and calculation procedures for the determination of equilibrium constants for all types of complex equilibria. Consequently, nowadays it cannot be regarded as forgivable to determine and publish erroneous constants as it was a quarter of century ago, in the time of 'gold fever' in coordination chemistry. It is a very important task of the studies to clean up the polluted areas.

We believe that the most important directions of future equilibrium studies are as follows:

(1) Determination of formation enthalpy and entropy of different species.

(2) Study of protonated, mixed ligand, polynuclear and outer-sphere complexes.

(3) Resolution of macroscopic thermodynamic constants to microconstants of well-defined isomeric species.

(4) Determination of stability constants of weak complexes.

(5) Study of complex equilibria in non-aqueous media and in the gas phase.

(6) Study of complexes of new ligands of fundamental or practical importance.

In the determination of formation enthalpies and entropies the application of direct calorimetry is preferable to the evaluation of these quantities from equilibrium measurements at different temperatures. Nevertheless, the two approaches can be regarded as complementary.

In most of the solutions which chemists use generally not only the mononuclear binary complexes exist but protonated (deprotonated), polynuclear, mixed ligand and outer-sphere complexes, too. For a while, these species used to be regarded as exotic types of complexes but now it is evident that these very species are the normally occurring constituents of the solutions, and that the simple parent complexes exist under carefully selected experimental conditions only. Therefore equilibrium studies of these types of complexes require much more attention in the future.

The resolution of thermodynamic constants to microconstants referring to well-defined isomeric species makes necessary the judicious application of the different spectroscopic (optical and resonance) techniques. After having enough data of this kind, it might be necessary to reconsider the different correlations between stability constants and other parameters.

The main task of equilibrium studies is not to decide the existence of the different complexes, but to learn the concentrations of these species under different conditions. Each judiciously imaginable complex exists in the solutions although its existence may not be manifested in the different properties of the solutions. This situation is due to either the small concentration of the complex and/or the small value of the corresponding intensive parameter. The small concentration may be the consequence of either the absolute or the relative instability of the species in question. In the former case the absolute value of the stability constant is small, in the latter case the absolute value of the stability constant can be quite big, but the stability constants of the related species are even larger. Both cases frequently occur, and the determination of the stability constants requires particular care. It seems likely that a number of unstable species may play important roles in different chemical phenomena where the corresponding intensive factor can be quite high. Such is the case with the kinetics of reaction where the rate studies may compellingly indicate the formation of unexpected species. For example, that dimeric and perhaps trimeric iodine species are present in CS_2 solution of iodine was first indicated by rate equation of iodination reactions of unsaturated organic compounds.

Recently, unexpectedly high orders were found in redox reactions involving oxyanions. This could be an indication of the formation of iso and heteropolyanions which are unstable because of irreversible redox reactions. One must bear in mind that very high degrees of aggregation were found in a number of anions. Equilibrium analysis undoubtedly proved the occurrence of species like $V_{10}O_{28}^{6-}$, $W_{12}O_{46}H_2^{10-}$ etc., even in rather dilute solutions. In case of oxyanions where an irreversible redox reaction is superimposed to the polycondensation or polymerization processes, the application of the traditional methods is not possible.

Statistical mechanical calculations have shown the possibility of ion-pair formation between ions of like charge. According to the considerations by Dang and Pettit [1], the strength of interaction in the $Cl^- - Cl^-$ ion pair is about three-four fold of the thermal energy, which mean that stability constant amounts rougly to 20–60. It seems likely that under the umbrella of the activity concept there is a considerable fraction of contributions of short range interactions. The difficulties of the chemical characterization of such species as Cl_2^{2-} are obvious and the efforts in the coming decades certainly will be rewarding.

It is likely that there is an interaction between the di- and triatomic anions, like CN^-, SCN^-, OCN^-, etc. and also between the corresponding acids. The study of the formation of such species both in solution and in the gas phase seems very promising.

The importance of study of complex equilibria in non-aqueous organic and inorganic solvents and solvent mixtures is obvious and the possibilities are literarily unlimited. Some of these studies might be necessary in connection with practical applications, other studies may contribute to the general understanding of chemistry of complex equilibria.

Complex equilibria are not restricted to the liquid phase. We do believe that such investigations will be rewarding, although a much faster increase of interest was expected in the time of the preparation of the first edition of this book.

All in all, we expect that most of the efforts in the equilibrium studies in the coming decades will be directed to determine the thermodynamic constants of complexes of new ligands. Either naturally occurring or synthetic organic compounds of biological interest will be selected in order to clarify the biological role of metal ions or to achieve and/or understand beneficial effects of different compounds.

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Appendix

A.1. An example for the transformation of the composition matrix

It was shown in Section 3.3 that the rows of the composition matrix relating to the components comprise a unit matrix. Thus, if we wish to pass from one component series of the equilibrium system to another, we must seek the matrix that transforms the square matrix formed from the vectors of the components to be selected into a unit matrix. This transformation matrix is the inverse of the square matrix relating to the species to be selected as components.

The new composition matrix for the components is obtained by performing the matrix inversion, and then multiplying the composition matrix from the right by the inverse matrix.

As an example, let us consider the system in Table 3.1, and characterize the system by the species HL, MeL and MeL$_2$ as components. The row vectors for these form the following square matrix:

		Starting components		
		H	L	Me
Species to be selected as components	HL	1	1	0
	MeL	0	1	1
	MeL$_2$	0	2	1

The determinant of the resulting matrix is -1 (i.e. not zero), therefore HL, MeL and MeL$_2$ are suitable for a description of the system. Inversion of the resulting matrix (subsequently denoted by **M**) leads to the following matrix

$$\mathbf{M}^{-1} = \begin{vmatrix} 1 & 1 & -1 \\ 0 & -1 & 1 \\ 0 & 2 & -1 \end{vmatrix}$$

i.e.

$$\begin{vmatrix} 1 & 1 & 0 \\ 0 & 1 & 1 \\ 0 & 2 & 1 \end{vmatrix} * \begin{vmatrix} 1 & 1 & -1 \\ 0 & -1 & 1 \\ 0 & 2 & -1 \end{vmatrix} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

$$\mathbf{M}^{-1} * \mathbf{M} = \mathbf{E}. \tag{A.1}$$

If the starting composition matrix is multiplied from the right by $\mathbf{M}^{-1}$, we obtain the composition matrix for the components HL, MeL and MeL_2

$$\begin{array}{c|ccc} & \multicolumn{3}{c}{\text{Starting components}} \\ & k_1 & k_2 & k_3 \\ \hline \text{Species} & H & L & Me \\ H & 1 & 0 & 0 \\ L & 0 & 1 & 0 \\ Me & 0 & 0 & 1 \\ HL & 1 & 1 & 0 \\ H_2L & 2 & 1 & 0 \\ MeL & 0 & 1 & 1 \\ MeL_2 & 0 & 2 & 1 \\ MeLH & 1 & 1 & 1 \\ MeLH_{-1} & -1 & 1 & 1 \end{array} * \begin{vmatrix} 1 & 1 & -1 \\ 0 & -1 & 1 \\ 0 & 2 & -1 \end{vmatrix} = \begin{array}{c|ccc} & \multicolumn{3}{c}{\text{New components}} \\ & k'_1 & k'_2 & k'_3 \\ \hline \text{Species} & HL & MeL & MeL_2 \\ H & 1 & 1 & -1 \\ L & 0 & -1 & 1 \\ Me & 0 & 2 & -1 \\ HL & 1 & 0 & 0 \\ H_2L & 2 & 1 & -1 \\ MeL & 0 & 1 & 0 \\ MeL_2 & 0 & 0 & 1 \\ MeLH & 1 & 2 & -1 \\ MeLH_{-1} & -1 & 0 & 1 \end{array}$$

$$\mathbf{A} * \mathbf{M}^{-1} = \mathbf{A}'. \tag{A.2}$$

The composition matrix for the starting components has been denoted by $\mathbf{A}$, and that for the new components by $\mathbf{A}'$.

Equation (3.6) defining the formation constants naturally remains valid; thus, the value of the formation constants relating to the new components is 1, and the other constants are transformed accordingly. The total concentrations likewise undergo transformation. By means of the transformation matrix $\mathbf{M}^{-1}$, the transformation between the total concentrations of the starting components and the total concentrations defined for the new components can be performed as follows

$$|T_{\mathrm{H}} T_{\mathrm{L}} T_{\mathrm{Me}}| * \begin{vmatrix} 1 & 1 & -1 \\ 0 & -1 & 1 \\ 0 & 2 & -1 \end{vmatrix} = |T_{\mathrm{HL}} T_{\mathrm{MeL}} T_{\mathrm{MeL_2}}|$$

i.e.

$$\begin{aligned} T_{\mathrm{HL}} &= T_{\mathrm{H}} \\ T_{\mathrm{MeL}} &= T_{\mathrm{H}} - T_{\mathrm{L}} + 2 * T_{\mathrm{Me}} \\ T_{\mathrm{MeL_2}} &= -T_{\mathrm{H}} + T_{\mathrm{L}} - T_{\mathrm{Me}}. \end{aligned} \qquad \text{(A.3)}$$

The composition matrix, formation constants and total concentrations relating to the components HL, MeL and MeL_2 are given in Table A.1, in a manner formally agreeing with that in Table 3.2.

Table A.1 Differential quotients of the r functions, expressed in terms of the differential

		$\mathrm{d}x$
		$\mathrm{d}\log[\mathrm{k}_1]$
Condition	$y = f(x)$	$\mathrm{d}y/\mathrm{d}x$
$[\mathrm{k}_1]$ = Constant	$\log r_{1(\mathrm{k}_1)} = \log[\mathrm{k}_1] - \log T_1$	
	$\log r_{2(\mathrm{k}_1)} = \log[\mathrm{k}_2] - \log T_2$	
$[\mathrm{k}_2]$ = Constant	$\log r_{1(\mathrm{k}_2)} = \log[\mathrm{k}_1] - \log T_1$	$1 - \left(\frac{\mathrm{d}\log T_1}{\mathrm{d}\log[\mathrm{k}_1]}\right)_{[\mathrm{k}_2]}$
	$\log r_{2(\mathrm{k}_2)} = \log[\mathrm{k}_2] - \log T_2$	$-\left(\frac{\mathrm{d}\log T_2}{\mathrm{d}\log[\mathrm{k}_1]}\right)_{[\mathrm{k}_2]}$
T_1 = Constant	$\log r_{1(T_1)} = \log[\mathrm{k}_1] - \log T_1$	1
	$\log r_{2(T_1)} = \log[\mathrm{k}_2] - \log T_2$	$\left(\frac{\mathrm{d}\log[\mathrm{k}_2]}{\mathrm{d}\log[\mathrm{k}_1]}\right)_{T_1} - \left(\frac{\mathrm{d}\log T_2}{\mathrm{d}\log[\mathrm{k}_1]}\right)_{T_1}$
T_2 = Constant	$\log r_{1(T_2)} = \log[\mathrm{k}_1] - \log T_1$	$1 - \left(\frac{\mathrm{d}\log T_1}{\mathrm{d}\log[\mathrm{k}_1]}\right)_{T_2}$
	$\log r_{2(T_2)} = \log[\mathrm{k}_1] - \log T_2$	$\left(\frac{\mathrm{d}\log[\mathrm{k}_2]}{\mathrm{d}\log[\mathrm{k}_1]}\right)_{T_2}$

The correlations in Tables 3.2 and A.1 are clearly equivalent from the mathematical description of the system. Indeed, a further 69, similarly equivalent arrangements could be made with the given transformation. However, the only arrangement containing the chemical content in illustrative form is that in which H, L and M feature as components. The importance of this transformation is that the rules governing the concentration distribution can be established comparatively simply (see Section 3.6), and similar transformations can essentially simplify and speed up the computational procedure involved in evaluation of the equilibrium measurements.

quotients of the total and equilibrium concentrations of the components

dx		
$d\log[k_2]$	dT_1	dT_2
dy/dx	dy/dx	dy/dx
$-\left(\frac{d\log T_1}{d\log[k_2]}\right)_{[k_1]}$	$-\frac{0.4343}{T_1}$	$-\left(\frac{d\log T_1}{dT_2}\right)_{[k_1]}$
$1-\left(\frac{d\log T_2}{d\log[k_2]}\right)_{[k_1]}$	$\left(\frac{d\log[k_2]}{dT_1}\right)_{[k_1]}-\left(\frac{d\log T_2}{dT_1}\right)_{[k_1]}$	$\left(\frac{d\log[k_2]}{dT_2}\right)_{[k_1]}-\frac{0.4343}{T_2}$
	$\left(\frac{d\log[k_1]}{dT_1}\right)_{[k_2]}-\frac{0.4343}{T_1}$	$\left(\frac{d\log[k_1]}{dT_2}\right)_{[k_2]}-\left(\frac{d\log T_1}{dT_2}\right)_{[k_2]}$
	$-\left(\frac{d\log T_2}{dT_1}\right)_{[k_2]}$	$-\frac{0.4343}{T_2}$
$\left(\frac{d\log[k_1]}{d\log[k_2]}\right)_{T_1}$		$\left(\frac{d\log[k_1]}{dT_2}\right)_{T_1}$
$1-\left(\frac{d\log T_2}{d\log[k_2]}\right)_{T_1}$		$\left(\frac{d\log[k_2]}{dT_2}\right)_{T_1}=\frac{0.4343}{T_2}$
$\left(\frac{d\log[k_1]}{d\log[k_2]}\right)_{T_2}-\left(\frac{d\log T_1}{d\log[k_2]}\right)_{T_2}$	$\left(\frac{d\log[k_1]}{dT_1}\right)_{T_2}-\frac{0.4343}{T_1}$	
1	$\left(\frac{d\log[k_2]}{dT_1}\right)_{T_2}$	

A.2. Differential connections of the r and p functions

The borate–proton two-component system has been chosen to illustrate the 24 different plotting modes (functions). The composition matrix of the system, the values of the formation constants are listed in Table A.2, and the log r functions are presented in Figs A.1–A.8. Logarithmic scale is used in the plotting, and an indication is always given of the fixed concentration.

Table A.2 Species formed in the H^+–$B(OH)_4^-$ equilibrium system, and their formation constants ($B = B(OH)_4^-$)

	H	B		
Species	p	q	$\log \beta_{pq}$	$\log K_{pq}$
HB	1	1	8.87	0
HB_3	1	3	10.31	−16.30
H_2B_3	2	3	19.71	−6.90
H_3B_5	3	5	30.55	−13.80
H_4B_5	4	5	37.80	−6.55

$$K_{pq} = \frac{[H_pB_q][H]^{p-q}}{[HB]^p}.$$

For clarity, the obvious results of the first step of differentiation are presented in Table A.3.

The Table demonstrates that the derivatives of the equilibrium and total concentrations of the components with respect to one another are necessary to give the differential correlations. These can be obtained most simply by starting from the equations generally describing two-component equilibrium systems

$$T_1 = \sum \alpha_{j1}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}} \tag{A.4}$$

$$T_2 = \sum \alpha_{j2}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}}. \tag{A.5}$$

We consider first the derivatives obtained at $[\mathrm{k}_1]$ = constant. Differentiation of A.4 with respect to $[\mathrm{k}_2]$ gives

$$\left(\frac{\mathrm{d}T_1}{\mathrm{d}[\mathrm{k}_2]}\right)_{[\mathrm{k}_1]} = \sum\alpha_{j1}\alpha_{j2}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}-1}. \tag{A.6}$$

Multiplying by $[\mathrm{k}_2]$

$$\left(\frac{\mathrm{d}T_1}{\mathrm{d}[\mathrm{k}_2]} * [\mathrm{k}_2]\right)_{[\mathrm{k}_1]} = \left(\frac{\mathrm{d}T_1}{\mathrm{d}\ln[\mathrm{k}_2]}\right)_{[\mathrm{k}_1]} = 0.4343\left(\frac{\mathrm{d}T_1}{\mathrm{d}\log[\mathrm{k}_2]}\right)_{[\mathrm{k}_1]} = \\ = p_{12} * T_1 = p_{21} * T_2. \tag{A.7}$$

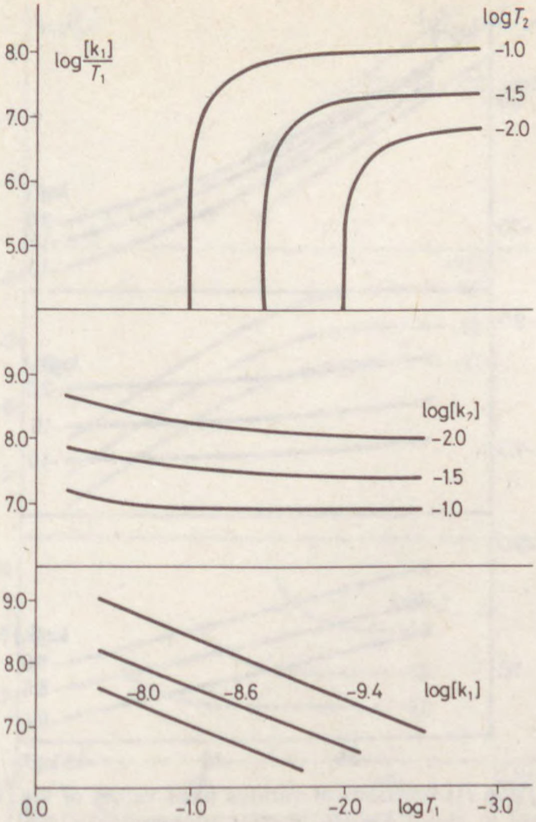

Fig. A.1. $\log r_1 = f(\log T_1)$ functions at various fixed values of $\log[\mathrm{k}_1]$, $\log[\mathrm{k}_2]$ and $\log T_2$, in the H^+–$\mathrm{B(OH)}_4^-$ system [12]

Equation (A.5) can be differentiated similarly, and leads to

$$0.4343\left(\frac{\mathrm{d}T_2}{\mathrm{d}\log[\mathrm{k}_2]}\right)_{[\mathrm{k}_1]} = p_{22} * T_2. \tag{A.8}$$

Dividing Eq. (A.7) by Eq. (A.8)

$$\left(\frac{\mathrm{d}T_2}{\mathrm{d}T_1}\right)_{[\mathrm{k}_1]} = \frac{p_{12} * T_1}{p_{22} * T_2} = \frac{p_{21}}{p_{22}}. \tag{A.9}$$

Under the condition $[\mathrm{k}_2]$ = constant, equations analogous to Eqs (A.7)–(A.9) are obtained, but the indices 1 and 2 are interchanged

$$0.4343\left(\frac{\mathrm{d}T_2}{\mathrm{d}\log[\mathrm{k}_1]}\right)_{[\mathrm{k}_2]} = p_{21} * T_2 = p_{12} * T_1 \tag{A.10}$$

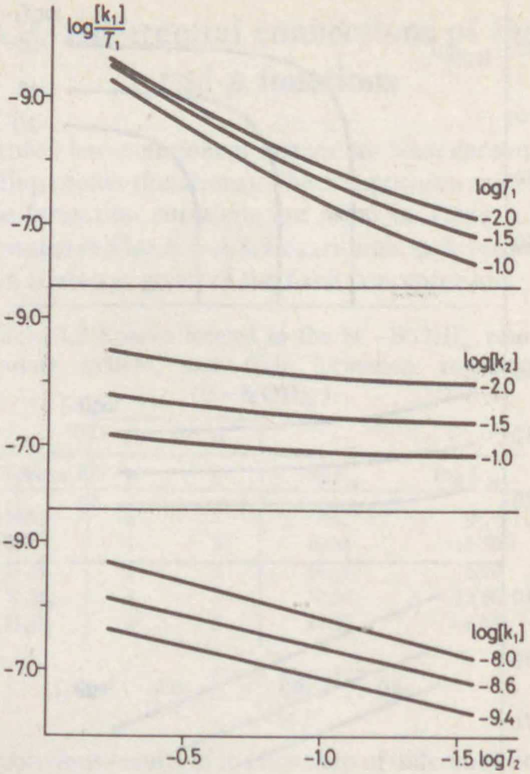

Fig. A.2. $\log r_1 = f(\log T_2)$ functions at various fixed values of $\log[\mathrm{k}_1]$, $\log[\mathrm{k}_2]$ and $\log T_1$, in H^+–$\mathrm{B(OH)}_4^-$ system [12]

$$0.4343\left(\frac{\mathrm{d}T_1}{\mathrm{dlog}\,[\mathrm{k}_1]}\right)_{[\mathrm{k}_2]} = p_{11} * T_1 \tag{A.11}$$

$$\left(\frac{\mathrm{d}T_2}{\mathrm{d}T_1}\right)_{[\mathrm{k}_2]} = \frac{p_{21} * T_2}{p_{11} * T_1} = \frac{p_{12}}{p_{11}}. \tag{A.12}$$

The derivatives defined by the condition $T_1 =$ constant are similarly produced by setting out from (A.4)

$$\left(\frac{\mathrm{d}T_1}{\mathrm{d}[\mathrm{k}_1]}\right)_{T_1} = 0 = \sum \alpha_{j1}^2 \beta_j [\mathrm{k}_1]^{\alpha_{j1}-1}[\mathrm{k}_2]^{\alpha_{j2}} + \sum \alpha_{j1}\alpha_{j2}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}-1}\left(\frac{\mathrm{d}[\mathrm{k}_2]}{\mathrm{d}[\mathrm{k}_1]}\right)_{T_1}. \tag{A.13}$$

By rearrangement

$$\left(\frac{\mathrm{d}[\mathrm{k}_2]}{\mathrm{d}[\mathrm{k}_1]} * \frac{[\mathrm{k}_1]}{[\mathrm{k}_2]}\right)_{T_1} = \left(\frac{\mathrm{dlog}\,(\mathrm{k}_2]}{\mathrm{dlog}\,[\mathrm{k}_1]}\right)_{T_1} = p_{11}/p_{12}. \tag{A.14}$$

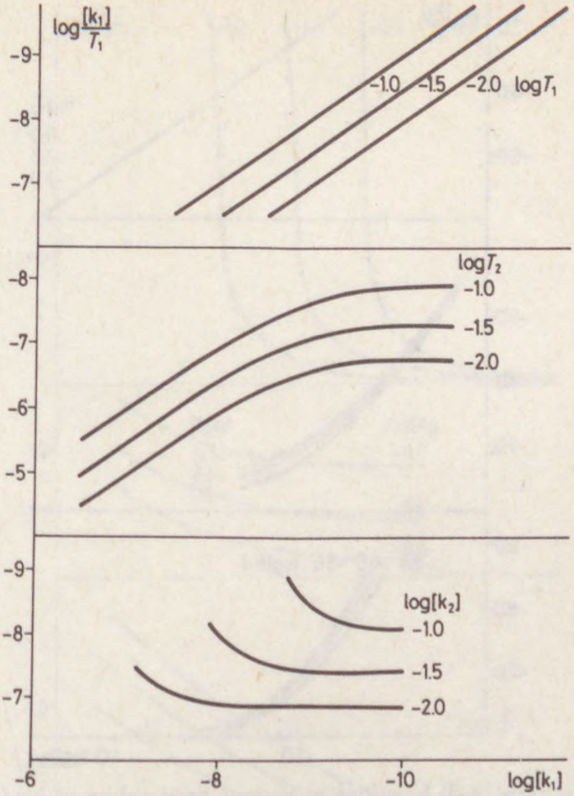

Fig. A.3. $\log r_1 = f(\log[k_1])$ functions at various fixed values of $\log[k_2]$, $\log T_2$ and $\log T_1$, in the H^+–$B(OH)_4^-$ system [12]

To obtain $(dT_2/d\log[k_1])_{T_1}$, (A.5) is differentiated at $T_1 = \text{constant}$

$$\left(\frac{dT_2}{d[k_1]}\right)_{T_1} = \sum \alpha_{j1}\alpha_{j2}\beta_j[k_1]^{\alpha_{j1}-1}[k_2]^{\alpha_{j2}} + \sum \alpha_{j2}^2\beta_j[k_1]^{\alpha_{j1}}[k_2]^{\alpha_{j2}-1}\left(\frac{d[k_2]}{d[k_1]}\right)_{T_1}. \tag{A.15}$$

Multiplying by $[k_1]$ and substituting Eq. (A.14)

$$0.4343\left(\frac{dT_2}{d\log[k_1]}\right)_{T_1} = T_2\left(p_{21} - p_{22}\frac{p_{11}}{p_{12}}\right) = T_1\left(p_{12} - \frac{p_{11} * p_{22}}{p_{21}}\right). \tag{A.16}$$

Table A.3 lists all of the differential connections between the r and p functions, obtained in the above manner.

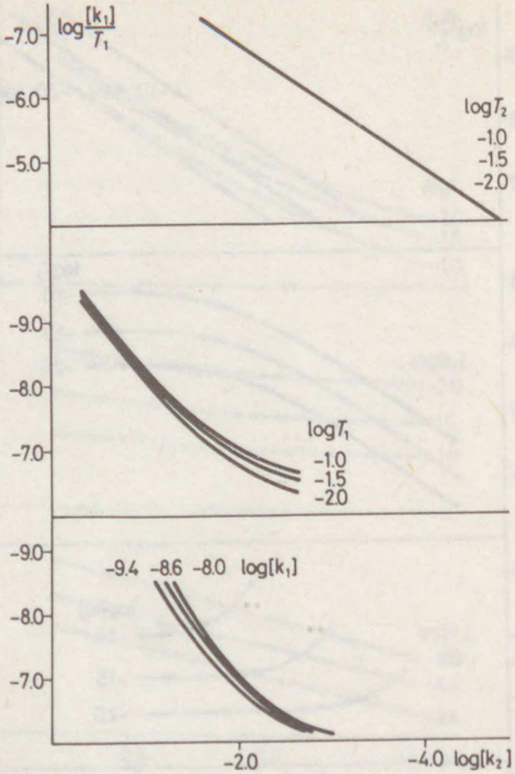

Fig. A.4. $\log r_1 = f(\log [k_2])$ functions at various fixed values of $\log [k_1]$, $\log T_1$ and $\log T_2$, in the H^+–$B(OH)_4^-$ system [12]

The system of differential correlations for the r and p functions defined by Eqs (3.46), (3.47) is not given here, because of the great space required. The manner of obtaining two of the derivatives in case of a three-component system will be presented merely as examples. On this basis, any optional derivative could be deduced.

One of the fundamental aims of complex equilibrium investigations is to determine the stoichiometric composition and stability of the main associations in the equilibrium systems, and hence to calculate the concentration distribution curves. In three-component systems, the concentration distribution curves are generally obtained by maintaining the total concentrations of two components at a constant value, and plotting the concentrations of the various associations as functions of the equilibrium concentration of the third component (usually the negative logarithm of this). In equilibrium systems containing the proton, a ligand and a metal ion, for instance, the concentrations of the complexes

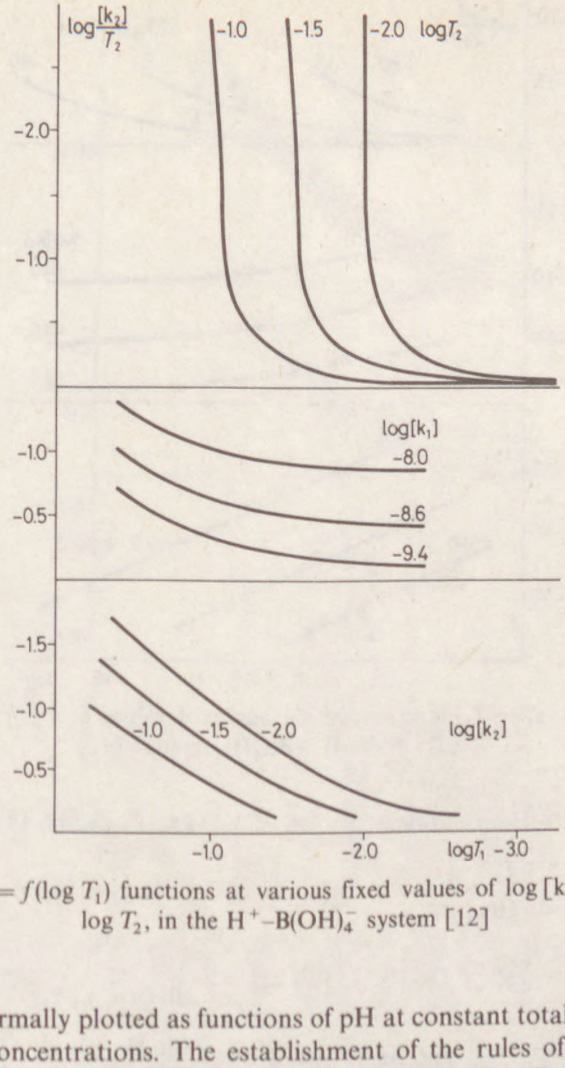

Fig. A.5. $\log r_2 = f(\log T_1)$ functions at various fixed values of $\log [k_2]$, $\log [k_1]$ and $\log T_2$, in the $H^+–B(OH)_4^-$ system [12]

formed are normally plotted as functions of pH at constant total metal ion and total ligand concentrations. The establishment of the rules of concentration distribution requires a knowledge of the function $d\log [k_3]/d\log [k_1]$ at constant T_2 and T_3. This function is obtained by setting out from the basic equations describing the three-component equilibrium systems

$$T_1 = \sum \alpha_{j1}\beta_j[k_1]^{\alpha_{j1}}[k_2]^{\alpha_{j2}}[k_3]^{\alpha_{j3}} \tag{A.17}$$

$$T_2 = \sum \alpha_{j2}\beta_j[k_1]^{\alpha_{j1}}[k_2]^{\alpha_{j2}}[k_3]^{\alpha_{j3}} \tag{A.18}$$

$$T_3 = \sum \alpha_{j3}\beta_j[k_1]^{\alpha_{j1}}[k_2]^{\alpha_{j2}}[k_3]^{\alpha_{j3}}. \tag{A.19}$$

The conditions $T_2 = \text{constant}$ and $T_3 = \text{constant}$ mean that $dT_2/d\ln [k_1] = 0$ and

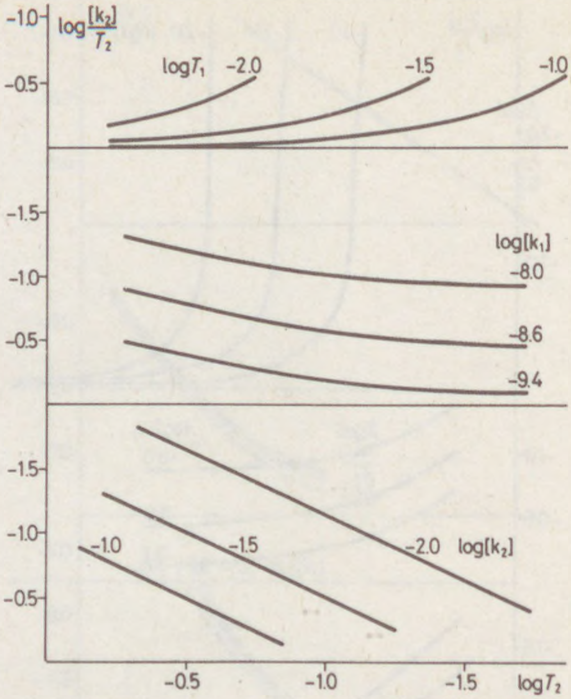

Fig. A.6. $\log r_2 = f(\log T_2)$ functions at various fixed values of $\log[k_2]$, $\log[k_1]$ and $\log T_1$, in the H^+–$B(OH)_4^-$ system [12]

$dT_3/d\ln[k_1] = 0$. Hence, differentiation of Eqs (A.18) and (A.19) gives

$$\left(\frac{dT_2}{d\ln[k_1]}\right)_{T_2,T_3} = \sum \alpha_{j1}\alpha_{j2}\beta_j[k_1]^{\alpha_{j1}}[k_2]^{\alpha_{j2}}[k_3]^{\alpha_{j3}} + \\ + \sum \alpha_{j2}^2\beta_j[k_1]^{\alpha_{j1}}[k_2]^{\alpha_{j2}}[k_3]^{\alpha_{j3}}\left(\frac{d\ln[k_2]}{d\ln[k_1]}\right)_{T_2,T_3} + \\ + \sum \alpha_{j2}\alpha_{j3}\beta_j[k_1]^{\alpha_{j1}}[k_2]^{\alpha_{j2}}[k_3]^{\alpha_{j3}}\left(\frac{d\ln[k_3]}{d\ln[k_1]}\right)_{T_2,T_3} = 0 \tag{A.20}$$

$$\left(\frac{dT_3}{d\ln[k_1]}\right)_{T_2,T_3} = \sum \alpha_{j1}\alpha_{j3}\beta_j[k_1]^{\alpha_{j1}}[k_2]^{\alpha_{j2}}[k_3]^{\alpha_{j3}} + \\ + \sum \alpha_{j2}\alpha_{j3}\beta_j[k_1]^{\alpha_{j1}}[k_2]^{\alpha_{j2}}[k_3]^{\alpha_{j3}}\left(\frac{d\ln[k_2]}{d\ln[k_1]}\right)_{T_2,T_3} + \\ + \sum \alpha_{j3}^2\beta_j[k_1]^{\alpha_{j1}}[k_2]^{\alpha_{j2}}[k_3]^{\alpha_{j3}}\left(\frac{d\ln[k_3]}{d\ln[k_1]}\right)_{T_2,T_3} = 0. \tag{A.21}$$

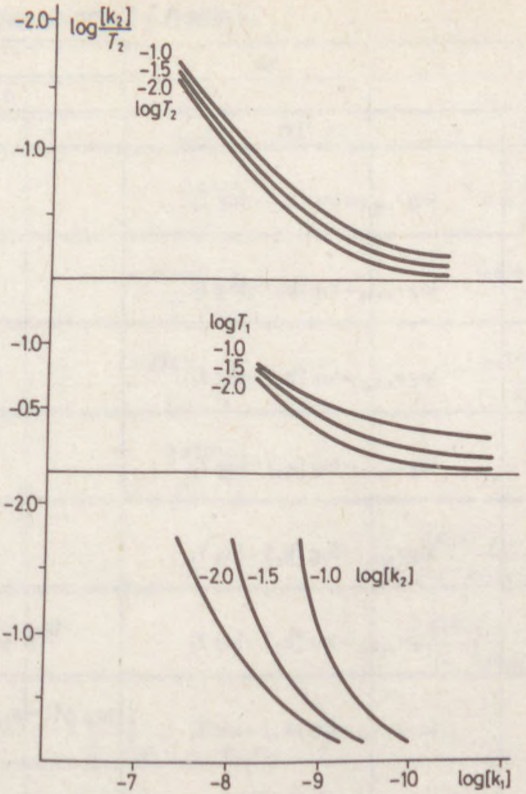

Fig. A.7. $\log r_2 = f(\log [k_1])$ functions at various fixed values of $\log [k_2]$, $\log T_1$ and $\log T_2$, in the H^+–$B(OH)_4^-$ system [12]

Equations (A.20) and (A.21) together can be regarded as a linear equation system involving two unknowns: $d\ln [k_3]/d\ln [k_1]$ and $d\ln [k_2]/d\ln [k_1]$. Through use of the appropriate determinants, we can write

$$\left(\frac{\ln [k_3]}{\ln [k_1]}\right)_{T_2,T_3} = \frac{\begin{matrix}\sum \alpha_{j1}\alpha_{j2}\beta_j[k_1]^{\alpha_{j1}}[k_2]^{\alpha_{j2}}[k_3]^{\alpha_{j3}} * \sum \alpha_{j2}\alpha_{j3}\beta_j[k_1]^{\alpha_{j1}}[k_2]^{\alpha_{j2}}[k_3]^{\alpha_{j3}} - \\ -\sum \alpha_{j1}\alpha_{j3}\beta_j[k_1]^{\alpha_{j1}}[k_2]^{\alpha_{j2}}[k_3]^{\alpha_{j3}} * \sum \alpha_{j2}^2\beta_j[k_1]^{\alpha_{j1}}[k_2]^{\alpha_{j2}}[k_3]^{\alpha_{j3}}\end{matrix}}{\begin{matrix}\sum \alpha_{j2}^2\beta_j[k_1]^{\alpha_{j1}}[k_2]^{\alpha_{j2}}[k_3]^{\alpha_{j3}} * \sum \alpha_{j3}^2\beta_j[k_1]^{\alpha_{j1}}[k_2]^{\alpha_{j2}}[k_3]^{\alpha_{j3}} - \\ -(\sum \alpha_{j2}\alpha_{j3}\beta_j[k_1]^{\alpha_{j1}}[k_2]^{\alpha_{j2}}[k_3]^{\alpha_{j3}})^2\end{matrix}}. \quad (A.22)$$

Further analysis of Eq. (A.22) leads to the rules of the concentration distribution in the equilibrium systems (see Section 3.6).

An important parameter characterizing the processes taking place in a proton–metal ion–ligand equilibrium system is the proton release factor at each fixed pH value. This quantity expresses the change in the total proton

Table A.3 Complete system of differential

		$\dfrac{dx}{d\log[\mathrm{k}_1]}$
Condition	$y=f(x)$	dy/dx
$[\mathrm{k}_1]=$ Constant	$\log r_{1(\mathrm{k}_1)}=\log[\mathrm{k}_1]-\log T_1$	
	$\log r_{2(\mathrm{k}_1)}=\log[\mathrm{k}_2]-\log T_2$	
$[\mathrm{k}_2]=$ Constant	$\log r_{1(\mathrm{k}_2)}=\log[\mathrm{k}_1]-\log T_1$	$1-p_{11}$
	$\log r_{2(\mathrm{k}_2)}=\log[\mathrm{k}_2]-\log T_2$	$-p_{21}$
$T_1=$ Constant	$\log r_{1(T_1)}=\log[\mathrm{k}_1]-\log T_1$	1
	$\log r_{2(T_1)}=\log[\mathrm{k}_2]-\log T_2$	$\dfrac{(p_{22}-1)p_{11}-p_{12}p_{21}}{p_{12}}$
$T_2=$ Constant	$\log r_{1(T_2)}=\log[\mathrm{k}_1]-\log T_1$	$\dfrac{(1-p_{11})p_{22}+p_{12}p_{21}}{p_{22}}$
	$\log r_{2(T_2)}=\log[\mathrm{k}_2]-\log T_2$	$-\dfrac{p_{21}}{p_{22}}$

concentration when the total concentration of the metal ion is varied, but the pH is kept constant. Let us denote the total concentration of the proton by T_1, and that of the metal ion by T_3. The proton release factor is then expressed by the differential coefficient $(dT_1/dT_3)_{[\mathrm{k}_1],T_2}$. At constant T_2 and constant $[\mathrm{k}_1]$, this is found by differentiating Eq. (A.18) with respect to $[\mathrm{k}_2]$

$$\left(\frac{dT_2}{d[\mathrm{k}_2]}\right)_{[\mathrm{k}_1],T_2}=0=\sum\alpha_{j2}^2\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}-1}[\mathrm{k}_3]^{\alpha_{j3}}+$$

$$+\sum\alpha_{j2}\alpha_{j3}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}}[\mathrm{k}_3]^{\alpha_{j3}-1}\left(\frac{d[\mathrm{k}_3]}{d[\mathrm{k}_2]}\right)_{[\mathrm{k}_1],T_2}. \tag{A.23}$$

connections between the *r* and *p* functions

dx		
$\mathrm{d}\log[\mathrm{k}_2]$	$\mathrm{d}T_1$	$\mathrm{d}T_2$
$\mathrm{d}y/\mathrm{d}x$	$\mathrm{d}y/\mathrm{d}x$	$\mathrm{d}y/\mathrm{d}x$
$-p_{12}$	$-\dfrac{0.4343}{T_1}$	$-\dfrac{0.4343\cdot p_{12}}{p_{22}\cdot T_2}$
$1-p_{22}$	$\dfrac{0.4343(1-p_{22})}{T_1\cdot p_{12}}$	$\dfrac{0.4343(1-p_{22})}{T_2\cdot p_{22}}$
	$\dfrac{0.4343(1-p_{11})}{p_{11}\cdot T_1}$	$\dfrac{0.4343(1-p_{11})}{p_{21}\cdot T_2}$
	$-\dfrac{0.4343\, p_{21}}{p_{11}\cdot T_1}$	$-\dfrac{0.4343}{T_2}$
$-\dfrac{p_{12}}{p_{11}}$		$\dfrac{0.4343\cdot p_{12}}{(p_{12}p_{21}-p_{11}p_{22})\,T_2}\equiv\left(\dfrac{\mathrm{d}\log[\mathrm{k}_2]}{\mathrm{d}T_1}\right)_{T_2}$
$\dfrac{(1-p_{22})p_{11}+p_{12}p_{21}}{p_{11}}$		$\dfrac{0.4343}{T_2}\left(\dfrac{p_{11}}{p_{22}p_{11}-p_{12}p_{21}}-1\right)$
$\dfrac{(p_{11}-1)p_{22}-p_{12}p_{21}}{p_{21}}$	$\dfrac{0.4343}{T_1}\left(\dfrac{p_{22}}{p_{11}p_{22}-p_{12}p_{21}}-1\right)$	
1	$\dfrac{0.4343\cdot p_{21}}{(p_{12}p_{21}-p_{11}p_{22})\,T_1}=\left(\dfrac{\mathrm{d}\log[\mathrm{k}_1]}{T_2}\right)_{T_1}$	

Hence

$$\left(\frac{\mathrm{d}[\mathrm{k}_3]}{\mathrm{d}[\mathrm{k}_2]}\right)_{[\mathrm{k}_1],\,T_2}=-\frac{\sum\alpha_{j2}^2\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}-1}[\mathrm{k}_3]^{\alpha_{j3}}}{\sum\alpha_{j2}\alpha_{j3}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}}[\mathrm{k}_3]^{\alpha_{j3}-1}}. \tag{A.24}$$

Differentiating (A.17) and (A.19) with respect to $[\mathrm{k}_2]$

$$\begin{aligned}\left(\frac{\mathrm{d}T_1}{\mathrm{d}[\mathrm{k}_2]}\right)_{[\mathrm{k}_1],\,T_2}&=\sum\alpha_{j1}\alpha_{j2}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}-1}[\mathrm{k}_3]^{\alpha_{j3}}+\\&+\sum\alpha_{j1}\alpha_{j3}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}}[\mathrm{k}_3]^{\alpha_{j3}-1}\left(\frac{\mathrm{d}[\mathrm{k}_3]}{\mathrm{d}[\mathrm{k}_2]}\right)_{[\mathrm{k}_1],\,T_2}.\end{aligned} \tag{A.25}$$

$$\begin{aligned}\left(\frac{\mathrm{d}T_3}{\mathrm{d}[\mathrm{k}_2]}\right)_{[\mathrm{k}_1],\,T_2}&=\sum\alpha_{j3}\alpha_{j2}\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}-1}[\mathrm{k}_3]^{\alpha_{j3}}+\\&+\sum\alpha_{j3}^2\beta_j[\mathrm{k}_1]^{\alpha_{j1}}[\mathrm{k}_2]^{\alpha_{j2}}[\mathrm{k}_3]^{\alpha_{j3}-1}\left(\frac{\mathrm{d}[\mathrm{k}_3]}{\mathrm{d}[\mathrm{k}_2]}\right)_{[\mathrm{k}_1],\,T_2}.\end{aligned} \tag{A.26}$$

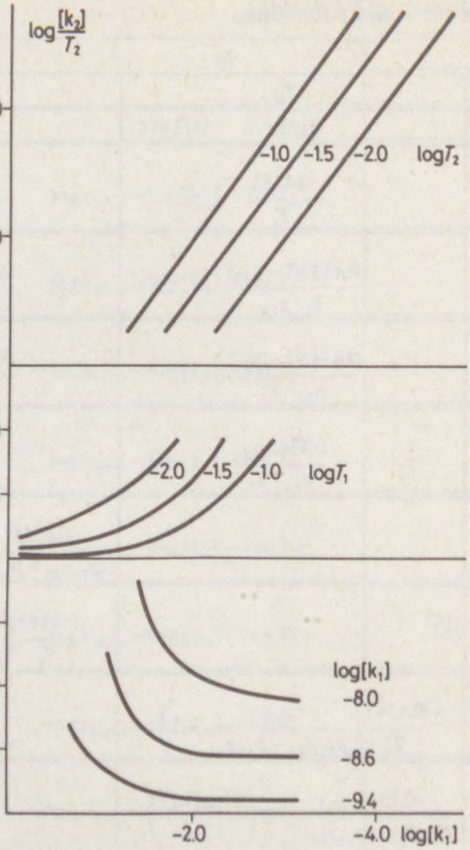

Fig. A.8. $\log r_2 = f(\log [k_2])$ functions at various fixed values of $\log [k_1]$, $\log T_1$ and $\log T_2$, in the H^+–$B(OH)_4^-$ system [12]

Substituting Eq. (A.24) into Eq. (A.25) and Eq. (A.26), dividing, simplifying and substituting the *p* functions leads to

$$\left(\frac{dT_1}{dT_3}\right)_{[k_1], T_2} = \frac{p_{21}p_{32} - p_{31}p_{22}}{p_{23}p_{32} - p_{22}p_{33}}. \tag{A.27}$$

Any differential quotient can be derived in an analogous way in three- or multicomponent equilibrium systems.

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