154. M. N. Shchukina, A. Ya. Berlin, and E. D. Sazonova, Zhur. Prikl. Khim., 18, 634 (1945).
155. R. Lukeš and J. Pliml, Chem. Listy, 48, 49 (1954); Coll. Czech. Chem. Comm., 19, 502 (1954).
156. R. Lukeš and J. Pliml, Chem. Zvesti, 4, 336 (1950); Coll. Czech. Chem. Comm., 15, 512 (1950).
157. K. Freudenberg, Ber., 51, 1668 (1918).
158. P. Karrer and H. Ruckstuhl, Helv. Chim. Acta, 27, 1698 (1944).
159. R. Willstätter, Annalen, 326, 23 (1903).
160. V. Prelog and A. Komzak, Ber., 74, 1705 (1941).
161. R. Foster and A. Carman, J. Pharmacol., 91, 195 (1947).
162. P. Chabrier, H. Najer, R. Giudicelli, and M. Joannic, Bull. Soc. chim. France, 1365 (1957).
163. A. Lasslo and P. Waller, J. Org. Chem., 22, 837 (1957).

Chemical Faculty,
Lomonosov State University,
Moscow

INVESTIGATION OF COMPLEX FORMATION IN SOLUTION BY THE DISTRIBUTION METHOD

A. P. Zozulya and V. M. Peshkova

Extraction with non-aqueous solvents is very widely employed in solving various problems in chemistry and chemical technology. The separation of elements with closely similar properties, the concentration and isolation of micro- and ultramicro-concentrations of metals, the clear separation and identification of difficultly separable organic substances, show why many investigators have evinced interest, especially in recent years, in the study of extraction processes[1-5]. The solubility of internal complexes and of a number of complexes of metals with inorganic ligands in organic solvents makes it possible to utilise the distribution method as a reliable means of studying the composition and many other physicochemical characteristics of complex compounds.

The principles of the distribution (or extraction) method were laid down by Nernst (1891). In the first paper on the constancy of the partition coefficient for species of the same molecular composition distributed between two immiscible solvents, Nernst established[6] the possibility of using his distribution law to study the dissociation equilibria of a number of substances in aqueous solution. Shortly afterwards Hendrixson[7] studied the distribution of benzoic and salicylic acids between water and benzene or chloroform and determined the dissociation constants K_{diss} of these acids in the aqueous phase, their dimerisation constants K_{dim} in the organic phase, and their distribution constants (partition coefficients) K_{part} between organic and aqueous phases*:

$$[H^+][A^-] = K_{diss}[HA]_{aq} , \quad (1)$$

$$[HA]_{org} = K_{part}[HA]_{aq} , \quad (2)$$

$$[H_2A_2]_{org} = K_{dim}[HA]^2_{org} . \quad (3)$$

* HA = molecule of acid, A^- = anion of acid, and H_2A_2 = = dimer molecule. We shall use the symbolic formula HA to denote reagents which dissociate as monobasic acids.

At about the same time similar investigations were carried out with inorganic compounds, e.g. thiocyanates of iron and halides of mercury[8]. In this work, however, the authors do not consider the possible formation of charged complex species. As far as we know, the first attempt to explain the experimental results by a stepwise mechanism of complex formation was published by Morse in 1902.[9] After studying the distribution of mercury complexes between toluene and an aqueous phase containing halide ions (A^-), Morse came to the conclusion that the aqueous phase contains, apart from Hg^{2+} and uncharged HgA_2 molecules, positively charged HgA^+. Assuming the impossibility of extracting charged particles with an organic solvent, Morse calculated from his results the distribution constant λ_N for HgA_2 between the phases and the successive formation constants k_1 and k_2:

$$[MA_{n-1}^{N-n+1}][A^-]k_n = [MA_n^{N-n}] , \quad (4)$$

$$[MA_N]_{org} = \lambda_N[MA_N]_{aq} . , \quad (5)$$

where $M^{N+} = Hg^{2+}$ and A^- is the halide ion.

Although the possibility of using the distribution method to study complex compounds in solution has been demonstrated so long ago, no attempt was made before 1941 to formulate quantitatively the relation between the partition coefficients for a metal in a given system and the parameters of the latter (concentration of metal ions, pH of aqueous phase, concentration of reagent, etc.). In 1941 Kolthoff and Sandell[10], studying the dithizone derivatives of certain metals, attempted to establish such a relationship on the basis of the distribution law and the law of mass action. Assuming that only free (hydrated) metal ions M^{2+} are present in the aqueous phase and excluding the possibility of association of the molecules of dithizone and the complex MA_2 in either phase, these authors accepted the following equations as correct:

$$K'_{part\ HA} = \frac{[HA]_{aq}}{[HA]_{org}} , \quad (6)$$

$$K'_{part\ MA_2} = \frac{[MA_2]_{aq}}{[MA_2]_{org}} \quad (7)$$

(according to the conventions which are now generally adopted these quantities are the reciprocals of the distribution constants of HA and the complex MA_2).

$$M^{2+} + 2HA \rightleftarrows MA_2 + 2H^+ , \quad (8)$$

(in the aqueous phase)

$$\frac{[MA_2]_{aq}}{[M^{2+}]_{aq}}\frac{[H^+]^2_{aq}}{[HA]^2_{aq}} = K_{eq} . \quad (9)$$

Substituting the concentrations of MA_2 and HA in the aqueous phase from Eqns. (6) and (7), they established the expression

$$\frac{[MA_2]_{org}}{[M^{2+}]_{aq}}\frac{[H^+]^2_{aq}}{[HA]^2_{org}} = K_{eq}\frac{K'^2_{part\ HA}}{K'_{part\ MA_2}} = K, \quad (10)$$

by means of which they arrived at Eqn. (12) linking the partition coefficient of the metal q with the characteristics of the system:

$$q = \frac{[MA_N]_{org}}{\sum_{n=0}^{n=N}[MA_n]_{aq}} , \quad (11)$$

$$q = \frac{[MA_2]_{org}}{[M^{2+}]_{aq}} = K\frac{[HA]^2_{org}}{[H^+]^2_{aq}} . \quad (12)$$

As can be seen from Eqn. (12), the partition coefficient of a bivalent metal increases proportionally to the square of the concentration of the reagent in the organic phase and

decreases proportionally to the square of the hydrogen-ion concentration in the aqueous phase. Kolthoff and Sandell allowed for the effect of hydrolysis on the extraction process, and introduced into Eqn. (12) the appropriate correction term (for the case of a bivalent metal ion):

$$q = \frac{[MA_2]_{org}}{[M]_{aq\ total}} = K \cdot \frac{[HA]^2_{org}}{([H^+]^2_{aq} + \beta_1[H^+]_{aq} + \beta_2)}, \qquad (13)$$

where β_1 and β_2 are hydrolysis constants.

Eqn. (12), obtained by Kolthoff and Sandell, has been repeatedly criticised[11,12]. In fact, the authors not only leave out of consideration the successive formation of complex species, but also in general neglect any complexes of the metal in the aqueous phase, which restricts their arguments to a limited number of systems and a limited range of concentrations. In spite of these limitations, a number of authors have subsequently used Kolthoff's equation (without any special changes) in the study of the stability of the dithizone complexes of metals[13-17]. For example, Babko and Pilipenko continued Kolthoff's investigations by studying the physicochemical characteristics of dithizone and its complexes with zinc, cadmium, and lead[13,14]. Babko and his coworkers determined the composition of the dithizone complexes by measuring the optical density of the extract after appropriate dilution with the organic solvent used. The limitations of such a method of determining the composition of a complex compound distributed between two phases have been pointed out in the Russian literature[18].

Eve and Strasheim[19] studied the effect of the hydrogen-ion concentration on the extraction of the dithizone derivatives of zinc, cobalt, nickel, and copper from tartrate solutions by means of chloroform*. Substitution of their experimental values for the partition coefficient and other quantities in the Kolthoff equation showed that the extraction process in general obeys Eqn. (10).

Subsequently, Irving and Williams[11] and other investigators[22] somewhat extended our ideas on the mechanism of complex formation and, besides allowing for the distribution of the reagent between the two solvents and its dissociation in the aqueous phase, took into account the formation of an uncharged complex in aqueous solution:

$$\begin{array}{ccc} H^+ + A^- \rightleftarrows & & HA \\ M^{N+} + NA^- \rightleftarrows MA_N & \Big\| & \Big\| \quad \text{in aqueous phase} \\ \downarrow\uparrow & & \downarrow\uparrow \quad \text{in organic phase} \\ MA_N & & HA \end{array}.$$

Irving put forward a simple quantitative treatment of the experimental results which took into account the relationship between the partition coefficient of the metal and the concentration of the reagent, the dissociation constant of the latter, the pH of the aqueous phase, the partition coefficient of the complexes, and other parameters of the system. If HA behaves as a monobasic acid over a given pH range and if the only complexes in the aqueous and organic phases are the mononuclear complexes MA_N, the relationship between q and the parameters of the system is represented by the simple equation

$$q = \frac{[MA_N]_{org}}{[MA_N]_{aq} + [M^{N+}]_{aq}} = \frac{1}{K'_{part\ MA_N} + ([H^+]^N_{aq}\ K \cdot [HA]^N_{org})}, \qquad (14)$$

where

$$K = \frac{(K_{diss\ HA}\ K'_{part\ HA})^N}{K_{inst.\ MA_N}\ K'_{part\ MA_N}}, \qquad (14a)$$

and $K_{inst\ MA_N}$ — the overall instability constant of the complex MA_N — is defined by the equation

$$K_{inst.\ MA_N} = \frac{[M^{N+}][A^-]^N}{[MA_N]}. \qquad (15)$$

It can be easily shown that, if

$$K'_{part\ MA_N} \ll \frac{[H^+]^N_{aq}}{K \cdot [HA]^N_{org}},$$

Eqn. (14) passes into the above Eqn. (12) of Kolthoff. Irving and Williams calculated the magnitude of the error due to neglecting the existence of MA_N complexes in the aqueous phase, and examined in detail the effect of change in pH, reagent concentration, and other factors on the extraction of various metals.

On the basis of the relationships deduced, Irving and his coworkers investigated complex formation between zinc and dithizone[23,24] and discussed earlier results[25]. The composition of the dithizone derivative of zinc was established from the graph of $\log q$ against $\log([HA]_{org} + pH)$ and spectrophotometrically by the method of continuous variations[26]. Buffered mixtures of varying composition were used in the work, which might have led to secondary complex formation and diminished the reliability of the results. No attempt was made in the above work, however, to examine in a general way the various processes of complex formation and distribution occurring in two-phase systems.

During the last ten years, the Scandinavian chemists, the Irving school and a number of other investigators (Diamond, Connick, etc.), whose work will be examined below, have extended the theoretical equipment required to calculate the characteristics of various types of complex from distribution data.

In its modern form, the distribution method consists of the study of the partition coefficients of a metal between immiscible solvents as a function of one or several variables. The process of extraction of a metal from an aqueous phase by means of an organic solvent is affected by many factors, such as the concentrations of ions of the element investigated and of other cations in the solution, of various anions, and of hydrogen ions, the nature of the organic solvent, etc. In most cases the partition coefficient depends in a complicated way on these variables.

In the treatments referred to above, one of the variables was generally examined, and a more or less satisfactory explanation given for the results obtained. The general picture was that the metal ion M^{N+} reacts in aqueous solution with the ligand A^- and the resulting complex MA_N is distributed between the phases. In fact complexes with different compositions and different charges exist in aqueous solution, and the complex (or series of complexes) extracted may include in their composition solvent molecules and other components. Preparative methods give no accurate indication either of the composition of the complexes in solution or even of the existence of many complexes, which in general exist only in solution. Analysis

* Many investigators have published papers on the role of pH in the extraction of internal complexes. Korenman and Sheyanova[20,21] attempted to obtain a theoretical basis for the influence of pH on the yield of reaction product in complex formation between metal ions and organic reagents.

of solid preparations sometimes shows the existence of extremely complicated compounds, containing metallic, A^-, and OH^- ions, uncharged molecules of HA, H_2O, organic solvent, etc. For example, the compounds $Th(OH)_2CrO_4 \cdot H_2O$,[27] $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$,[28] etc. are known. The isolation of a compound in the solid form, however, does not always prove its existence in solution. In the second of these substances the benzene molecules are only held in the spaces between the $Ni(CN)_2 \cdot NH_3$ molecules, and are linked to the latter by weak van der Waals forces. In solution, however, $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$ molecules do not exist at all or else their number is insignificant. A similar position is observed with hydroxyquinoline molecules in the compound $ScA_3 \cdot HA$,[29] where A represents the quinolinoxy ion. Definite conclusions as to the composition of the complexes which are extracted and those which are in the aqueous phase can be drawn only on the basis of a physicochemical analysis of the solutions. Practically all the fundamental characteristics of complexes can be obtained by studying the distribution of the metal when the variables enumerated above are changed. Until recently the opinion was expressed that the distribution method could be used only to ascertain the comparative stability of complex compounds, and doubt was entertained as to its suitability for the quantitative determination of their stability constants[30].

In 1949 Rydberg and other Scandinavian investigators demonstrated the full value of the distribution method for the quantitative study of complex formation in solution. To interpret data relating to the extraction of a metal complex by an organic solvent from an aqueous phase of low and constant ionic strength, these authors took into account the influence of temperature and examined the following variables: concentrations of metal ion M^{N+}, anion A^-, HA, OH^-, and solvents [organic (Org) and H_2O].[31-33] In the general case complexes of type I may be formed in aqueous solution (the charges on the ions are omitted):

$$\underset{(I)}{M_mA_n(OH)_p(HA)_r(Org)_s(H_2O)_t},$$

and their formation constants may be written in the general form

$$\kappa_{m,n,p,r,s,t} = \frac{[M_mA_n(OH)_p(HA)_r(Org)_s(H_2O)_t]}{[M]^m[A]^n[OH]^p[HA]^r[Org]^s[H_2O]^t} \quad . \qquad (16)$$

Taking into account the interrelationship of some of the variables in Eqn. (1), and the ionic product of water,

$$[H_2O]\ K_{H_2O} = [H^+][OH^-] \quad , \qquad (17)$$

Eqn. (16) can be written in the form

$$\kappa_{m,n,p,r,s,t} = \frac{[M_mA_n(OH)_p(HA)_r(Org)_s(H_2O)_t]}{[M]^m[HA]^{n+r}[H]^{-n-p}[H_2O]^{p+t}[Org]^sK^n_{\text{diss HA}}K^p_{H_2O}} \quad . \qquad (18)$$

Writing $n + r = x$, $n + p = y$, and $p + t = z$, formula I can be rewritten in a simpler form:

$$\underset{(II)}{M_m(HA)_x(H)_{-y}(H_2O)_z(Org)_s} \quad .$$

In the majority of cases it is quite difficult to determine the number of water molecules incorporated in a complex in aqueous solution. However, it can be found by an indirect method if we know the coordination number of the element with respect to all the ligands in the complex, and also the number of coordination positions occupied by all the ligands other than H_2O. Usually all experiments are carried out at constant ionic strength, and the effect of hydration is normally included in the formation constant for the complex. In such a case complex II can be written in a still simpler form:

$$\underset{(III)}{M_m(HA)_x(H)_{-y}(Org)_s},$$

and the formation constant of the complex is represented by the equation

$$\kappa_{m,x,y,s} = \frac{[M_m(HA)_x(H)_{-y}(Org)_s]}{[M]^m[HA]^x[H]^{-y}[Org]^s} \quad . \qquad (19)$$

The physical meaning of x and y is clear: x is equal to the total number of HA and A^-, and y the total number of A^- and OH^- per atom of complex-forming metal. The charge on the complex is then $mN - y$. All the subsequent arguments of Rydberg are based on the assumption that only uncharged complexes pass into the organic solvent. This assumption is correct for solvents of low dielectric constant. When it is known that only a neutral complex will pass into the organic layer (distribution constant $\lambda_{m,x,-mN,s}$), and the mole fraction of the solvents is constant (ionic strength I = = const.), the partition coefficient for the metal can be written in the form

$$q = \frac{\sum_1^m \sum_0^x \sum_0^s m\kappa_{m,x,mN,s}\ \lambda_{m,x,mN,s}\ [M]^m[HA]^x[H]^{-mN}[Org]^s}{\sum_1^m \sum_0^x \sum_0^y \sum_0^s m\kappa_{m,x,y,s}\ [M]^m[HA]^x[H]^{-y}[Org]^s} \quad . \qquad (20)$$

Eqn. (20) is greatly simplified if only mononuclear complexes are considered. For the majority of metallic ions, other than those which are strongly hydrolysed, it is legitimate to ignore polynuclear complexes ($m > 1$), provided that the experiments are carried out with $[M] \leqslant 10^{-3}$ g-ion/litre. A range of concentrations of metal ions can usually be found in which formation of polynuclear complexes, hydrolysis products, or polymeric forms can be neglected. The search for such a range reduces to a study of the dependence of the partition coefficient on the concentration of metal ions in the aqueous phase with other conditions the same. If it is established that q does not depend on the metal-ion concentration over a given range, the formation of polynuclear complexes can be safely ignored. In the work of Rydberg only mononuclear complexes are considered. In both the Russian and foreign literature methods have already been described for studying the composition and characteristics of several systems containing polynuclear complexes[34-39]. Such a study can be carried out by means of distribution, spectrophotometric, etc. methods. The equations considered below are applicable only if it has been established that q is independent of the metal-ion concentration.

The distribution method enables us to elucidate the influence of the organic solvent on the distribution of the metal, and also to establish whether the water-immiscible solvent molecules enter the complex. The effect of the organic solvent can be ascertained by varying $[Org_1]$ by adding a third component Org_2, also immiscible with water. However, even if this third component does not interact with the complex, its addition may cause a considerable change in the activity coefficients. A different approach is possible, consisting in a study of the distribution of the metal in the two systems H_2O-Org_1 and H_2O-Org_2 for identical hydrogen-ion and reagent concentrations. If mononuclear complexes are formed in both systems, the ratio of

the partition coefficients for the metal is given by the following expression:

$$\frac{q_1}{q_2}=\frac{\sum_0^x\sum_0^s \kappa_{x,N,s}\ \lambda'_{x,N,s}\ [HA]^x[H]^{-N}[Org_1]^s \sum_0^x\sum_0^y\sum_0^s \kappa''_{x,y,s}\ [HA]^x[H]^{-y}[Org_2]^s}{\sum_0^x\sum_0^s \kappa''_{x,N,s}\ \lambda''_{x,N,s}\ [HA]^x[H]^{-N}\ \ Org_2]^s \sum_0^x\sum_0^y\sum_0^z \kappa'_{x,y,s}\ [HA]^x[H]^{-y}[Org_1]^s}, \tag{21}$$

where κ' and κ'' are the formation constants and λ' and λ'' the distribution constants for the complexes in the two systems. At constant ionic strength under equilibrium conditions $[Org_1]$ = const. and $[Org_2]$ = const., and we may therefore write

$$\kappa'_{x,y}=\sum_0^s \kappa'_{x,y,s}\ [Org_1]^s, \tag{22}$$

and analogous expressions for $\kappa''_{x,y}$, $\kappa'_{x,N}\lambda'_{x,N}$, and $\kappa''_{x,N}\lambda''_{x,N}$. After substitution of these in (21), the latter simplifies to

$$\frac{q_1}{q_2}=\frac{\sum_0^x \kappa'_{x,N}\ \lambda'_{x,N}\ [HA]^x[H]^{-N}\sum_0^x\sum_0^y \kappa''_{x,y}\ [HA]^x[H]^{-y}}{\sum_0^x \kappa''_{x,N}\ \lambda''_{x,N}\ [HA]^x[H]^{-N}\sum_0^x\sum_0^y \kappa'_{x,y}[HA]^x[H]^{-y}}. \tag{23}$$

If complexes are formed with one or both solvents $\lambda'_{x,N} \neq \lambda''_{x,N}$ and with rare exceptions $\kappa'_{x,N} \neq \kappa''_{x,N}$, and the ratio q_1/q_2 will change with change in [H] when [HA] = const. and vice versa.

If under these conditions q_1/q_2 = const., it can be regarded as established that the complex contains no solvent molecules*. Fig. 1 shows the curves for $\log q = f(pH)$: in the case of Org_1 and Org_2 the vertical distances h are equal to one another ($S = 0$); in the case of Org_2 and Org_3, $h'_1 \neq h'_2 \neq h'_3$ ($S \neq 0$).

The formation of complexes containing molecules of the organic solvent was established by Rydberg[33] in a study of the extraction of thorium acetylacetonate with isobutyl methyl ketone (hexone). The curves for the distribution of thorium between hexone and the aqueous phase in the presence of acetylacetone differ from those between water and benzene or chloroform. This difference was due to the formation of complexes between $ThA_n^{(4-n)+}$ and hexone molecules (hex). Rydberg was able to calculate the equilibrium constants for the reactions:

$$ThA_2hex_4^{2+} + A^- \rightleftarrows ThA_3hex_2^+ + 2hex,$$

and

$$ThA_3hex_2^+ + A^- \rightleftarrows ThA_4 + 2hex,$$

where A^- is the acetylacetonate ion.

Thus we can always ascertain beforehand whether we are dealing only with mononuclear complexes containing no molecules of the organic solvent used. If it has been established that $m = 1$ and $S = 0$, the partition coefficient for the metal is given by

$$q=\frac{\sum_0^x \kappa_{x,N}\ \lambda_{x,N}\ [HA]^x[H]^{-N}}{\sum_0^x\sum_0^y \kappa_{x,y}\ [HA]^x[H]^{-y}}. \tag{24}$$

Eqn. (24) enables all or nearly all the constants in it to be calculated provided the type of complexes formed is known. The composition of the complexes formed in the aqueous phase is established from the relationship between $\log q$ and pH or $\log [HA][H]^{-1}$ (proportional to -pA).

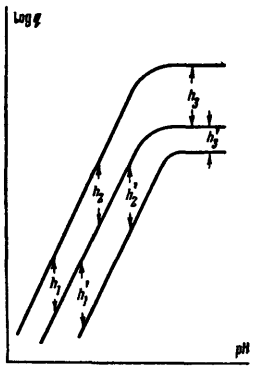


Fig. 1. Log q vs. pH for complexes with $S=0$ ($h_1 = h_2 = h_3$) and with $S \neq 0$ ($h'_1 \neq h'_2 \neq h'_3$).

As Rydberg showed, the distribution of metal between the phases varies with [H] or $[HA][H]^{-1}$ differently for various types of complexes. The curves for $\log q = f(pH)$ or $\log q = f(\log [HA][H]^{-1})$ have a different but fully determined form depending on the composition of the complex compounds in the aqueous phase. Distribution curves obtained for complexes of the types MA_n, $MA_n(OH)_p$, and $MA_n(OH)_p(HA)_r$ are shown in Fig. 2. The composition of the complexes is established experimentally by studying the distribution of the metal at several different concentrations of the reagent in the organic solvent layer (and consequently also in the aqueous phase) with other conditions the same. The descending portion of the curves at high concentrations of the ligand (shown by the broken curves) with or without a plateau may be due to the formation of negatively charged complexes. By carrying out experiments over a sufficiently wide range of HA concentrations, distribution curves can be obtained which establish unambiguously the type of complex formed.

For each type of complex appropriate formulae have been established by means of which it is possible to calculate the stability constants of the various complexes and the distribution constants of the uncharged complexes in the system under consideration. Thus for complexes of the type MA_n the equation linking the partition coefficient for the metal with the concentration of free ligand can be presented in the form

$$q=\frac{\kappa_N\ \lambda_N\ [A]^N}{\sum_0^n \kappa_n [A]^n}, \tag{25}$$

and that for complexes of the $MA_n(OH)_p$ type in the form

$$q=\frac{\sum_0^n \kappa_{n,N-n}\ \lambda_{n,N-n}\ [A]^n\ [OH]^{N-n}}{\sum_0^n\sum_0^p \kappa_{n,p}\ \ [A]^n\ [OH]^p}. \tag{26}$$

Many cases have been described in which the distribution of metal between the phases, in the presence of a reagent which dissociates as a monobasic acid, is represented by Eqn. (25).[41-47]

Several methods have been suggested for calculating stability constants from Eqn. (24).[48] The widely known methods of Leden[49], Bjerrum[50], Fronaeus[51], and also the

* The method suggested by Rydberg[40] for determining very large and very small partition coefficients is based on the same principle.

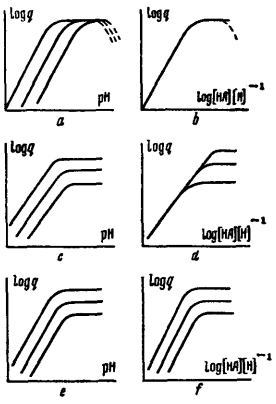


Fig. 2. Curves for the distribution of metal between the phases with $[HA]_1 > [HA]_2 > [HA]_3$ for different types of complexes: *a*), *b*) MA_n; *c*), *d*) $MA_n(OH)_p$; *e*), *f*) $MA_n(OH)_p \cdot (HA)_r$.

graphical "two-parameter" method suggested by Dyrssen and Sillén[52] can be used to calculate the characteristics of complex formation from distribution data.

Calculation of the constants in Eqn. (24) is usually carried out by methods similar to that of Leden, as follows. By introducing a series of functions of [HA], defined by the equations

$$f_\lambda = \sum_0^x \kappa_{x,N} \lambda_{x,N} [HA]^x , \quad (27)$$

$$f_y = \sum_0^x \kappa_{x,y} [HA]^x , \quad (28)$$

into Eqn. (24), we obtain the expression

$$q = \frac{f_\lambda [H]^{-N}}{\sum_0^y f_y [H]^{-y}} = \frac{f_\lambda [H]^{-N}}{f_0 + f_1 [H]^{-1} + f_2 [H]^{-2} + f_3 [H]^{-3} \ldots} \quad (29)$$

Eqn. (29) is readily put into the following form:

$$q^{-1}[H]^{-N} = P_0 = f_0 f_\lambda^{-1} + f_1 f_\lambda^{-1} [H]^{-1} + f_2 f_\lambda^{-1} [H]^{-2} + \ldots \quad (30)$$

and solved for $f_0 f_\lambda^{-1}$, $f_1 f_\lambda^{-1}$, etc. Actually the graph of $P_0 = f([H]^{-1})$ will be a curve with a limiting value $f_0 f_\lambda^{-1}$ and a limiting slope $f_1 f_\lambda^{-1}$ when $[H]^{-1}$ tends to zero:

$$\lim_{[H]^{-1} \to 0 \text{ (or } [H] \to \infty)} P_0 = f_0 f_\lambda^{-1} + (f_1 f_\lambda^{-1} [H]^{-1} + f_2 f_\lambda^{-1} [H]^{-2} + \ldots) . \quad (31)$$

The value of $f_0 f_\lambda^{-1}$ [numerically equal to the intercept on the ordinate axis of the curve $P_0 = f([H]^{-1})$] enables us to calculate the values of the functions P_1, P_2, etc., given by Eqns. (32a) and (32b); the limiting values of these functions for $[H]^{-1} \to 0$ allow $f_1 f_\lambda^{-1}$, $f_2 f_\lambda^{-1}$, etc., to be found (e.g. $f_2 f_\lambda^{-1}$ can be obtained as the value of the limiting slope of P_1 and as the limiting value of P_2):

$$P_1 = \frac{P_0 - f_0 f_\lambda^{-1}}{[H]^{-1}} = f_1 f_\lambda^{-1} + f_2 f_\lambda^{-1} [H]^{-1} + f_3 f_\lambda^{-1} [H]^{-2} + \ldots , \quad (32a)$$

$$P_2 = \frac{P_1 - f_1 f_\lambda^{-1}}{[H]^{-1}} = f_2 f_\lambda^{-1} + f_3 f_\lambda^{-1} [H]^{-1} + \ldots . \quad (32b)$$

By successive formation of the functions P_3, P_4, etc., for different values of [HA] all the required values of $f_y f_\lambda^{-1}$ can be obtained.

According to Eqn. (28)

$$f_{y=0} = \sum_0^x \kappa_{x,0} [HA]^x = \kappa_{0,0} + \kappa_{1,0} [HA] + \kappa_{2,0} \cdot [HA]^2 + \ldots . \quad (33)$$

By definition $\kappa_{0,0} = 1$ [see Eqn. (19)]. The subsequent values of κ with $x > 0$ and $y = 0$ relate to complexes containing a metal ion M^{N+} and one or several uncharged reagent molecules but no other ligands, i.e. an addition complex $M(HA)_x^{N+}$. On the assumption that the concentration of such complexes can be neglected in comparison with that of free (hydrated) metal ions (which is true in many cases), we find that $f_0 = 1$ [Eqn. (33)]. In such a case Eqn. (34) is valid, and enables f_λ to be calculated for all concentrations of HA studied:

$$\frac{f_0}{f_\lambda} = \frac{\sum_0^x \kappa_{x,0} [HA]^x}{\sum_0^x \kappa_{x,N} \cdot \lambda_{x,N} [HA]^x} \cong \frac{1}{f_\lambda} . \quad (34)$$

Using the values of $f_0 f_\lambda^{-1}$, $f_1 f_\lambda^{-1}$, etc. obtained earlier for corresponding values of [HA] and knowing that $f_0 = 1$, it is easy to obtain the different values f_y. For example, the following expression is valid for f_1:

$$f_1 = \frac{f_1 f_\lambda^{-1}}{f_0 f_\lambda^{-1}} = \frac{f_1}{f_0} = \sum_0^x \kappa_{x,1} [HA]^x . \quad (35)$$

With the aid of f_λ and f_y, values of $\kappa_{x,N} \lambda_{x,N}$ and $\kappa_{x,y}$ are calculated, allowing the distribution constants $\lambda_{x,N}$ to be found for the various uncharged complexes.

If formation of complexes of the type $M(HA)_x^{N+}$ cannot be neglected, the calculation is greatly complicated and the accuracy of the results diminished. An approach to a solution of such a complicated expression has been suggested by Rydberg[31].

It is much simpler to calculate the stability and distribution constants for complexes of the type $MA_n^{(N-n)+}$, the general form of whose partition coefficient is given by Eqn. (25). In fact, on introducing into (25) the auxiliary constants φ_n given by (36),

$$\varphi_{N-n} = \frac{[MA_n] [A]^{N-n}}{[MA_N]} = \kappa_n \kappa_N^{-1} , \quad (36)$$

Eqn. (25) is readily converted to the form

$$q = \lambda_N \left(\sum_{n=0}^{n=N} \varphi_{N-n} [A]^{n-N} \right)^{-1} , \quad (37)$$

which is convenient for the calculation of the constants appearing in it. It is not difficult to show that the equation

$$q = \frac{\lambda_N}{1 + \varphi_1 [A]^{-1} + \varphi_2 [A]^{-2} + \varphi_3 [A]^{-3} + \ldots \varphi_N [A]^{-N}} , \quad (38)$$

which is identical with (37), can be transformed into an equation for the function F_0,

$$F_0 = \frac{1}{q} = (1 + \varphi_1 [A]^{-1} + \varphi_2 [A]^{-2} + \ldots \varphi_N [A]^{-N}) \lambda_N^{-1} . \quad (39)$$

the calculation of which is quite simple. As can be seen from (39)

$$\lim_{[A]^{-1} \to 0} F_0 = \lambda_N^{-1} , \quad (40)$$

and the limiting slope is numerically equal to φ_1 / λ_N. By setting up the succeeding functions F_n in a manner analogous to that used for f_y and f_λ, all the φ_n values may be calculated and with their aid all the κ_n values (and also the successive formation constants) may be found.

The calculation of stability constants from distribution data can also be carried out by utilising the concept of the mean number of ligands $\bar{n}$ per atom of metal[50]:

$$\bar{n} = \frac{\sum_{n=1}^{n} n [MA_n]_{aq}}{[M]_{\text{total aq}}} . \quad (41)$$

The fraction of the total concentration of metal occurring

in complexes of the type $MA_n^{(N-n)+}$ (n is an integral number) is expressed by the equation

$$\alpha_n = \frac{[MA_n]}{[M]_{\text{total aq}}} \quad . \qquad (42)$$

As Rydberg showed[41], the relationship between $\bar{n}$ and $\log q$ is of the form

$$\bar{n} = N + \frac{d \log q}{d\,pA}, \qquad (43)$$

where pA is the logarithm of the reciprocal of the concentration of free ligand [for the derivation of Eqn. (43) see p. 112]. By graphical differentiation of the distribution curve $\log q = f(pA)$* the curve for the formation of the complex in solution, $\bar{n} = f(pA)$, is constructed by means of (43). Each point on the curve thus obtained satisfies the following equation, obtained by transformation of (41).

$$\bar{n} + (\bar{n} - 1)\kappa_1 [A] + (\bar{n} - 2)\kappa_2 [A]^2 + \ldots (\bar{n} - N)\kappa_N [A]^N = 0 \quad . \qquad (44)$$

By choosing points on the curve $\bar{n} = f(pA)$ which are convenient for calculation and setting up a system of equations of the type of (44), all the values of the constants κ_n can be found. By means of the latter it is not difficult to obtain φ_n, and then also the successive formation constants k_n for the complexes in aqueous solution [see Eqn. (4)].

Apart from the above methods, the "two-parameter" method suggested by Dyrssen and Sillén[52] can be used to calculate stability and distribution constants from the distribution curves. Their graphical method** is based essentially on the assumption that the overall stability constant κ_N and the ratio of successive formation constants k_n may be represented by the following equations:

$$\kappa_N = 10^{S\,a} \quad , \qquad (45a)$$

$$\frac{k_n}{k_{n+1}} = 10^{2b} \quad , \qquad (45b)$$

where S is the maximum number of ligands which can add on to the metal ion and a and b are constants. Two asymptotes are drawn to the distribution curve $\log q = f(pA)$, their slopes being equal to zero and to the charge on the metal ion respectively. The value of pA at the base of the perpendicular dropped from the point of intersection of the asymptotes on to the pA axis and the distance between the distribution curve and the point of intersection of the asymptotes are used to calculate the parameters a and b by means of appropriate formulae (depending on the valency of the metal ions the factor a is to be multiplied by different whole numbers). Knowing the parameters a and b, it is easy to obtain κ_N, κ_n, and k_n. The distribution constant λ_N for the uncharged complex is numerically equal to the intercept on the $\log q$ axis of the asymptote of zero slope. If the distribution curve after reaching a maximum value (plateau) then exhibits a drop (formation of negatively charged complexes), it is possible by means of the "two-parameter" method to calculate, although with considerable error, the formation constants of some or all of the complexes having $S > N$ (in the case of univalent ligands only). The two-parameter method, giving only rough values of the stability constants (cases of systems in which k_n/k_{n+1} = const. are very rare), may be employed when it is impossible to obtain a sufficient quantity of experimental data, or if the accuracy of such data is inadequate for the independent calculation of the constants. A check of the two-parameter method on systems for which results had been calculated by other methods was carried out in several cases[44,45,52] and its suitability demonstrated for approximate calculations.

TABLE 1. Stability and distribution constants of acetylacetonates of certain actinides.

Metal	Organic solvent	$\log k_1$	$\log k_2$		$\log k_4$	$\log \lambda_N$	Ionic strength of aqueous phase
Th^{4+}	C_6H_6	7.8±0.3	7.7±0.15	6.3±0.1	5.0 ±0.05	2.50±0.05	0.01
	$CHCl_3$	7.7±0.2	7.2±0.15	5.9±0.1	4.95±0.05	2.55±0.05	0.1
	$C_4H_9COCH_3$ (hexone)			8.0±0.15	4.3 ±0.15	1.5 ±0.1	0.1
U^{4+}	C_6H_6	8.6±0.2	8.4±0.4	6.4±0.3	6.1 ±0.2	3.62±0.05	0.1
	$CHCl_3$					4.0 ±0.2	0.1
	$C_4H_9COCH_3$					1.6 ±0.1	0.1
Pu^{4+}	C_6H_6	10.5±11.0	9.2±0.5	8.4±0.5	6.0 ±0.4	2.5 ±0.2	0.1
	$CHCl_3$					2.6 ±0.3	0.1
	$C_4H_9COCH_3$					1.4 ±0.1	0.1

By means of the procedures described above, many systems which form internal complexes capable of extraction by various organic solvents have been investigated. Rydberg studied the formation of complexes by acetylacetone with thorium using benzene[41], chloroform[43], and other solvents[32,33]. He studied also the formation of complexes by uranium(IV),[45] plutonium*[44], lanthanum, samarium, hafnium, and other elements[58] with this reagent. In the majority of cases mononuclear complexes of the type $MA_n^{(N-n)+}$, containing no organic solvent molecules in their composition, were formed in the aqueous phase. Eqn. (37) is applicable to this type of complex. Calculations on such systems were carried out mainly by Leden's method, more rarely by Bjerrum's method, and only in exceptional cases by the Dyrssen–Sillen two-parameter method. It is noteworthy that Rydberg was able to study the stability of compounds of quadrivalent uranium, the ready oxidation of which to the sexivalent state has frequently hindered the employment of other methods.

Values of the successive formation constants of the acetylacetonato complexes of Th^{4+}, U^{4+}, and Pu^{4+} and the distribution constants of the uncharged complexes λ_N found by Rydberg and his coworkers for various solvent systems are given in Table 1.[12]

In the case of the acetylacetonato complexes of sexivalent uranium the distribution of metal between the phases cannot be represented by Eqn. (37). As Rydberg showed, complexes of the general type $M(HA)_x(H)_{-y}$ are formed in this case. By appropriate treatment of the distribution curves

* Graphical differentiation of the curve is conveniently carried out by means of a special instrument designed by Chmutov[53,54]. For methods of graphical differentiation see the books cited in the next two references[55,56].

** The reader is advised to consult ref. 52, pp. 665–674 (Ed. of Translation).

* The distribution of Pu(IV) between an aqueous phase and benzene has also been studied by Harvey[57], but not with the aim of determining the stability of the complexes formed.

Rydberg was able to calculate the equilibrium constants of the following reactions:

$$UO_2^{2+} + OH^- \rightleftarrows UO_2OH^+ \qquad K_{eq} = 10^{9.6},$$
$$UO_2^{2+} + 2OH^- \rightleftarrows UO_2(OH)_2 \qquad K_{eq} = 10^{18.2},$$
$$UO_2^{2+} + OH^- + A^- \rightleftarrows UO_2AOH \qquad K_{eq} = 10^{15.6},$$
$$UO_2^{2+} + A^- \rightleftarrows UO_2A^+ \qquad K_{eq} = 10^{6.8},$$
$$UO_2^{2+} + A^- + HA \rightleftarrows UO_2AHA^+ \qquad K_{eq} = 10^{8.7},$$
$$UO_2^{2+} + 2A^- \rightleftarrows UO_2A_2 \qquad K_{eq} = 10^{13.1},$$
$$UO_2^{2+} + 2A^- + HA \rightleftarrows UO_2A_2HA \qquad K_{eq} = 10^{14.8},$$
$$UO_2^{2+} + HA \rightleftarrows UO_2HA^{2+} \qquad K_{eq} < 1,$$
$$UO_2^{2+} + 2HA \rightleftarrows UO_2(HA)_2^{2+} \qquad K_{eq} < 10,$$
$$UO_2^{2+} + 3HA \rightleftarrows UO_2(HA)_3^{2+} \qquad K_{eq} < 100,$$
$$(UO_2A_2)_{aq} \rightleftarrows (UO_2A_2)_{CHCl_3} \qquad K_{part} = 3.3,$$
$$(UO_2A_2HA)_{aq} \rightleftarrows (UO_2A_2HA)_{CHCl_3} \qquad K_{part} = 22.$$

As was noted earlier (p. 104 etc.), if the complexes formed in the aqueous phase do not include any solvent in their composition, their stability constants are independent, within the limits of experimental error, of which solvent is used in the investigation. This is fully confirmed in the case of the acetylacetonatothorium complexes (see Table 1).

It is interesting to compare data obtained by the distribution method with the results of a study of the stability of the same complex compounds by other, e.g. potentiometric, methods. Izatt, Fernelius, and their coworkers[59-67] carried out a major investigation of the complexes of acetylacetone and other β-diketones with various metals. They determined in particular the formation constants of the acetylacetonato complexes of thorium and uranium(VI) in aqueous solution. Comparison of the data of Rydberg[33,41] with those of Izatt[66] shows that both methods — distribution and potentiometric — give very similar results. The fourth formation constant of acetylacetonatothorium is an exception. In Izatt's experiments this constant was calculated from data obtained at quite high pH values, at which the effect of hydrolysis of the metal ions is most evident. Rydberg, using the data of Hietanen[68] on the hydrolysis of thorium ions, established that a considerably greater proportion of the thorium ions were hydrolysed in Izatt's experiments than in the distribution experiments* (the concentration of thorium ions in the aqueous phase after equilibrium had been reached with the organic phase was about 10^5 times as great in Izatt's experiments as in Rydberg's). Rydberg[12] obtained a thermodynamic formation constant of $\log k_4 = 5.1$, which is more likely to be correct than Izatt's value.

Izatt, Fernelius, and Block found the thermodynamic formation constants of the acetylacetonatouranyl complexes UO_2A^+ and UO_2A_2 to be $10^{7.7}$ and $10^{6.4}$ respectively. Applying the necessary corrections for the activity coefficients in 0.1 M $NaClO_4$ solutions, Rydberg[12] obtained values of $\sim 10^{7.1}$ and $\sim 10^{13.6}$ for the analogous constants (see above). Thus, although the former value shows satisfactory agreement with Izatt's data, a considerable difference is observed with the latter constant. Such a divergence in the results may be caused by insufficient variation of the acetylacetone concentration by Izatt and his coworkers. This would probably not allow him to detect other complexes formed between UO_2^{2+} and acetylacetonate ions (e.g. UO_2A_2HA, etc. — see above), and this would produce an error in the determination of the constants.

* For the mechanism of the hydrolysis of quadrivalent thorium, uranium, and other actinides, see e.g. refs. 69-72.

On the basis of the results of the study of the acetylacetone complexes of actinides by the distribution method[12] Rydberg concluded that the formation constants for quadrivalent Th, U, and Pu increase as the ionic radius decreases. He was not able to detect any direct relationship between the distribution constants for the uncharged complex in the organic and aqueous phases and the stability constants of the complexes (or radii of the metal ions). Nor did he observe any direct relationship between the distribution constant for the reagent HA and that for the corresponding uncharged complex MA_N with a given solvent. In Rydberg's opinion this shows that some caution is necessary in comparing distribution data with data on the stability of internal complexes. However, in investigations of several reagents of one and the same class a definite relationship is sometimes observed between the distribution constants of the reagent and of the complex compounds formed by it[73-75].

Apart from the acetylacetone complexes, a number of complex compounds of thenoyltrifluoroacetone, widely used in practice for the separation, purification, and study of various elements, were investigated[76-82]. Huffman et al.[82], studying the possibility of separating zirconium and hafnium by means of various fluorinated β-diketones, showed that in 2 M perchloric-acid solution the species containing Zr(IV) and Hf(IV) are mainly monomers, the formation of which can be represented by the equation:

$$M^{4+} + 4HA \rightleftarrows MA_4 + 4H^+.$$

The equilibrium constant for the extraction process at constant hydrogen-ion concentration is represented by the equation

$$\log K_{eq} = \log q - 4 \log [HA], \qquad (46)$$

where $q = [MA_4]_{org}/\Sigma[M]$, and [HA] is the activity of the β-diketone in the organic phase.

They established that the $\log q = f(\log [HA])$ curves for different solvents have the same slope, equal to 4, and that when complexes are formed between isovaleroyltrifluoroacetone and Zr or Hf the distribution constants of the corresponding compounds in the n-hexane–H_2O system are higher than those for the benzene–H_2O system, whereas the converse holds for the reagent itself. An equation analogous to (46) was obtained by Keenan and Suttle[76] in a study of complex formation between praseodymium and thenoyltrifluoroacetone. They plotted the graph of $\log q = f(pH)$ and calculated its slope by the method of least squares, obtaining values of 2.96 and 2.93 for different reagent concentrations (the composition of the complex is thus PrA_3). The preparation of complex compounds of 2-furoyltrifluoroacetone, benzoylacetone, and dibenzoylmethane with thorium, uranium(IV), samarium, and other elements, has been described[83-86], but, as far as we know, their physicochemical characteristics have so far been little studied.

A large amount of work using the above methods has also been carried out on the formation of complexes between actinides and organic reagents important in analytical chemistry. Thus Dyrssen investigated complex formation between thorium, lanthanum, yttrium, and uranium and tropolone[87], cupferron[42], 1-nitroso-2-naphthol and 2-nitroso-1-naphthol[88], and 5,7-dihalogenated derivatives of hydroxyquinoline[89]. In addition, a study was made of the stability of compounds of samarium, lanthanum, hafnium, strontium, and other elements with several of these reagents[90-92]. Hök-Bernstrom and Dyrssen investigated the formation of complexes of thorium, uranium(VI), and in

TABLE 2. Composition of complex compounds of certain actinides established by the distribution method.

System			Type of complex		Reference
M	HA	Org	aqueous phase	organic phase	
Th^{4+}	acetylacetone	C_6H_6 / $CHCl_3$	$MA_n^{(4-n)+}$	MA_N	33
Th^{4+}	"	hexone	$MA_n(Org)_s$	MA_N	33
U(VI)	"	C_6H_6 / $CHCl_3$ / hexone	$MA_n(OH)_p$ / $MA_n(HA)_r$	$MA_N(HA)_r$	33
U^{4+}	"	C_6H_6	$MA_n^{(4-n)+}$	MA_N	45
U(VI)	salicylic acid	hexone	$MA_n(OH)_p$	$MA_N(HA)_r$	94
Th^{4+}	"	"	$MA_n^{(4-n)+}$	$MA_N(HA)_r$	93
U(VI)	methoxybenzoic acid	"	$MA_n(OH)_p$	MA_N	94
Th^{4+}	"	" / $CHCl_3$	$MA_n^{(4-n)+}$	MA_N	93

certain cases tervalent lanthanum with salicylic, methoxybenzoic, cinnamic, *N*-phenylbenzohydroxamic, and other benzene carboxylic acids [93-97]. Table 2 shows the results of a study of the composition of some of these complex compounds in various solvent systems.

On the basis of the results obtained Dyrssen discussed the influence of the structure of the organic reagent on the stability of its complex compounds with metals [98]; he also worked out methods for separating and determining certain elements [99].

The values of the successive stability constants of complex compounds make it possible to calculate the percentage distribution of the metal between complexes of differing composition and the mole fractions of the latter as functions of the concentration of free ligand (see p. 106). Curves of this type are given in a number of papers [41,47].

As can be seen from the above account, with any method of treating the experimental results it is necessary to know the functional dependence of the partition coefficient of the metal on the concentration of free ligand. Calculation of the latter is impossible without a preliminary detailed investigation of the reagent under the given experimental conditions. If the concentrations of metal ions and ligand are similar, it is necessary to take into account the decrease in concentration of the ligand due to complex formation. This always complicates the calculations, and therefore it is much more convenient to work with sufficient excess of reagent to make this decrease negligible. This is quite possible when radioactive isotopes are used. The distribution of metal between the phases can then be measured at extremely low concentrations of metal ions, which allows not only the amount of ligand combined in the complexes to be neglected but also the range of experimental concentrations to be considerably widened with far less risk of polymerisation or of exceeding the solubility products of the compounds under investigation.

The preliminary investigation of the reagent consists in effect in the determination of its dissociation constants (for acid dissociation in the overwhelming majority of cases) and the distribution constants between the aqueous phase and a few — at least two — organic solvents at a given ionic strength and temperature. The dissociation constant of the reagent can be determined spectrophotometrically, potentiometrically, by a two-phase titration method, etc. [100-109]. The distribution constants of the reagent in several two-phase systems (organic solvents which are subsequently to be used in the study of complex formation are chosen) are determined at various concentrations of the reagent in the organic–solvent layer, covering a sufficiently wide range. If the distribution constant is practically constant for different concentrations of the reagent, it may be accepted that the reagent does not undergo molecular association in the organic layer, or in other words that the molecular weight of the reagent is the same in the two phases*. Possible association of the reagent molecules in the organic phase may also be detected spectrophotometrically [112,113]. In the absence of any polymerisation of the reagent in either phase, the concentration of free ligand in an aqueous solution of a definite low and constant ionic strength is calculated from the equation

$$pA = pK_{diss\,HA} + \log[H] - \log[HA]^{0}_{org} + \log(K_{part\,HA}+1 + K_{diss\,HA}[H]^{-1}), \quad (47)$$

where pA = -log [A], $pK_{diss\,HA}$ is the logarithm of the reciprocal of the dissociation constant and $K_{part\,HA}$ is the distribution constant of the reagent, both at given ionic strength and temperature, $[HA]^{0}_{org}$ is the concentration of the reagent in the original solution (in the organic solvent used), and [H] is the hydrogen-ion concentration under equilibrium conditions. If the phases have different volumes, appropriate correction factors are introduced into Eqn. (47). When such solvents as C_6H_6, $CHCl_3$, and certain others are used, the changes in volume undergone by the phases on prolonged shaking are insignificant and can be neglected [33,44].

In certain cases the phenomenon of keto–enol tautomerism must be taken into account in calculating the concentration of the ligand in the aqueous phase. It is known, for example, that β-diketones exist in aqueous solution in two forms, the keto form and the enol form. The latter dissociates, splitting off a hydrogen ion and forming an anion which can add on to various metal ions to form internal complexes. Many workers have investigated the keto–enol tautomerism of β-diketones [114-117]. Rydberg [101] determined the keto–enol tautomerism constant for acetylacetone and the distribution constants of its keto and enol forms in the benzene–water system. (The distribution constant for acetylacetone between benzene and water according to Rydberg is 5.95 ± 0.05 over the pH range 1–7.) The acid dissociation constant of acetylacetone and other β-diketones determined in the usual way [Eqn. (1)] will contain a certain error if the concentration of the enol form is taken as equal to the total concentration of the reagent. Frequently, however, this error is insignificant. As Calvin and Wilson [118] remark: "The K_{diss} as written here (see p. 101) represents a characteristic of the acid strength of the enol form as such. This, however, is not quite the constant which we have measured and called K_{diss}. The measured value represents the apparent dissociation constant and includes the constant for the keto–enol tautomerism in the following manner:

$$K_{enol} = K_{appar}\ (1 + K_1),$$

where K_1 = [keto]/[enol]. It is clear that for aromatic compounds $K_1 \cong 0$, so that $K_{enol} \cong K_{appar} = K_{diss}$. For the aliphatic compounds, however, K_1 will have an appreciable

* For methods of studying association equilibria of organic molecules in organic solvents by the distribution method see e.g. refs. 110 and 111.

value, thus making K_{diss} for these compounds a lower limit for the acidity of the enol". The correction for K_1 will hardly affect the results in the case of acetylacetone and similar reagents, and therefore many authors in their calculations employ values of the dissociation constants of β-diketones without any correction for K_1. The acid dissociation constant of acetylacetone was also determined by Eidinoff[119], and the distribution of the reagent between $CHCl_3$ and aqueous solutions of perchloric acid was studied by Salvinien[120]. The latter found the distribution constant of acetylacetone in the system to fall from 23.7 to 10.2 with increase in the $HClO_4$ concentration from 0 to 1.94 M. In the water–CCl_4 system the distribution constant diminishes from 3.3 to 1.4. In general, the results obtained by Salvinien are in satisfactory agreement with Rydberg's data[106].

The distribution method has been successfully used to investigate hydrolysis and polymerisation reactions occurring in aqueous solutions of metal ions. Here we should first consider, perhaps, the study of the chemistry of aqueous solutions of zirconium. The great difficulties caused by the extreme readiness with which this element is hydrolysed make it understandable why, until very recently, nothing definite was known about the state of Zr(IV) in aqueous solution. The earlier results indicated the formation of polynuclear complexes[121], but the composition of the latter could not be regarded as reliably established. In recent years Connick, Reas, and other authors[121-128] have carried out a series of investigations with the aim of establishing the composition and in some cases the stability of the zirconium-containing complexes formed in solutions of perchloric and other acids. The nature of this element compelled these workers to pay more attention to complexes of mixed type $MA_n(OH)_p$ than had hitherto been done by other investigators[10,14]. By studying the distribution of Zr(IV) between aqueous perchloric acid and benzene in the presence of thenoyltrifluoroacetone, Connick, Zielen, and others attempted to establish the composition of the complex compounds extracted and of the zirconium-containing species present in the aqueous phase, and also to determine the characteristics of the process of complex formation by Zr(IV) with the majority of the most frequently encountered anions. The usual methods of investigating the composition of complexes in solution (potentiometric, spectrophotometric, solubility measurement, freezing-point determination, etc.) would not, in the view of the above authors, yield reliable results owing to the great tendency of Zr(IV) to hydrolysis even in very acid solutions. They therefore chose a method based on the distribution equilibria of zirconium between the aqueous phase to be investigated and an organic solvent containing the complex-forming reagent.

In the aqueous phase zirconium forms complexes with thenoyltrifluoroacetone to an insignificant extent, but the internal complex formed dissolves readily in the organic solvent (benzene, chloroform, etc.) and is in equilibrium with all the species in the aqueous phase. Thus any change in the complex formation in the aqueous solution should be quantitatively reflected in the passage of metal into the organic–solvent layer. Connick and McVey[124], with the aim of establishing the composition of the complex which is extracted, studied first of all the variation of the partition coefficient of the metal with thenoyltrifluoroacetone concentration for a constant hydrogen-ion concentration in the aqueous phase. Using a solvent of low dielectric constant (benzene) and assuming that only neutral, uncharged particles pass into the organic solvent layer (similarly as was done later by Rydberg[31-33] and other Scandinavian investigators) Connick and his coworkers examined the process represented by the equation

$$Zr(OH)_nA_m^{(4-n-m)+} + (p-m)HA \rightleftarrows Zr(OH)_{4-p}A_p + (4-m-n)H^+ + (n+p-4)H_2O, \quad (48)$$

the equilibrium constant of which is

$$K_{eq\ m,n,p} = \frac{[Zr(OH)_{4-p}A_p][H^+]^{4-m-n}[H_2O]^{n+p-4}}{[Zr(OH)_nA_m^{(4-n-m)+}][HA]^{p-m}}. \quad (49)$$

(A represents the thenoyltrifluoroacetonate ion.) By means of (49) and certain transformations we can obtain an equation relating the partition coefficient to the reagent concentration and other parameters of the system*:

$$\frac{\partial \ln q}{\partial \ln [HA]} = -4f_0 - 3f_1 - 2f_2 - f_3 + 4f_0' + 3f_1' + 2f_2' + f_3', \quad (50)$$

where f_n is the fraction of the total metal concentration in complexes with a definite number of ligands (thenoyltrifluoroacetonate or hydroxyl ions). By measuring the slope of the curve for $\log q$ plotted against $\log [HA]$ it is possible to obtain the number of ligands combined with Zr(IV) in the extracted complex and in all the complexes in the aqueous phase. By means of the distribution method Connick and other investigators have obtained the degree of polymerisation as a function of the variables of the system (concentration of metal ions, acidity of solution, etc.), and have calculated the equilibrium constants of the successive polymerisation processes. The results obtained for analogous systems by other methods (spectrophotometric, chromatographic, etc.)[129-132] are fundamentally in agreement with those obtained by the distribution method. Certain divergencies (e.g. in the degree of polymerisation or the existence of the unhydrolysed ion Zr^{4+}) are perhaps due to different experimental conditions (ionic strength of the solution, difference in properties of the individual mineral acids, etc.).

The work of Connick and his coworkers has established the possibility of using the distribution method to determine the composition and stability of complexes which are not extracted by solvents of low dielectric constant. This is done by adding a secondary ligand (HSO_4^-, F^-, and certain other anions) to a two-phase system containing water, organic solvent, metal ions, and an organic reagent giving on dissociation the primary ligands which form a complex readily extracted by the organic solvent used. The relationship found between the partition coefficient of the metal and the concentration of the secondary ligand gives an indication of the composition of the complexes in the aqueous solution, and in certain cases makes possible a quantitative treatment of the complex formation between the metal ions and the secondary ligand. This procedure (introduction of a secondary ligand) substantially widens the possibilities of the distribution method and suggests that it will prove very effective in many cases for the investigation of other systems, including both extractable and non-extractable complex compounds. This method has been used to study the formation of complexes by Th(IV) with iodate ions[133], the anions of various monobasic acids (HCl, HF, HNO_3, $HClO_3$, $HBrO_3$, $ClCH_2COOH$, and HCOOH), and other ligands[134-136]. Day and Stoughton[135] thus demonstrated the existence in the aqueous phase of mixed complexes of the type $Th(NO_3)F^{2+}$

* The reader is advised to consult ref. 124, p. 3184 (Ed. of Translation).

and $Th(NO_3)F_2^+$, and calculated the equilibrium constants for the following reactions (ionic strength $I = 0.5$):

$$Th^{4+} + HF \rightleftarrows ThF^{3+} + H^+ \qquad K_{eq} = 4.3 \cdot 10^4,$$
$$Th^{4+} + 2HF \rightleftarrows ThF_2^{2+} + 2H^+ \qquad K_{eq} = 3.1 \cdot 10^7,$$
$$Th^{4+} + IO_3^- \rightleftarrows Th(IO_3)^{3+} \qquad K_{eq} = 7.6 \cdot 10^2,$$
$$Th^{4+} + 2IO_3^- \rightleftarrows Th(IO_3)_2^{2+} \qquad K_{eq} = 6.2 \cdot 10^4,$$
$$Th^{4+} + 3IO_3^- \rightleftarrows Th(IO_3)_3^+ \qquad K_{eq} = 1.4 \cdot 10^7,$$
$$Th^{4+} + BrO_3^- \rightleftarrows Th(BrO_3)^{3+} \qquad K_{eq} = 6.4,$$
$$Th^{4+} + 2BrO_3^- \rightleftarrows Th(BrO_3)_2^{2+} \qquad K_{eq} = 8.2,$$
$$Th^{4+} + ClO_3^- \rightleftarrows Th(ClO_3)^{3+} \qquad K_{eq} = 1.84,$$
$$Th^{4+} + NO_3^- \rightleftarrows Th(NO_3)^{3+} \qquad K_{eq} = 4.73,$$
$$Th^{4+} + Cl^- \rightleftarrows ThCl^{3+} \qquad K_{eq} = 1.76,$$
$$Th^{4+} + ClCH_2COOH \rightleftarrows Th(ClCH_2COO)^{3+} + H^+ \qquad K_{eq} = 1.33,$$
$$Th^{4+} + Cl_2CHCOOH \rightleftarrows Th(Cl_2CHCOO)^{3+} + H^+ \qquad K_{eq} = 5.74,$$
$$Th^{4+} + 2Cl_2CHCOOH \rightleftarrows Th(Cl_2CHCOO)_2^{2+} + 2H^+ \qquad K_{eq} = 12.7,$$
$$Th^{4+} + CCl_3COOH \rightleftarrows Th(CCl_3COO)^{3+} + H^+ \qquad K_{eq} = 8.23,$$
$$Th^{4} + 2CCl_3COOH \rightleftarrows Th(CCl_3COO)_2^{2+} + 2H^+ \qquad K_{eq} = 26.7.$$

Rossotti and Rossotti[137] investigated the hydrolysis of In^{3+}. They established the existence of the hydroxo complexes $In(OH)^{2+}$ and $In(OH)_2^+$, and calculated their formation constants. Their results are in good agreement with the potentiometric data of Biedermann for an analogous system* [138].

Allen[141] studied the sulphate complexes of UO_2^{2+} by the above method of introducing a secondary ligand, and Betts and Leigh[142] used the same method to study complex formation between U(IV) and HSO_4^-. The latter detected the complexes $U(SO_4)^{2+}$ and $U(SO_4)_2$, with formation constants of 338 and 0.74 respectively**.

Connick, Reas, and their coworkers investigated only zirconium compounds. The theory of the distribution method has been more widely developed in recent years by a group of English investigators led by Irving. In a series of papers Irving, Williams, Rossotti, and others have considered the general form of the distribution law for a metal distributed between organic and aqueous phases, and have described the application of their results to the investigation of a number of systems[137,144-153]. Irving and his collaborators have considered the case of non-ideal systems and their proposed methods for interpreting the results are therefore somewhat more general than those described by Rydberg and others. The main theoretical arguments of Irving and his coworkers are briefly examined below.

Irving has considered both ideal and non-ideal systems. By the former are understood systems in which wide variation in the experimental conditions produces no changes in the properties of either solvent, and in which the degree of solvation (by water or organic solvent molecules) of any species remains unchanged in either phase. In other words, in ideal systems the average numbers of water and organic solvent molecules associated with each species are constant, as are also the stability constants and partition coefficients. In non-ideal systems a change in one or more variables (concentrations of hydrogen ions, metal ions, reagent, and ligand) produces changes in the composition of both phases (the mutual miscibility of the solvents changes), and consequently the partition coefficients, stability "constants", etc., are no longer constant.

Irving[144] divides all the types of extracted compounds into the following four main classes: (1) covalent compounds of the type of SO_2, Cl_2, OsO_4, etc.; (2) internal complexes of metals with organic reagents (dithizone, acetylacetone, dimethylglyoxime, etc.); (3) mineral acids and their salts and acido complexes (e.g. $HFeCl_4$, etc.); and (4) certain salts containing bulky anions or cations (e.g. the compound of Fe(II) tri-1,10-phenanthrolinate with alkylsulphonates or alkyl sulphates, etc.) [154,155]. Extraction of compounds of the first type is readily explained on the basis of Nernst's theory[6]. The interpretation of the extraction results for compounds of the fourth type is basically similar to that for internal complexes. The greatest differences in behaviour on partition in two-phase systems are observed with compounds of the second and third types, namely, internal complexes and complexes with inorganic ligands.

In the case of internal complexes a quite stable unsolvated monomeric complex MA_n is formed at such a low concentration of the ligand A^- that the properties of the aqueous phase as a solvent remain practically unchanged. Internal complexes which are very sparingly soluble in water are at the same time, as a rule, readily soluble in non-polar organic solvents (benzene, chloroform, carbon tetrachloride, etc.). The organic reagent HA, the anion of which is a ligand in MA_n, also dissolves well in the same organic solvents. Addition of foreign ions to the aqueous phase and the resulting change in composition do not affect the composition of the (usually neutral) species which is extracted, and the absence of hydration in the extracted complexes eliminates the possibility of any change in the composition of the organic phase. Thus the mutual miscibility of two phases is practically unchanged even when the concentration of HA and A^- is varied over a wide range in order to obtain partition coefficients which are more convenient to measure. In such a case the stability constants of the complexes in the aqueous solution, and also the distribution constants of the extracted species, will be constant provided that the ionic strength of the aqueous phase is kept constant, and their values can be obtained by carrying out a sufficiently large number of experiments. In other words, the system is "ideal", and when different solvents are employed the $\log q = f(pA)$ curves will be parallel to one another (see p. 104). Parallel curves will not be obtained if the solvation in the different organic solvents is different.

In the extraction of compounds of the third type, strongly hydrated species may pass into the organic layer, causing considerable changes in composition of both phases. Besides, two or more complex species may be extracted together instead of one extracted with compounds of the second class. Such a marked change in composition of the phases may lead to a change in the values of the stability and distribution constants, or may cause the system to diverge from ideal behaviour. In certain cases this may be avoided by appropriate choice of organic solvent or of the other components of the system[146,147]. The maintenance of a constant ionic strength in the organic phase would considerably diminish such complications, but up to now control of the ionic strength in an organic solvent has hardly been possible in the study of the distribution of acido complexes and inorganic salts in two-phase systems. The extraction of an uncharged internal complex takes place at an insignificant total concentration, and therefore cannot produce any appreciable change in the activity coefficients

* For the hydrolysis of In^{3+} in aqueous solution see also refs. 139, 140, etc.

** For complex formation between U(VI) and SO_4^{2-} see, for example, ref. 143.

in either phase. Addition of a neutral salt to the aqueous solution to keep the ionic strength constant during extraction of compounds of the third type can markedly change the behaviour of the system, and this also distinguishes systems of the third and second types from one another. Apart from this the partition coefficient for the extraction of internal complexes is frequently independent of the concentration of metal ions (over a certain range of concentrations), but in the case of acido complexes it may increase, decrease, or remain constant depending on the nature of the extracted species.

The above complications occurring in the extraction of inorganic salts and acido complexes were taken into account by Irving and his coworkers in working out a general method for interpreting distribution data. Their analysis of complex formation using extraction techniques was based on a combination of Bjerrum's concept of a stepwise mechanism of complex formation[156] and Nernst's distribution law[6]. Irving first considered the equilibria between simple ions and all the complex species in a system containing two immiscible solvents. Such equilibria are quantitatively described by the successive formation constants which determine the relative concentrations of various complexes in aqueous solutions, and a series of distribution constants for such complexes in the two-phase system under examination. Irving et al. did not consider the possibility of a stepwise equilibrium between the extracted complexes in the organic phase, since it is not possible to establish from distribution data whether a particular complex found in the organic layer has migrated from the aqueous phase or whether it has been formed in the organic phase from components in distribution equilibrium with similar components in the aqueous solution.

Assuming that, in the aqueous phase saturated with organic solvent (Org) and containing metal ions M, hydrogen ions H^+, and ligand A^-, the concentration of the acid and the anion A^- is such that hydrolysis of any cation can be neglected, all the complexes of type MA_n, acido complexes H_hMA_n, polynuclear molecules M_2A_6, $H_2M_3A_{12}$, etc., in equilibrium with one another can be represented as a complex of the general type (IV):

$$H_hM_mA_n(H_2O)_p(Org)_s .$$

The concentration of type IV complexes is determined by their stability constants κ:

$$k_{h,m,n,p,s} = \frac{[H_hM_mA_n(H_2O)_p(Org)_s]}{[H]^h[M]^m[A]^n[H_2O]^p[Org]^s}, \quad (51)$$

and the distribution in the two-phase system by the distribution constant:

$$\gamma_{h,m,n,p,s} = \frac{[H_hM_mA_n(H_2O)_p(Org)_s]_{org}}{[H_hM_mA_n(H_2O)_p(Org)_s]_{aq}}. \quad (52)$$

The partition coefficient of the metal between the phases, numerically equal to the ratio of the total concentrations of all forms of metal-containing complexes in the organic and in the aqueous phases, can be represented as follows:

$$q = \frac{\sum m[H_hM_mA_n(H_2O)_p(Org)_s]_{org}}{\sum m[H_hM_mA_n(H_2O)_p(Org)_s]_{aq}} = \quad (53)$$

$$\frac{\sum \gamma_{h,m,n,p,s}\ \kappa_{h,m,n,p,s}\ m[H]^h[M]^m[A]^n[H_2O]^p[Org]^s}{\sum \kappa_{h,m,n,p,s}\ m\ [H]^h[M]^m[A]^n[H_2O]^p[Org]^s}.$$

Eqn. (53) differs from (20) in that its numerator contains the distribution constants of all the species distributed between the phases instead of the distribution constant of the uncharged complex $\lambda_{m,x,mN,s}$ in Eqn. (20). The mean composition of the complexes in the organic and aqueous phases may not be the same. Using the concept of a mean number $\bar{E}$ of metal atoms per complex molecule in the organic phase and the corresponding mean $\bar{\epsilon}$ in the aqueous solution, and applying similar concepts to the mean numbers of hydrogen ions, ligand ions, water molecules, and organic solvent molecules per atom of metal, Irving put forward an expression for q in the form

$$q = \frac{\bar{\theta}\bar{B}[H]^{\bar{E}\bar{H}}[M]^{\bar{E}}[A]^{\bar{E}\bar{N}}[H_2O]^{\bar{E}\bar{P}}[Org]^{\bar{E}\bar{S}}}{\bar{\kappa}[H]^{\bar{\epsilon}\bar{h}}[M]^{\bar{\epsilon}}[A]^{\bar{\epsilon}\bar{n}}[H_2O]^{\bar{\epsilon}\bar{p}}[Org]^{\bar{\epsilon}\bar{s}}}, \quad (53a)$$

where $\bar{H}$ and $\bar{h}$ are the mean numbers of hydrogen ions, $\bar{N}$ and $\bar{n}$ are the mean numbers of ligands, $\bar{P}$ and $\bar{p}$ are the mean numbers of water molecules, and $\bar{S}$ and $\bar{s}$ are the mean numbers of organic solvent molecules, per atom of metal in the averaged complex molecule in organic and aqueous phases: correspondingly $\bar{\theta}$ and $\bar{B}$ are the distribution and stability constants of the averaged complex molecule in the organic phase, and $\bar{\kappa}$ is the stability constant of the averaged complex molecule in the aqueous phase. On taking logarithms, (53a) readily yields the expression

$$\log q = \log\left(\frac{\bar{\theta}\bar{B}}{\bar{\kappa}}\right) + \log\left(\frac{\bar{E}}{\bar{\epsilon}}\right) + (\bar{E}\bar{H} - \bar{\epsilon}\bar{h})\log[H] + (\bar{E} - \bar{\epsilon})\log[M] + (\bar{E}\bar{N} - \bar{\epsilon}\bar{n})\log[A] + (\bar{E}\bar{P} - \bar{\epsilon}\bar{p})\log[H_2O] + (\bar{E}\bar{S} - \bar{\epsilon}\bar{s})\log[Org] \quad (53b)$$

In ideal systems the stability constants of the averaged complexes in the organic and the aqueous phases, $\bar{B}$ and $\bar{\kappa}$, the distribution constant of the averaged complex in the organic phase $\bar{\theta}$, and also the indices $\bar{P}$, $\bar{p}$, $\bar{S}$, and $\bar{s}$ are constant. With constant ionic strength in the aqueous phase, the mutual solubility of the solvents is constant, and expression (53b) may be written in the form

$$\log q = \Psi + \log\left(\frac{\bar{E}}{\bar{\epsilon}}\right) + (\bar{E}\bar{H} - \bar{\epsilon}\bar{h})\log[H] + (\bar{E} - \bar{\epsilon})\log[M] + (\bar{E}\bar{N} - \bar{\epsilon}\bar{n})\log[A], \quad (54)$$

where Ψ is a constant independent of [M], [H], and [A]. With the help of Eqn. (54) it is possible to draw definite conclusions as to the composition of the various complexes existing in the organic and aqueous phases, and it is also possible, if a sufficient number of measurements are made, to calculate the values of the constants which it contains.

To find the mean number of metal atoms per averaged complex molecule, the so-called "polymerisation factor"[144], Eqn. (54) is differentiated with respect to the concentration of metal ions at constant concentrations of ligand and hydrogen ions. It is easy to show that

$$\left(\frac{\partial \log q}{\partial \log[M]}\right)_{[H],[A]} = (\bar{E} - \bar{\epsilon}) . \quad (55)$$

Thus if the value of the partial derivative (55) is found to be zero, the degree of polymerisation of the metal-containing complexes is the same in each phase. In the limiting case, when the concentration [M] tends to zero, the values of E and ϵ tend to unity: i.e. at very low concentrations of metal ions only mononuclear complexes are formed in organic and aqueous phases. This has been established for the majority of metals, the only possible exception being elements that are extremely readily hydrolysed. It is also obvious that, if $(\partial \log q/\partial \log[M])_{[H],[A]} > > 0$, the degree of polymerisation in the organic phase is higher than in the aqueous phase, and conversely if the value of this derivative is less than zero. By means of Eqn. (55) it is possible to obtain information as to the relative polymerisation of the complexes in each of the phases,

but, as noted above, it is impossible to judge the nature of the species undergoing such polymerisation in the organic phase. Relationships of the type (55) were investigated in particular by Connick and Reas in their work on the polymerisation of zirconium in aqueous solution[125]. All the cases covered by Eqn. (55) have been described in the literature. Thus the condition $\bar{E} = \bar{\epsilon}$ is achieved in practice in the extraction of internal complexes[31-33], and cases of association of the extracted molecules in the organic phase have been established in a study of the extraction of halide complexes of iron, gold, and other elements[157,158]. The formation of dimers in the aqueous phase ($\bar{\epsilon} > \bar{E}$) has been observed by Irving and Rossetti in the extraction of In^{3+} from hydrobromic acid solutions[147].

The difference in the mean number of ligands associated with each complex-forming metal atom in the averaged complexes in each phase is indicated by the value of the partial derivative of the partition coefficient with respect to the ligand concentration for [M] = const. and [H] = const.:

$$\left(\frac{\partial \log q}{\partial \log [A]}\right)_{[H],[M]} = \bar{E}\bar{N} - \bar{\varepsilon}\bar{n} \quad . \qquad (56)$$

What has been said about Eqn. (55) is applicable also to (56). The value of the derivative obtained indicates either the same or different mean numbers of ligands in each averaged complex in organic and aqueous phases. If mononuclear complexes are formed, $\bar{E} = \bar{\epsilon} = 1$, and Eqn. (56) may be written in the form:

$$\left(\frac{\partial \log q}{\partial \log [A]}\right)_{[H],[M]} = \bar{N} - \bar{n} \quad . \qquad (57)$$

If it is established that a single neutral complex is transferred to the organic solvent layer (such a case usually occurs in the extraction of internal complexes by non-polar solvents), Eqn. (57) can be used to find all the stability constants of the complex compounds formed in the aqueous phase. A similar equation was deduced by Rydberg for the particular case of the distribution of acetylacetonato complexes of thorium between benzene and an aqueous phase[41]. The formation of compounds $ThA_n^{(4-n)+}$, was established in the latter system, the extracted complex having $\bar{N} = 4$ (p. 106). In this way the following equation was obtained:

$$\left(\frac{\partial \log q}{\partial \log \left(\frac{1}{[A]}\right)}\right) = -\frac{\partial \log q}{\partial p\,A} = 4 - \bar{n}, \text{ or}$$
$$\bar{n} = 4 + \frac{\partial \log q}{\partial p\,A} \quad . \qquad (58)$$

The method of finding the successive stability constants by means of Eqn. (58) has already been indicated briefly (p. 106).

The relative degree of association of hydrogen ions with metal-containing molecules in each of the phases can be determined by differentiating Eqn. (54) with respect to the hydrogen-ion concentration for constant concentrations of the metal ions and ligand:

$$\left(\frac{\partial \log q}{\partial \log [H]}\right)_{[M],[A]} = (\bar{E}\bar{H} - \bar{\varepsilon}\bar{h}). \qquad (59)$$

If MA_n molecules, which are not acido complexes, pass into the organic layer, the value of the derivative (59) is equal to zero for the case of mononuclear complexes, provided that no acido complexes are formed in aqueous solution, i.e. $\bar{h} = 0$. A possible value of this derivative indicates the extraction of acido complexes. If

$$\left(\frac{\partial \log q}{\partial \log [H]}\right)_{[M],[A]} < 0,$$

the species which had lost hydrogen ions pass into the organic solvent layer, and acido complexes are present in the aqueous solution, their distribution constants being extremely small or zero. In the extraction of internal complexes whose ligands are anions of weak acids HA, mononuclear complexes MA_n are generally formed in the aqueous phase, for which $\bar{E} = \bar{\epsilon} = 1$ and $\bar{H} = \bar{h} = 0$. By using well known equations for the dissociation and distribution constants of HA in the given system and substituting the expression for [A] in Eqn. (54) it is possible to obtain

$$\log q = \Psi + (\bar{N} - \bar{n})(\log [HA]_{org} + pH - \log K_{diss\ HA}\ K_{part\ HA}). \qquad (60)$$

Thus from the slope of the $\log q = f(pH)$ curves for $[HA]_{org}$ = const. or the $\log q = f([HA]_{org})$ curves for pH = = const. the value of $\bar{N} = \bar{n}$ can be obtained. In the limiting case equations are obtained which had been deduced earlier by Kolthoff[10] and Irving[11]:

$$\log q = \Psi' + \bar{N}(\log [HA]_{org} + pH), \qquad (61)$$

where the constant Ψ' combines Ψ of Eqn. (60) with the remaining constants. As can be seen from Eqn. (61), the slope of the curve $\log q = f(pH)$ for $[HA]_{org}$ = const. is in the limiting case the value of $\bar{N}$, i.e. the mean number of ligands associated with a metal atom. In the case of mononuclear complexes $\bar{N}$ defines the composition of the extracted complex ($\bar{H} = \bar{h} = 0$). In certain systems this method was successful in establishing the composition of the extracted molecules[76,90,124,159]. Sometimes, owing to a number of causes (different ratios of stability and distribution constants[144]) the value of $\bar{N} - \bar{n}$ is obtained instead[24,41-43,91]. Particular cases of the determination of the composition of complex compounds in this way will be noted below. In certain cases it is necessary, in order to establish the composition of the complex species in each of the phases, to consider not one derivative but two in combination with supplementary information obtained by an independent method. If the acid HA is very strong (mineral acids such as HCl, HBr, etc.) and if the H^+ and A^- ions in the aqueous solution result solely from its dissociation, and provided that $[M] \ll [HA]_{total}$, then the concentrations can be equated: $[H] = [A] = [HA]_{total}$. Substituting these values in Eqn. (54) and differentiating yields the following equation for mononuclear complexes:

$$\left(\frac{\partial \log q}{\partial \log [HA]_{total}}\right)_{[M]} = \bar{E}(\bar{H} + \bar{N}) - \bar{\varepsilon}(\bar{h} + \bar{n}) = (\bar{H} - \bar{h}) + (\bar{N} - \bar{n}) \quad . \qquad (62)$$

The value of the derivative (62) in combination with such derivatives as

$$\left(\frac{\partial \log q}{\partial \log [H]}\right)_{[M],[A]} \quad \text{and} \quad \left(\frac{\partial \log q}{\partial \log [A]}\right)_{[M],[H]}$$

can give valuable information about the composition of the extracted complexes. For example, if the complex MA_3 passes into the organic phase, the values of the derivatives

$$\left(\frac{\partial \log q}{\partial \log [HA]_{total}}\right)_{[M]} \quad \text{and} \quad \left(\frac{\partial \log q}{\partial \log [A]}\right)_{[M],[H]}$$

are $(3 - \bar{n})$. At the same time if the organic phase contains an acido complex HMA_4 which dissociates strongly in aqueous solution into H^+ and MA_4^-, the values of these derivatives will no longer be $(3 - \bar{n})$, but $(5 - \bar{n})$ and $(4 - \bar{n})$ respectively, since for this case $\bar{H} = 1$, $\bar{h} = 0$, and $\bar{N} = 4$. If the acido complex is appreciably associated in the aqueous phase, or even if it dissociates appreciably in the organic phase, the position is greatly complicated and may require independent determinations of $\bar{n}$ or measurements of the electrical conductivity of the organic layer[144].

If it is established that a complex of type MA_n is extracted, it is easy to find its concentration in the aqueous phase when the extent of its formation, the total concentration of metal, and the concentration of free ligand [A] are known:

$$\frac{[MA_n]}{[M]_{total}} = \alpha_n = \frac{\kappa_n [A]^n}{\sum_0^n \kappa_n [A]^n}. \quad (63)$$

In such a case the partition coefficient of the metal is expressed by the equation

$$q = \frac{[MA_n]_{org}}{\sum [M]_{aq}} = \gamma_n \alpha_n = \frac{\gamma_n \cdot \kappa_n \cdot [A]^n}{\sum_0^n \kappa_n [A]^n}. \quad (64)$$

An analogous equation was obtained by Rydberg (see p. 104) and other investigators for the extraction of many internal complexes (e.g. for the distribution of thorium in two-phase systems in the presence of acetylacetone, oxine, cupferron, etc.). Eqn. (64) establishes a general relation between the partition coefficient of a metal, the distribution constant of the extracted mononuclear complex, and the stability constants of the various complexes in the aqueous phase.

If the acido complex HMA_{n+1} is involved in the distribution in addition to the complex MA_n, a new term will be introduced into the equation relating the partition coefficient to the parameters of the system:

$$q = \alpha_n \cdot \gamma_n + \alpha_{n+1} \cdot \gamma_{acido} \kappa'_{acido} [H], \quad (65)$$

where γ_{acido} is the distribution constant of HMA_{n+1}, and $\kappa'_{acido} = [HMA_{n+1}]/[H][MA_{n+1}]$ is its dissociation constant. The concentration of HMA_{+1} in the organic phase is obviously $\gamma_{acido}\kappa'_{acido}[H][MA_{n+1}]$. If several complexes are involved in the distribution, the equation can be given in the general form

$$q = \sum_0^n \alpha_i \gamma_i + \alpha_{n+1} \gamma_{acido} \kappa'_{acido} [H]. \quad (66)$$

If a sufficient number of experiments are carried out, Eqns. (64)–(66) can be used to calculate all the constants (distribution, stability, etc.) occurring in them. On the other hand, if the values of the stability and distribution constants are known, the proportion of each complex can be calculated as a function of the concentration of the free ligand [A]. More complicated equations are obtained if alkali-metal salts of acids of the type HMA_{n+1} take part in the distribution[144], but by appropriate modification of expressions similar to (65) and (66) formulae convenient for calculation can be obtained. In order to simplify equations of this type, it should be noted which of the complexes predominates in one of the phases, and whether its concentration in the other phase can be neglected.

A large number of complex compounds of metal ions with inorganic ligands have been investigated by the above procedures. Halide complexes have been studied in considerable detail, and among them perhaps the greatest attention has been devoted to the halide complexes of tervalent iron. The extraction of Fe(III) from chloride solutions by means of ether has been known for very many years[160-164], but the composition of the compounds formed in the aqueous phase, or distributed between the phases, let alone the stability of such compounds, remained unknown for a long time. It was noted that the partition coefficient depended on the components of the system[165,166], and subsequently many investigators, using various methods, studied the formation of complexes between Fe(III) and chloride ions, the composition of the extracted compound and of the complexes formed in the aqueous phase[145,157,158,167-176]. But when the results of all this work are collated, it is hardly possible to regard the problem of the composition or stability of these complexes as finally solved.

Other halide complexes which have been studied include chloride complexes of gallium[174,179-181], manganese[180], arsenic[182-184], thallium[152,174,185], and indium[150-152,186,187], bromide and iodide complexes of thallium[152], gallium[152], indium[150-152], and other elements[188]. In some cases the data obtained by the distribution method can be compared with the results of other methods of physicochemical analysis (e.g. chromatographic[189] or conductimetric[190]).

Irving and his collaborators[146-152] made a detailed study of the processes of complex formation in the systems In^{3+} – –hydrogen halide–organic solvent–aqueous phase. By using equations deduced previously[144], representing in a general form the extraction of complexes of this type, they were able to show that only the mononuclear complexes* $InBr^{2+}$, $InBr_2^+$, $InBr_3$, $HInBr_4$, and $InBr_4^-$ and free (hydrated) In^{3+} ions are formed at a concentration of $In^{3+} < 10^{-5}$ M in the aqueous phase in the presence of Br^- ions. At higher In^{3+} concentrations the formation of polynuclear complexes becomes possible. Irving and Rossotti found that, with trace concentrations of In^{3+} and the condition $1.0\ M \geqslant [Br^-] \leqslant 0.2\ M$ (pH $\geqslant 3$), every In^{3+} ion is combined on an average with 1.6 Br^- ions, but does not add on H^+ or OH^-. From solutions of low H^+ concentration ($\sim 10^{-3}$ M) $InBr_3$ and $MInBr_4$ (M = alkali metal) pass into the organic solvent layer. At higher acidities ($[H^+] > 0.1$ M) the acido complex $HInBr_4$ is preferentially extracted, and to a lesser extent $InBr_3$. Investigation of the extraction of In^{3+} from aqueous HBr solutions by isobutyl methyl ketone and diethyl ether, with $[In^{3+}] > 10^{-5}$, showed the presence in the aqueous phase of polymeric (associated) molecules containing In^{3+}. The value of the derivative $-1 \leqslant (\partial \log q/\partial \log[In])_{[HBr]} \leqslant 0$ [see Eqn.55)] indicates that mono- and dinuclear complexes exist in the aqueous phase and also that the monomeric form alone passes into the organic layer. Irving and Rossotti concluded from their results that the dimer In_2Br_6 ($In_2Br_7^-$ in the presence of KNO_3) predominates in the aqueous phase, and not hydroxylated dimers.

Recently Horrocks and Voigt[185] attempted to establish the composition of the complex compound extracted by ether from chloride solutions of $TlCl_3$. They showed that the partition coefficient of Tl(III) depends substantially on the ionic strength of the solution, the concentration of the ligand, and the hydrogen-ion concentration. With high ionic strength in the aqueous phase and a high Cl^- concentration in the ether layer, the complex of empirical formula $HTlCl_4$ is extracted, but not H_2TlCl_5. It was not possible, however, to explain the extraction process at low Cl^- and H^+ concentrations by

* Data on the stability of halide complexes of indium obtained by other methods (see for example Carleson and Irving[19]) also indicate that complexes of more complicated composition are absent.

this mechanism, and this forced Horrocks and Voigt to postulate that under these conditions either $TlCl_5$ is extracted or else $HTlCl_4$ dissociates in the organic phase.

The above equations are applicable only to ideal systems. In the case of "non-ideal" systems additional complications arise, and the distribution results can be interpreted either from a consideration of the phase diagrams[144] or by application of the Gibbs–Duhem equation, as was done by McKay et al.[192]. In the investigation of complex formation in solution by the distribution method non-ideal systems are encountered comparatively rarely, and they will therefore not be considered here.

Certain additional factors, which extend Irving's treatment were considered by Diamond in a series of papers on the extraction of complex compounds of sexivalent molybdenum. Nelidow and Diamond[193–196] measured the partition coefficient of Mo(VI) between various organic solvents (ketones, ethers, etc.) and aqueous HCl and HBr (occasionally with the addition of $HClO_4$ or trifluoroacetic acid) and studied its variation with the hydrogen-ion concentration and the concentration of the metal ions (between 10^{-9} and 10^{-2} M). From their results they attempted to deduce the nature of the complexes which were extracted and of those which remained in the aqueous phase. It was assumed that the mechanism of extraction is governed by four main factors: (1) association and polymerisation of metal-containing molecules in one or both phases (q should depend on $[M]_{aq}$); (2) ionisation of metal-containing species as an acid (q depends on the hydrogen-ion concentration and on the concentrations of any substances which dissociate with the formation of H^+); (3) complex formation with halide ions (q depends on the concentration of these and on the presence of components yielding halide ions on dissociation); and (4) solvation and hydration of complexes in each phase (q should consequently depend on the nature of the solvent). From a study of the variation of the partition coefficient with the metal-ion and hydrogen-ion concentrations, it appeared that the first two factors are of little significance, i.e. that the extracted molecules are monomers possessing no acidic properties. At the same time the effects of the third and fourth factors are quite distinct, and this led Diamond to conclude that the molecule which is extracted is MoO_2Cl_2 containing a variable number of added water and organic-solvent molecules (change in solvation with change in concentration of the acid is probably also significant).

Alimarin and Polyanskii[196] and also Zharovskii[197] studied an analogous system and explained the distribution curves they obtained by the formation of complex acids of the type $H[MoCl_5]$ and $H[MoO_2Cl_3]$.

Subsequently Diamond[194,195] made a further examination of the influence of the various parameters of the system (concentrations of halide ions, hydrogen ions, and foreign halide salts, acid strength, total concentration of metal) on the partition coefficients of halide complexes between aqueous solutions of hydrogen halides and various organic solvents. Apparently on the basis of considerations put forward in a short but interesting paper by Saldick[186], Diamond obtained general equations expressing the nature of the variation of q with change in the above parameters, taking into account the possible formation of cationic, neutral, anionic, and polymeric (associated) species containing ions of the metal under investigation. In contrast to the above method[144] of interpreting results for similar systems, the work of Diamond showed that the partition coefficient might be affected by the presence of substances containing an ion common to the ions of the complex compound formed, if such a substance predominates in one of the phases.

Diamond checked his equations for the distribution of molybdenum between aqueous solutions of HCl, HBr, and $HCl–HNO_3$ and $HBr–HClO_4$ mixtures, and various oxygen-containing organic solvents (diethyl, bis-2-chloroethyl, and dibutyl ethers, etc.). He showed that the change in partition coefficient with variation in the concentration of metal in the aqueous phase $[M]_{aq}$ might be caused by two main processes — polymerisation of metal-containing species in the aqueous phase and the influence of a common ion — which can be distinguished experimentally. If the decrease in the partition coefficient is due to polymerisation of metal-containing species in the aqueous phase, the slope of the $\log q = f(\log [M]_{aq})$ curve remains constant with different organic solvents and on introducing a second acid, which is more soluble in the organic solvent and dissociates more strongly in it than the hydrogen halide under investigation. If the change in the partition coefficient is due to the common ion effect the slope of the curve will depend on the nature of the solvent, and the partition coefficient of the metal in the given two-phase system will fall to a lower constant value on introducing the second acid (anions containing the metal then predominate in the organic phase, and halide ions in the aqueous phase). In this way it was shown that, at a concentration of the hydrogen halide below 6 M and a concentration of molybdenum ions below 0.1 M in the aqueous solution, polymeric forms can exist, but not monomeric cations to any appreciable extent, and the predominant species are apparently anions of acids which are stronger than HCl.

The distribution method is widely used in the investigation of nitrate complexes of actinides, lanthanides, and other elements. Such solvents as isobutyl methyl ketone[198], diisopropyl ether[199] and dibutyl ether[200] are comparatively seldom used for this purpose, but complex formation is very often studied by means of the distribution of the metal between an aqueous phase containing NO_3^- ions and a benzene solution of tri-n-butyl phosphate[201,202] (occasionally the benzene is replaced by paraffin oil [kerosene] and other solvents).

Fomin and Maiorova[203] investigated the distribution of HNO_3 between an aqueous phase and a solution of tri-n-butyl phosphate (TBP) in benzene. Povitskii and Solovkin and their collaborators[204,205] determined the equilibrium constant for complex formation between $HClO_4$ and TBP. Dyrssen[206] studied the dissociation, distribution, and dimerisation of dibutyl phosphate in an organic solvent.

The nitrates of many elements dissolve comparatively readily in TBP, forming complexes with the latter. The composition of such complexes can be established either by direct analysis of the compound formed (if this is possible, as in the case of $UO_2(NO_3)_2 \cdot 2TBP$ for example) or by studying the distribution of $M(NO_3)_p$ between H_2O and TBP. With constant ionic strength in the aqueous phase and a varying TBP concentration in the benzene (or other inert solvent) the partition coefficients of M^{p+} are determined for trace concentrations of the latter. Assuming that complexes $M(NO_3)_p \cdot n\,TBP$ exist in the organic layer and writing the equilibrium constant for the reaction $M^{p+} + p\,NO_3^- + n\,TBP \rightleftharpoons M(NO_3)_p \cdot n\,TBP$, it is easy to represent the partition coefficient,

$$q = \frac{[M(NO_3)_p \cdot n\ TBP]_{org}}{[M]_{aq}}, \qquad (67)$$

as a function of the TBP concentration. From the slope of the $q = f([TBP])$ curve we can find the number of TBP molecules associated with one molecule of the metal nitrate.

It is found that, depending on the experimental conditions, complexes are sometimes formed with different numbers of TBP molecules. In the case of $Th(NO_3)_4$ complexes are found with two [207-212] and four TBP molecules [213-215]. For other elements the following complexes are known:

$UO_2(NO_3)_2 \cdot 2$ TBP [207, 209, 213, 215-217], $Zr(NO_3)_4 \cdot 2$ TBP [209, 218, 219], $Zr(NO_3)_4$ TBP [220], $ZrCl_4 \cdot 2$ TBP [219, 221], $Y(NO_3)_3 \cdot 3$ TBP, $Ce(NO_3)_3 \cdot 3$ TBP, $Am(NO_3)_3 \cdot 3$ TBP [209, 222], $Ce(NO_3)_4 \cdot 2$ TBP, $Np(NO_3)_4 \cdot 2$ TBP, $NpO_2(NO_3)_2 \cdot 2$ TBP [209], $PuO_2(NO_3)_2 \cdot 2$ TBP $Pu(NO_3)_4 \cdot 2$ TBP [223].

The composition of the last complex has been confirmed by spectrophotometric measurements [224]. The extraction of compounds of uranium, thorium, ruthenium, lanthanum, and other elements by means of pure TBP and its solutions in various inert solvents has been studied by a number of Russian and foreign investigators [205,225-231]. The distribution of nitrate complexes of Ce(IV) between an aqueous phase and a solution of tri-n-butyl phosphate was studied by Warf [232]. Subsequently Blaustein and Gryder [199] detected polymeric molecules in aqueous solutions of cerium nitrate. They showed also that the complex $H_2Ce(NO_3)_6$ passed into the organic solvent layer*. Analogous results were obtained also by Wylie [234]. The distribution method has been used to study complexes of protactinium with alkyl hydrogen phosphates [235,236], mixed complexes of thorium with sulphate and nitrate ions [237], and several complexes of astatine [238] and uranium [239].

A number of investigations have been made into the composition of thiocyanate complexes of metals. As early as 1931 Schlesinger and Van Valkenburgh [240] attempted to establish spectrophotometrically the composition of the thiocyanate complex of Fe(III) extracted by ether. They concluded that the dimer $Fe[Fe(SCN)_6]$ exists in the ether. MacDonald, Mitchell, et al. [241,242], by making a detailed study of all the factors influencing the extraction of iron thiocyanate, proved subsequently that this conclusion was erroneous. They showed that the ether layer contains the complex $Fe(SCN)_3$, while the aqueous phase contains a series of complexes $Fe(SCN)_x^{(3-x)+}$, where $x = 1-6$. The extraction of thiocyanate complexes of Fe(III) and of a number of other elements by means of n-butyl phosphate, tri-n-butyl phosphate, and diethyl ether was also studied by Freiser [243,244] and Bock [245].

Other types of complex compounds which have been studied include complexes of nickel with organic acids and amines [246-249], compounds of calcium with hydrazine [250], phosphate complexes of uranium [251], and certain perrhenates [252]. Work has been done on the reactions of iodine in aqueous solutions and on other special problems [253-258]. In certain cases results obtained by the distribution method are in very good agreement with data obtained by other methods (e.g. potentiometric [259] or chromatographic [249]).

---o0o---

This account shows that appropriate mathematical procedures for treating the experimental results to obtain information on the composition and physicochemical characteristics of complex compounds are available for every system. A complete study of the process of complex formation in systems containing internal complexes falls into a series of stages, none of which can in general be excluded: (1) determination of the dissociation constants of an organic reagent HA for a given constant ionic strength and temperature; (2) study of the distribution of the reagent between the aqueous phase and several (at least two) organic solvents over a fairly wide range of HA concentrations in the organic layer; (3) ascertaining the range of concentration of metal ions in the aqueous phase within which formation of polynuclear complexes and hydrolysis products may be neglected; (4) an examination of the possible formation of complexes containing molecules of the organic solvent; (5) establishment of the composition of the complexes formed in the aqueous phase; (6) plotting of the distribution curve for a reasonable selection of the above factors and its mathematical treatment by one or more methods of calculation [48-52,260] (sometimes both arithmetical and graphical* methods can be employed in the treatment of experimental results). The examination of various special systems (complex formation with organic or inorganic ligands, employment of polar or non-polar organic solvents, etc.) may sometimes require appropriate modification of the above equations to allow for the peculiarities of the particular system.

The mathematical procedures employed in the study of complex formation by the distribution method are now quite well developed. Almost all the types of complexes that can be formed in aqueous solutions have been discussed theoretically. Many such complexes have been studied experimentally, at least in solutions of low and constant ionic strength.

The theoretical principles discussed here and the brief account of the vast range of systems investigated by the distribution method show it to be reliable, rapid, and comparatively simple. The determination of the stability constants of complex compounds, and also of such important properties as the partition coefficient of the metal and the distribution constant of complex molecules in various two-phase systems opens up wide opportunities for the solution of both theoretical and practical problems in analytical and other fields of chemistry.

1. V.I. Kuznetsov, Uspekhi Khim., 23, 654 (1954).
2. L.C. Craig, Analyt. Chem., 28, 723 (1956).
3. A.K. Babko and A.T. Pilipenko, "Kolorimetricheskii Analiz" (Colorimetric Analysis), Goskhimizdat, Moscow: Leningrad, 1951.
4. E. Hecker, Verteilungsverfahren im Laboratorium, 1955.
5. L. Craig, D. Gregory, and G. Barry, in "Aminokisloty i Belki" (Amino-Acids and Proteins), (Translated into Russian), Inostr. Lit., Moscow 1952, p. 32.
6. W. Nernst, Z. phys. Chem., 8, 110 (1891).
7. W.S. Hendrixson, Z. anorg. Chem., 13, 73 (1897).
8. A. Hantzsh and F. Sebaldt, Z. phys. Chem., 30, 258 (1899).
9. H. Morse, ibid., 41, 709 (1902).
10. I.M. Kolthoff and E.B. Sandell, J. Amer. Chem. Soc., 63, 1906 (1941).
11. H. Irving and R.J. Williams, J. Chem. Soc., 1841 (1949).
12. J. Rydberg, Svensk. kem. Tidskr., 67, 499 (1955).
13. A.K. Babko and A.T. Pilipenko, Zhur. Anal. Khim., 1, 275 (1946).
14. Idem, ibid., 2, 33 (1947).
15. A.T. Pilipenko, ibid., 5, 14 (1950).

* These results may be compared with the data of Newton and Arcand obtained with sulphate complexes of cerium [233].

* For graphical treatment of the results of investigations of complex formation see, for example, Rossotti et al. [261-264].

16. Idem, ibid., 8, 286 (1953).
17. R. E. Chernitskaya, Zhur. Obshch. Khim., 22, 403, 408 (1952).
18. N. P. Komar', Trudy Khim. Fak. i Nauch.-Issled. Inst. Kharkov. Gos. Univ., 14, 135 (1956).
19. D. T. Eve and A. Strasheim, J. South African Chem. Inst., 9, 5 (1956).
20. I. M. Korenman and F. R. Sheyanova, Zhur. Obshch. Khim., 26, 1849 (1956).
21. Idem, Zhur. Anal. Khim., 12, 285 (1957).
22. N. H. Furman, W. B. Mason, and J. S. Pekola, Analyt. Chem. 21, 1325 (1949).
23. H. Irving, S. J. H. Cooke, S. C. Woodger, and R. J. P. Williams, J. Chem. Soc., 1847 (1949).
24. H. Irving, C. F. Bell, and R. J. P. Williams, ibid., 356 (1952).
25. H. Irving, G. Andrew, and E. J. Risdon, ibid., 541 (1949).
26. W. C. Vosburgh and G. R. Cooper, J. Amer. Chem. Soc., 63, 437 (1941).
27. G. Ljunggren and L. G. Sillen, Arkiv. Kemi, 1, 277 (1949).
28. J. H. Rayner and H. M. Powell, J. Chem. Soc., 319 (1952).
29. L. Pokras, M. Kilpatrick, and P. M. Bernays, J. Amer. Chem. Soc., 75, 1254 (1953).
30. A. E. Martell and M. Calvin, Chemistry of Metal Chelate Compounds, N. Y., 1952.
31. J. Rydberg, Arkiv. Kemi, 8, 101 (1955).
32. J. Rydberg, Rec. Trav. Chim., 75, 737 (1956).
33. J. Rydberg, Arkiv. Kemi, 8, 113 (1955).
34. L. G. Sillén, Acta Chem. Scand., 8, 299 (1954).
35. L. G. Sillén, ibid., 8, 320 (1954).
36. B. Hedström, ibid., 9, 613 (1955).
37. G. Biedermann and L. G. Sillen, ibid., 10, 1011 (1956).
38. L. G. Sillén, Rec. Trav. chim., 75, 705 (1956).
39. N. P. Komar', Zhur. Fiz. Khim., 28, 2142 (1954).
40. J. Rydberg, Arkiv. Kemi, 5, 517 (1953).
41. J. Rydberg, Acta Chem. Scand., 4, 1503 (1950).
42. D. Dyrssen, Svensk. kem. Tidskr., 65, 43 (1953).
43. J. Rydberg, Arkiv Kemi, 5, 413 (1953).
44. J. Rydberg, ibid., 9, 109 (1956).
45. J. Rydberg and B. Rydberg, ibid., 9, 81 (1956).
46. V. M. Peshkova and A. P. Zozulya, Nauch. Dokl. Vys. Shkoly, Khim. i Khim. Tekhnol., 1, 470 (1958).
47. Idem, Zhur. Neorg. Khim., 4, 379 (1959) [Rus. J. Inorg. Chem., 168 (1959)].
48. J. C. Sullivan and J. C. Hindman, J. Amer. Chem. Soc., 74, 6091 (1952).
49. J. Leden, Z. phys. Chem., A188, 160 (1941).
50. J. Bjerrum, Chem. Rev., 46, 381 (1950).
51. S. Fronaeus, Acta Chem. Scand., 4, 72 (1950).
52. D. Dyrssen and L. G. Sillén, ibid., 7, 663 (1953).
53. K. V. Chmutov and V. E. Ermishin, Zhur. Fiz. Khim., 29, 930 (1955).
54. K. V. Chmutov, Zavod. Lab., 23, 94 (1957).
55. L. M. Batuner and M. E. Pozin, "Matematicheskie Metody v Khimicheskoi Tekhnike" (Mathematical Methods in Chemistry), Goskhimizdat, Leningrad, 1955.
56. K. P. Yakovlev, "Matematicheskaya Obrabotka Rezul'tatov Izmereniya" (Mathematical Treatment of Experimental Results), GITTL, Moscow, 1953.
57. R. G. Harvey, H. G. Heal, A. G. Maddock, and E. L. Rowley, J. Chem. Soc., 1010 (1947).
58. J. Rydberg, Arkiv Kemi, 9, Part 2, 95 (1956).
59. L. G. Van Uittert and C. G. Haas, J. Amer. Chem. Soc., 75, 451 (1953).
60. L. G. Van Uittert, W. C. Fernelius, and B. E. Douglas, ibid., 75, 455 (1953).
61. L. G. Van Uittert, W. C. Fernelius, and B. E. Douglas, ibid., 75, 457 (1953).
62. L. G. Van Uittert, W. C. Fernelius, and B. E. Douglas, ibid., 75, 2736 (1953).
63. L. G. Van Uittert, W. C. Fernelius, and B. E. Douglas, ibid., 2739 (1953).
64. L. G. Van Uittert, W. C. Fernelius, and B. E. Douglas, ibid., 75, 3577 (1953).
65. L. G. Van Uittert and W. C. Fernelius, ibid., 75, 3862 (1953).
66. R. M. Izatt, W. C. Fernelius, C. G. Haas, and B. P. Block, J. Phys. Chem., 59, 170 (1955).
67. R. M. Izatt, W. C. Fernelius, and B. P. Block, ibid., 59, 80 (1955).
68. S. Hietanen, Acta Chem. Scand., 8, 1626 (1954).
69. S. Hietanen, Rec. Trav. chim., 75, 711 (1956).
70. K. A. Kraus and R. W. Holmberg, J. Phys. Chem., 58, 325 (1954).
71. S. Heitanen, Acta Chem. Scand., 10, 1531 (1956).
72. J. A. Hearne and A. G. White, J. Chem. Soc., 2168 (1957).
73. I. Stary, Candidate Thesis, (Ph. D. Equivalent), Moscow University, 1958.
74. I. Stary and N. P. Rudenko, Nauch. Dokl. Vys. Shkoly, Khim. i Khim Tekhnol., 1, 624 (1958).
75. N. P. Rudenko and I. Stary, Trudy Kom. Anal. Khim. Akad. Nauk SSSR, 9, (12), 28 (1958).
76. T. K. Keenan and J. F. Suttle, J. Amer. Chem. Soc., 76, 2184 (1954).
77. R. Bolomey and L. Wish, ibid., 72, 4483, 4486 (1950).
78. D. C. McCarty, B. E. Dearing, and J. F. Flagg, U. S. Atomic Energy Comm. Report KAPL-180, 45 (1949); cited in Chem. Abs., 50, 9828 (1956).
79. M. Calvin, J. C. Reid, R. E. Connick, and H. W. Grandall, University of California, Berkeley, California, 1944-1946.
80. J. C. Sullivan and J. C. Hindman, J. Amer. Chem. Soc., 76, 5931 (1954).
81. L. B. Magnusson and M. L. Anderson, ibid., 76, 6207 (1954).
82. E. H. Huffman, G. M. Iddings, R. M. Osborne, and G. V. Shalimoff, ibid., 77, 881 (1955).
83. L. Sacconi and R. Ercoli, Gazzetta, 79, 731 (1949).
84. W. Forsling, Acta Chem. Scand., 3, 1133 (1949).
85. R. T. McIntyre, E. W. Berg, and D. N. Campbell, Analyt. Chem. 28, 1316 (1956).
86. C. Musante, Gazzetta, 76, 123 (1946).
87. D. Dyrssen, Acta Chem. Scand., 9, 1567 (1955).
88. D. Dyrssen, M. Dyrssen, and E. Johanson, ibid., 10, 106 (1956).
89. D. Dyrssen, M. Dyrssen, and E. Johanson, ibid., 10, 341 (1956).
90. D. Dyrssen and V. Dahlberg, ibid., 7, 1186 (1953).
91. D. Dyrssen, Svensk. kem. Tidskr., 66, 234 (1954).
92. D. Dyrssen, ibid., 67, 311 (1955).
93. B. Hök-Bernstrom, Acta Chem. Scand., 10, 174 (1956).
94. B. Hök-Bernstrom, ibid., 10, 163 (1956).
95. D. Dyrssen, ibid., 10, 353 (1953).
96. B. Hök-Bernstrom, Svensk. kem. Tidskr., 68, 34 (1956).
97. M. Dyrssen, Rec. Trav. chim., 75, 748 (1956).
98. D. Dyrssen, ibid., 75, 753 (1956).
99. B. Hök, Svensk. kem. Tidskr., 65, 1106 (1953).
100. W. Strenström and N. Goldsmith, J. Phys. Chem., 30, 1683 (1926).
101. J. Rydberg, Svensk. kem. Tidskr., 62, 179 (1950).
102. C. V. Banks and A. B. Carlson, Analyt. Chim. Acta, 7, 291 (1952).
103. A. P. Zozulya, N. N. Mezentseva, V. M. Peshkova, and Yu. K. Yur'ev, Zhur. Anal. Khim., 14, 17 (1959).
104. D. Dyrssen and B. Hök, Svensk. kem. Tidskr., 64, 80 (1952).
105. D. Dyrssen, ibid., 64, 213 (1952).
106. J. Rydberg, ibid., 65, 37 (1953).
107. B. Hök, ibid., 65, 182 (1953).
108. D. Dyrssen, Acta Chem. Scand., 8, 1394 (1954).
109. D. Dyrssen and E. Johanson, ibid., 9, 763 (1955).
110. M. Davies and H. E. Hallen, J. Chem. Educ., 33, 322 (1956).
111. D. S. Goodman, J. Amer. Chem. Soc., 80, 3887 (1958).

112. N. P. Komar', Trudy Khim. Fak. i Nauch.-issled. Inst. Kharkov. Gos. Univ., 14, 119 (1956).
113. Idem, ibid., 14, 119 (1956).
114. R. A. Morton, A. Hassan, and T. C. Calloway, J. Chem. Soc., 883 (1934).
115. M. L. Eidinoff, J. Amer. Chem. Soc., 67, 2073 (1945).
116. L. J. Bellamy and L. Beacher, J. Chem. Soc., 4487 (1954).
117. L. J. Bellamy and L. Beacher, ibid., 4491 (1954).
118. M. Calvin and K. W. Wilson, J. Amer. Chem. Soc., 67, 2003 (1945).
119. M. L. Eidinoff, ibid., 67, 2072 (1945).
120. I. Salvinien and C. Garrigues, Compt. rend., 242, 504 (1956).
121. M. Adolf and W. Pauli, Kolloid Z., 29, 173 (1921).
122. R. E. Connick and W. H. McVey, "The Aqueous Chemistry of Zirconium", UCLP-101, March, 1948.
123. W. H. Reas, Thesis, University of California, 1948.
124. R. E. Connick and W. H. McVey, J. Amer. Chem. Soc., 71, 3182 (1949).
125. R. E. Connick and W. H. Reas, ibid., 73, 1171 (1951).
126. A. I. Zielen and R. E. Connick, ibid., 78, 5785 (1956).
127. W. B. Blumenthal, J. Chem. Educ., 26, 472 (1949).
128. E. Huffman and L. Beaufait, J. Amer. Chem. Soc., 71, 3179 (1949).
129. K. A. Kraus and J. S. Johnson, ibid., 75, 5768 (1953).
130. J. S. Johnson and K. A. Kraus, ibid., 78, 3937 (1956).
131. B. A. J. Lister and L. A. McDonald, J. Chem. Soc., 4315 (1952).
132. E. M. Larsen and P. Wang, J. Amer. Chem. Soc., 76, 6223 (1954).
133. R. W. Stoughton, et al., Atomic Energy Comm. Report, AECD-2429, 1948; cited in ref. [135].
134. T. L. Zebroski, H. W. Alter, and G. K. Heumann, J. Amer. Chem. Soc., 73, 5646 (1951).
135. R. A. Day and R. W. Stoughton, ibid., 72, 5662 (1950).
136. W. C. Waggener and R. W. Stoughton, J. Phys. Chem., 56, 1 (1952).
137. F. J. C. Rossotti and H. Rossotti, Acta Chem. Scand., 10, 779 (1956).
138. G. Biedermann, Arkiv Kemi, 9, 175, 227 (1956).
139. T. Moeller, J. Amer. Chem. Soc., 63, 1206 (1941).
140. L. G. Hepler and Z. Z. Hugus, ibid., 74, 6115 (1952).
141. K. A. Allen, ibid., 80, 4133 (1958).
142. R. H. Betts and R. K. Leigh, Canad. J. Res., 28B, 1514 (1950).
143. R. H. Betts and R. H. Michels, J. Chem. Soc., 286 (1949).
144. H. M. Irving, F. J. C. Rossotti, and R. J. P. Williams, ibid., 1906 (1955).
145. D. E. Chalkley and R. J. P. Williams, ibid., 1920 (1955).
146. H. Irving and F. J. C. Rossotti, ibid., 1927 (1955).
147. H. Irving and F. J. C. Rossotti, ibid., 1938 (1955).
148. H. Irving and F. J. C. Rossotti, ibid., 1946 (1955).
149. F. J. C. Rossotti, Rec. Trav. chim., 75, 743 (1956).
150. H. Irving and F. J. C. Rossotti, J. Chem. Soc., 2475 (1956).
151. H. Rossotti, Rec. Trav. chim., 75, 763 (1956).
152. H. Irving and F. J. C. Rossotti, Analyst, 77, 801 (1952).
153. H. M. Irving and R. J. P. Williams, ibid., 77, 813 (1952).
154. H. L. Friedman and G. R. Haugen, J. Amer. Chem. Soc., 76, 3294 (1954).
155. R. Powell and C. G. Taylor, Chem. and Ind., 726, (1954).
156. J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions" Copenhagen, 1941.
157. N. H. Nachtrieb and J. G. Conway, J. Amer. Chem. Soc., 70, 3547 (1948).
158. N. H. Nachtrieb and R. E. Fryxell, ibid., 70, 3552 (1948).
159. F. W. Cornish, Atomic Energy Research Establishment, S/R 891; cited in ref. [144].
160. J. W. Rothe, Stahl und Eisen, 12, 1052 (1892).
161. J. W. Rothe, Chem. News, 66, 182 (1892).
162. A. C. Langmuir, J. Amer. Chem. Soc., 22, 102 (1900).
163. E. F. Kern, ibid., 23, 689 (1901).
164. F. N. Speller, Chem. News, 83, 124 (1901).
165. N. Kolossowsky, Bull. Soc. chim. France, 37, 372 (1925).
166. R. M. Dodson, G. Forney, and E. H. Swift, J. Amer. Chem. Soc., 58, 2573 (1936).
167. I. Axelrod and E. H. Swift, ibid., 62, 33 (1940).
168. S. Kato and R. Ishii, Sci. Papers Inst. Phys. Chem. Res. Tokyo, 36, 82 (1939).
169. B. V. Nekrasov and V. V. Ovsyankina, Zhur. Obshch. Khim., 11, 573 (1941).
170. N. H. Nachtrieb and R. A. Fryxell, J. Amer. Chem. Soc., 74, 897 (1952).
171. R. J. Myers, D. E. Metzler, and E. H. Swift, ibid., 72, 3767 (1950).
172. R. J. Myers and D. E. Metzler, ibid., 72, 3772 (1950).
173. D. E. Metzler and R. J. Myers, ibid., 72, 3776 (1950).
174. D. E. Campbell, A. H. Laurene, and H. M. Clark, ibid., 75, 6193 (1952).
175. A. H. Laurene, D. E. Campbell, S. E. Wiberley, and H. M. Clark, J. Phys. Chem., 60, 901 (1956).
176. H. L. Friedman, J. Amer. Chem. Soc., 74, 5 (1952).
177. D. E. Campbell, T. M. Clark, and W. H. Bauer, J. Phys. Chem., 62, 506 (1958).
178. G. A. Gamlen and D. O. Jordan, J. Chem. Soc., 1435 (1953).
179. E. H. Swift, J. Amer. Chem. Soc., 46, 2375 (1924).
180. D. C. Grahame and G. T. Seaborg, J. Amer. Chem. Soc., 60, 2524 (1938).
181. N. H. Nachtrieb and R. A. Fryxell, J. Amer. Chem. Soc., 71, 4035 (1949).
182. F. C. Edwards and H. F. Viogt, Analyt. Chem., 21, 1204 (1949).
183. G. M. Arcand, J. Amer. Chem. Soc., 79, 1865 (1957).
184. G. O. Brink, P. Kafalas, R. A. Sharp, E. L. Weiss, and J. W. Irvine, ibid., 79, 1303 (1957).
185. D. L. Horrocks and H. F. Voigt, ibid., 79, 2440 (1957).
186. J. Saldick, J. Phys. Chem., 60, 500 (1956).
187. J. F. Steinbach and H. Freiser, Analyt. Chem., 26, 375 (1954).
188. W. A. E. McBryde and J. H. Yoe, ibid., 20, 1094 (1948).
189. R. H. Herbert and J. W. Irvine, J. Amer. Chem. Soc., 76, 987 (1954).
190. H. L. Friedman and H. Taube, ibid., 72, 3362 (1950).
191. B. G. F. Carleson and H. Irving, J. Chem. Soc., 4390 (1954).
192. E. Glueckauf, H. A. C. McKay, and A. R. Mathieson, Trans. Faraday Soc., 47, 437 (1951).
193. I. Nelidow and R. M. Diamond, J. Phys. Chem., 59, 710 (1955).
194. R. M. Diamond, ibid., 61, 69 (1957).
195. R. M. Diamond, ibid., 61, 74 (1957).
196. I. P. Alimarin and V. N. Polyanskii, Zhur. Anal. Khim., 8, 266 (1953).
197. F. G. Zharovskii, Zhur. Neorg. Khim., 2, 623 (1957).
198. J. Rydberg and B. Bernstrom, Acta Chem. Scand., 11, 86 (1957).
199. B. D. Blaustein and J. W. Gryder, J. Amer. Chem. Soc., 79, 540 (1957).
200. V. M. Vdovenko, A. A. Lipovskii, and M. G. Kuzina, Zhur. Neorg. Khim., 2, 975 (1957).
201. F. R. Bruce, J. M. Fletcher, and H. H. Hyman (Eds.), "Progress in Nuclear Energy", Series 3, "Process Chemistry", Pergamon Press, London.
202. E. K. Hyde, ibid., p. 393.
203. V. V. Fomin and E. P. Maiorova, Zhur. Neorg. Khim., 3, 540 (1958).
204. N. S. Povitskii, A. S. Solovkin, and I. V. Shilin, ibid., 3, 222 (1958).
205. V. B. Shevchenko, I. V. Shilin, and A. S. Solovkin, ibid., 3, 225 (1958).
206. D. Dyrssen, Acta Chem. Scand., 11, 1771 (1957).
207. H. A. MacKay, see ref. 201, p. 496.
208. E. Hesford, H. A. C. McKay, and D. Scargill, J. Inorg. Nuclear Chem., 4, 321 (1957).

209. T.V.Healy and H.A.C.McKay, Rec.Trav.chim., 75, 730 (1956).
210. V.V.Fomin and E.P.Maiorova, Zhur.Neorg.Khim., 1, 1703 (1956).
211. Idem, ibid., 1, 2749 (1956).
212. W.H.Hardwick, R.Todd, and P.Swift, Atomic Energy Research Establishment, C/M 152 (1955); cited in ref.[208]
213. F.L.Kuller, see ref. 201, p. 258.
214. D.F.Peppard, G.W.Mason, and J.L.Maier, J.Inorg.Nuclear Chem., 3, 215 (1956).
215. A.T.Greski, see ref. 201, p.141
216. S.M.Karpacheva, L.P.Khorkhorina, and A.M.Rozen, Zhur. Neorg.Khim., 2, 1441 (1957).
217. H.A.C.McKay, Trans.Faraday Soc., 52, 39 (1956).
218. F.Hadswel and J.M.Hayden, see ref. 201, p.541.
219. A.Alcock, F.C.Bedrod, W.H.Hardwick, and H.A.C.McKay, J.Inorg.Nuclear Chem., 4, 100 (1957).
220. A.S.Solovkin, Zhur.Neorg.Khim., 2, 611 (1957).
221. A.E.Levitt and H.Freund, J.Amer.Chem.Soc., 78, 1545 (1956).
222. D.Scargill, K.Alcock, J.M.Fletcher, E.Hesford, and H.A.C.McKay, J.Inorg.Nuclear Chem., 4, 304 (1957).
223. G.F.Best, H.A.C.McKay, and P.R.Woodgate, ibid., 4, 315 (1957).
224. T.V.Healy and H.A.C.McKay, Trans. Faraday Soc., 52, 633 (1956).
225. A.V.Nikolaev, A.A.Sorokina, and A.S.Maslennikova, Zhur. Neorg.Khim., 3, 160 (1958).
226. R.L.Andelin, E.L.Anderson, and W.H.McVey, U.S.Atomic Energy Comm.Report, IDO-14381, 26 (1956); cited in Chem. Abs., 51, 2361 (1957).
227. V.D.Nikol'skii and V.S.Shmidt, Zhur.Neorg.Khim., 2, 2746 (1957).
228. M.Chatelet and C.Nicaud, Compt.rend., 242, 1891, 1471 (1956).
229. V.B.Shevchenko, A.S.Solovkin, and I.V.Shilin, Zhur.Neorg. Khim., 3, 1965 (1958).
230. T.H.Siddall, U.S.Atomic Energy Comm.Report, DP-181, 22 (1956); cited in Chem.Abs., 51, 12718a (1957).
231. B.Bernstrom and J.Rydberg, Acta Chem.Scand., 11, 1173 (1957).
232. J.C.Warf, J.Amer.Chem.Soc., 71, 3257 (1949).
233. T.W.Newton and G.M.Arcand, ibid., 75, 2449 (1953).
234. A.W.Wylie, J.Chem.Soc., 1474 (1951).
235. V.B.Shevchenko, V.A.Mikhailov, and Yu.P.Zaval'skii, Zhur.Neorg.Khim., 3, 1955 (1958).
236. V.A.Mikhailov, V.B.Shevchenko, and V.A.Kolchanov, ibid., 3, 1959 (1958).
237. E.P.Maiorova and V.V.Fomin, ibid., 3, 1937 (1958).
238. H.M.Neumann, J.Inorg.Nuclear Chem., 4, 349 (1957).
239. H.A.C.McKay and A.R.Mathieson, Trans. Faraday Soc., 47, 427 (1951).
240. H.I.Schlesinger and H.E.Van Valkenburgh, J.Amer.Chem. Soc., 53, 1212 (1931).
241. K.M.Mitchell and J.Y.MacDonald, J.Chem.Soc., 1310 (1951).
242. J.Y.McDonald, K.M.Mitchell, and A.T.S.Mitchell, ibid., 1574 (1951).
243. L.Melnick and H.Freiser, Analyt.Chem., 25, 856 (1953).
244. L.Melnick and H.Freiser, ibid., 27, 462 (1955).
245. R.Bock, Z.anal.Chem., 133, 110 (1951).
246. C.S.Shaw, Z.phys.Chem., 204, 194 (1955).
247. C.S.Shaw, ibid., 204, 207 (1955).
258. C.S.Shaw, ibid., 205, 6 (1955).
249. J.Schubert, E.L.Lind, W.M.Westfall, R.Pfleger, and N.C.Li, J.Amer.Chem.Soc., 80, 4799 (1958).
250. R.P.Seward, ibid., 76, 4850 (1954).
251. B.I.Thamer, ibid., 79, 4298 (1957).
252. H.L.Friedman and G.R.Haugen, ibid., 76, 2060 (1954).
253. R.G.Wille and M.L.Cood, ibid., 79, 1040 (1957).
254. C.F.Baes, U.S.Atomic Energy Comm. Report ORNL-1930, 36 (1955); cited in Chem.Abs., 50, 6877a (1956).
255. Y.Tsuzuki, Bull.Chem.Soc.Japan, 13, 337 (1938).
256. C.Columbic and S.Weller, J.Amer.Chem.Soc., 74, 3739 (1952).
257. H.C.Moser and A.F.Voigt, J.Inorg.Nuclear Chem., 4, 354 (1957).
258. Z.Hagimura, Technol.Repts.Tohoku Univ., 18, 16 (1953).
259. I.Qvarfort and L.G.Sillén, Acta Chem.Scand., 3, 505 (1949).
260. K.B.Yatsimirskii, Zhur.Neorg.Khim., 1, 2306 (1956).
261. F.J.C.Rossotti and H.S.Rossotti, Acta Chem.Scand., 9, 1166 (1955).
262. F.J.C.Rossotti, H.Rossotti, and L.G.Sillén, ibid., 10, 186 (1956).
263. F.J.C.Rossotti, H.Rossotti, and L.G.Sillén, ibid., 10, 203 (1956).
264. L.G.Sillén, ibid., 10, 803 (1956).

Zhdanov State University,
Leningrad