

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON EQUILIBRIUM DATA*

**Critical Evaluation of Equilibrium Constants in Solution
Part A: Stability Constants of Metal Complexes**

**CRITICAL SURVEY OF STABILITY
CONSTANTS OF NTA COMPLEXES**

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*Membership of the Commission for 1981-83 is as follows:

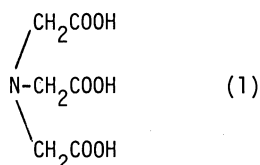
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CRITICAL SURVEY OF STABILITY CONSTANTS OF NTA COMPLEXES

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1. INTRODUCTION

Nitrilotriacetic acid (1) is one of the simplest aminopolycarboxylic acids which, in the fully deprotonated form, can act as a general sequestering agent for all metal ions (61 S).



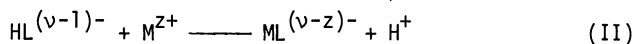
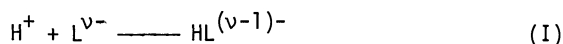
This is due to the presence of one selective N donor and of three general O donors which can form, by coordination, three stable 5-membered chelate rings. Because of the presence of a basic nitrogen atom, its sequestering tendency is strongly dependent on the pH value of the solution. Ionic equilibria involving (1) has been of interest to both analytical chemists and to industry (detergent, plant nutrition, pulp and paper manufacture, industrial and boiler cleaning (75 M)). Almost 150 papers have appeared in which equilibria involving this ligand with hydrogen or metal ions are discussed and described by means of numerical data. In this survey all numerical data for these equilibria are critically discussed, especially in relation to the systems used (salts, solutions, apparatus, techniques, ...) to obtain the experimental data and the methods used for the calculations and refinements. A question mark indicates situations where the required information is not given in the literature or for cases for which the literature was inaccessible. The numerical data are then classified according to four categories: recommended, tentative, doubtful and rejected (75 W). In this introduction the methods used for the investigations and calculations are presented chronologically. In this way it is possible to follow the reasons which have led to the introduction of new methods and devices. Indeed, dating from the publication of Jannik Bjerrum's thesis, the techniques for the determination of equilibrium data have received impulses from different scientific approaches and from technological progress.

2. INVESTIGATION OF EQUILIBRIA

For each method a selection of papers is considered and discussed in detail. No attempt has been made to be exhaustive and the choice of the literature simply reflects the questions

to be discussed. NTA as a tetradentate ligand can form not only 1 : 1 but also 1 : 2 complexes. Further, in the presence of other ligands L^* , mixed complexes $M(NTA)L^*$ can also be formed (the data for such species are given in a separate chapter). The values of the thermodynamic functions ΔG^0 , ΔH^0 and ΔS^0 for the equilibria are tabulated in the appendix.

Although nitrilotriacetic acid was synthesized by Heintz^a in 1862, the first observation of its strong sequestering power for alkaline earth cations was discovered approximately seven decades later. Heintz mentioned the initial deep blue color of neutral solutions of this acid in the presence of copper salts, followed by precipitation of a solid phase (the solution remaining was observed to be acidic); however these observations were not understood and not further explored. In 1917, Dubsy and Spritzmann (17 D) concluded from the composition of the copper(II) complex salts that coordination of the nitrilotriacetate ion occurs via four donor atoms. The water softening properties of aminocarboxylic acids were first mentioned in a patent of the I.G. Farbenindustrie in Frankfurt am Main (D.R.P.N. 718981) of 31 October 1935. In particular, if such acids have more than one carboxylate group per nitrogen atom: "It seems, as if the calcium ion would be bound in complex form by the mentioned aminoacids". In this, NTA was one of the more efficient of the acids investigated. After the discovery of this water softening property, some preparative work was carried out by Pfeiffer (42 P) who obtained, in the presence of calcium ions, a 1 : 2 complex salt, $K_2Ca(NTA)_2 \cdot 4H_2O$ ^b. It was at this time that Schwarzenbach began an investigation of the equilibria between aminocarboxylic acids and metal ions using potentiometric pH measurements. The direct pH method is based on the fact that the pH values of solutions of the protonated ligand alone (case A) or in the presence of a metal ion (case B) when neutralized by stepwise addition of a strong base, allow the evaluation of the constants for the equilibria involved:



Equilibria I and II refer to the simple case of a monoprotic acid whose anion forms 1 : 1 complexes only. The equilibrium constant for I is identical to the protonation constant $K_{1,H}$ ($\text{dm}^3 \text{mol}^{-1}$) for the anion, where brackets are used to denote the concentration expressed

$$K_{1,H} = \frac{[HL]}{[H][L]}$$

in mol dm^{-3} . From the equilibrium constant of II, K_{II} , it is possible to obtain the stability constant K_f of ML as follows:

Note a. W. Heintz, *Annalen* 122, 260 (1862)

Note b. For information about other complex salts: see Gmelin Vol.IV, III Supplement

$$K_1 = \frac{[ML]}{[M][L]} = \frac{[H][ML]}{[M][HL]} \frac{[HL]}{[H][L]} = K_{II} K_{1,H}$$

For the sake of simplicity the charges are omitted. The relations between the total concentration of the ligand $[L]_t$, the metal ion $[M]_t$, and the dissociable protons $[H]_t$, are:

$$\begin{array}{l} \text{case A} \\ \text{case B} \end{array} \left\{ \begin{array}{l} [L]_t = [L] + [HL] \\ [H]_t = [H] + [HL] - [OH] = [L]_t - [OH]_t \\ \\ [L]_t = [L] + [HL] + [ML]; \quad [M]_t = [M] + [ML] \\ [H]_t = [H] + [HL] - [OH] = [L]_t - [OH]_t \end{array} \right.$$

where $[OH]_t$ is the concentration of strong base added to the solution of the monoprotonic acid. These relationships are reduced in the first case to:

$$\bar{p} + (\bar{p} - 1) K_{1,H} [H] = 0 \quad \text{with } \bar{p} = [HL]/[L]_t$$

and in the second to:

$$\bar{n} + (\bar{n} - 1) K_1 [L] = 0$$

$$\text{with } \bar{n} = [ML]/[M]_t = \{[L]_t - ([L]_t - [OH]_t + [OH] - [H]) / ([H] K_{1,H})\} / [M]_t$$

The above relationships remain linear in the unknown constants if the maximum number of protons bound to L (= P) is > 1 and that of ligand molecules (= N) bound to M is > 1 (61 R, 65 A):

$$\sum_0^P (\bar{p} - p) \kappa_p [H]^p = 0$$

$$\sum_0^N (\bar{n} - n) \beta_n [L]^n = 0$$

$$\text{with } \kappa_p = [H_p L] / ([H]^p [L]) \quad \text{and} \quad \beta_n = [ML_n] / ([M] [L]^n) = K_1 K_2 \dots K_n$$

For each pair of values \bar{p} , [H] or \bar{n} , [L] one linear equation in the involved unknown ($K_{1,H}$ or K_1) or unknowns (κ_p or β_n) is obtained. If the number of pairs of values is equal to or greater than that of the unknowns, the calculation of the constants can be done with standard methods. Normally the number of pairs is high, which allows the use of statistical (least squares) methods giving not only the "best values" for the constants but also their standard deviations as well as the precision of the measurements. Concerning the basis of these methods

in ionic equilibria calculations the papers of Sillén (63 Sa, 63 Sb) give the needed information. It is not difficult to develop procedures for the computer calculation of the stability constants (77 P). The literature does not always list sufficient information concerning determined stability constants to evaluate the reliability of the experiments used. For simple systems involving formation of mononuclear species, it is normally sufficient to list the standard deviation of the constants $\sigma(\beta_n)$ or $\sigma(\kappa_p)$, but in more complicated cases the standard deviation of the proton number $\sigma(\bar{p})$ and/or the ligand number, $\sigma(\bar{n})$ should also be included since they give a measure of the precision of each single result from the "expected". On the contrary, the value of the standard deviation of a constant depends also on the relative concentration of the species involved.

These relationships are no longer valid if protonated or hydroxo metal complexes are formed. Their use is straightforward if the measurements are made at constant ionic strength, because it is then possible to measure the hydrogen ion concentration ($[H^+] = 10^{-pH}$) of the solution after calibrating the cell with solutions of known hydrogen ion concentration (using strong acids or buffer solutions). The constant ionic strength should preferably be maintained with the same inert salt as that used in the measurements. With this precaution it is possible to minimize the diffusion potential if cells with a liquid junction are used. Corrections are necessary for solutions in which the concentrations of H^+ or OH^- are higher than 0.5% of the ionic strength on a molarity scale, because of the extremely high mobility of these ions. The above method had already been used by different authors (e.g., in the determination of pK values of acids by Simms (26 S) and of stability constants of complexes by Cannan and Kibrick (38 C)) before Bjerrum gave the first complete and detailed description of the procedure in his dissertation (41 B).

Graphical representation of titration curves allows the following information to be obtained:

- (i) the purity of the protonated ligand can be estimated from the calculated equivalent weight and the shape of the curve
- (ii) detection of the presence of undesired pH buffering impurities
- (iii) data concerning the compositions of the complexes formed (if the stability constants are $> 10^4$).

The last information is especially important in relation to the calculation of stability constants. On the basis of such results it was possible, for instance, to demonstrate that only 1 : 1 and 1 : 2 complexes (60 A) are present in acidic solutions of trivalent lanthanide ions and NTA and with the absence of 2 : 3 complexes (57 N). In Fig. 1 are given the titration curves of (i) the triprotonated ligand alone (A); (ii) the ligand in the presence of Ca^{2+} (B); and (iii) in the presence of Cu^{2+} (C), at $I = 0.1$ (KNO_3) and $25^\circ C$. The total concentration of the cations ($1 \cdot 10^{-3} M$) is half that of the ligand ($2 \cdot 10^{-3} M$), so that formation of both ML^- and ML_2^{4-} can be realized during the titration. With both metal ions the formation of the 1 : 1 and 1 : 2 complexes takes place in two distinct pH ranges. For Ca^{2+} (and Cu^{2+}) the complex CaL^- (CuL^-) is formed at pH 5 - 7 (< 4) and CaL_2^{4-} (CuL_2^{2-}) and pH 9 - 11 (8 - 10). Evaluation using least squares procedures gives the following constants:

$$\text{Ca}^{2+} \log K_1 = 6.41 (1) \quad \log K_2 = 2.47 (5)$$

$$\text{Cu}^{2+} \log K_1 = 11.2 (1) \quad \log K_2 = 4.24 (3) \quad \log \frac{[\text{CuL}(\text{OH})] [\text{H}]}{[\text{CuL}]} = 9.17 (3)$$

Standard deviation of the ligand number: $\sigma_{\bar{n}} = 0.005$

In parentheses three times the standard deviation of the last digits are shown. Because CuL^- is already formed at the beginning of the titration its formation constant is very uncertain; this fact will be further discussed.

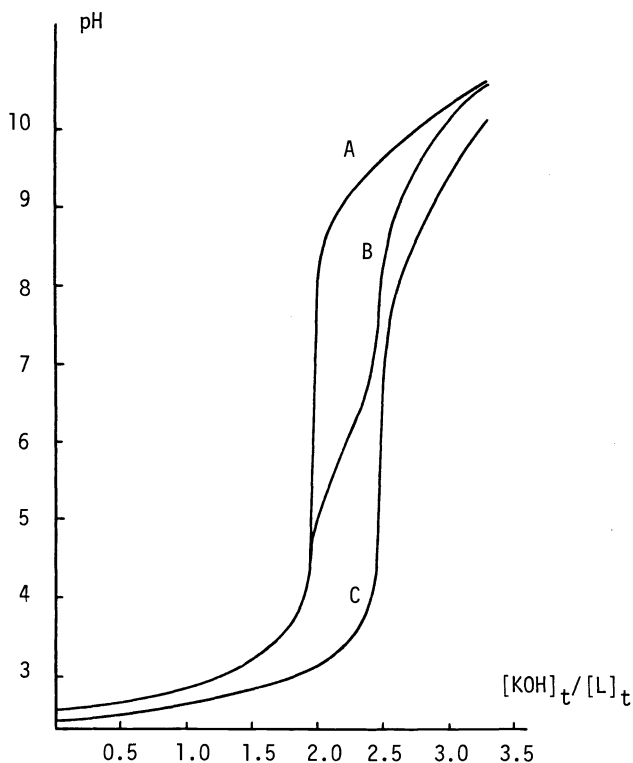
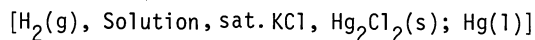


Fig. 1. Titration curves of nitrilotriacetic acid

Sometimes a large error in a constant results from the presence of other species in low concentration. An exact understanding of the situation is often possible only after large variations of the total concentrations of the components have been studied. This can be done only if the ionic strength of the system is high enough to allow such alteration of the composition without significant interference with the ionic medium (activity). At ionic strength 0.1 M (the most widely used ionic strength), such alterations are practically impossible! More recent studies have therefore employed an ionic strength of 1 M or more.

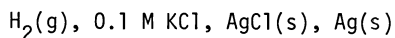
In the first communication of the series "Komplexe", Schwarzenbach (45 S) gave a list of constants for 1 : 1 complexes of Li^+ , Na^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} . As no inert salt was present the ionic strength of the solutions changed during the titration, the calculation of

the constants at ionic strength $\rightarrow 0$ is appropriate. This implies the use of the activity coefficients of the species involved, but since the total concentration of the ions present was approximately millimolar, the use of the Debye-Hückel limiting law is justified. Activities instead of concentrations were then inserted in the expressions to obtain the thermodynamic constants. Schwarzenbach used the following cell:



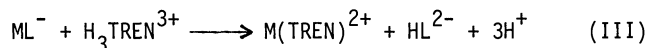
with a sat. KCl agar bridge. The standardization of the cell with the hydrogen electrode was carried out by titration of acetic and benzoic acids. The pK values obtained for H_3L and H_2L^- (3.03 and 3.07) are very questionable if compared with those obtained at $I = 0.1$ (1.89 and 2.49) and this has been discussed by Schwarzenbach. In the dissertation of Kampitsch published some years later (1949), the inadequacy of the method is considered "because of the impossibility of the mathematical or experimental elimination of the diffusion potential" (49 K). It should be further mentioned that anomalous pK values were also obtained for uramildiacetic acid which has two deprotonation equilibria in acidic solution. The pK values also "became" reasonable at ionic strength 0.1 (1.7 and 2.67) (63 I) compared with the values for $I = 0$ (3.75 and 2.86 (46 S)). A correction for liquid junction potential was introduced in Schwarzenbach's laboratory only after 1954; mathematical elimination of this potential was carried out by use of the formula of Henderson (7 H). Because of this difficulty, Schwarzenbach in 1949 introduced KCl as inert salt, and this enabled the use of an AgCl, Ag electrode directly in the solution without liquid junction.

In a second paper Schwarzenbach (48 S) demonstrated that the "thermodynamic stability constants" of Cd^{2+} , Co^{2+} , Fe^{2+} , Mn^{2+} , Ni^{2+} , Zn^{2+} , Ce^{3+} , Al^{3+} and Fe^{3+} should be greater than 10^{10} and therefore not able to be evaluated using the pH method just described because the complex is already formed in the initial solution and the titration corresponds to neutralization of free hydrogen ions as well as those bound to excess of the ligand. The further neutralization of the mixture enables the formation of 1 : 2 complexes and the formation of hydroxo complexes to be followed. The values of the equilibrium constants for these two complex types for $I \rightarrow 0$ are given with a precision of ± 0.2 in logarithmic units. Another difficulty in the investigation of equilibria involving variable and low ionic strength arises from the uncertainty in the calculated activity coefficients especially if the ionic charge is high as, for instance, it is the case for aminopolycarboxylate anions. The measurements involving nitrilotriacetic acid and alkaline earth cations were therefore repeated by Schwarzenbach (49 S) with the following cell, in which the concentration of chloride was held constant at 0.1 M. For standardization, titration of acetic acid using the

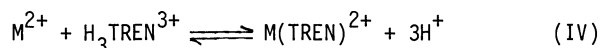


pK value of Harned and Owen (43 H) was employed. This practice could be followed because Ag^+ forms weak complexes with aminopolycarboxylate anions. To maintain a constant chloride concentration, the solution of strong base used for the titration was made 0.1 M in KCl (50 W). The difficulties encountered in the investigation of stable 1 : 1 complexes have been overcome by Ackermann and Schwarzenbach (49 A) by use of pH measurements applied to the exchange

reaction III. The stable complex ML^- reacts with a protonated amine, TREN (2, 2', 2''-tri-



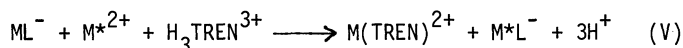
aminotriethylamine), in a suitable pH range to allow an exact determination of the equilibrium constant involved. This has been carried out for the system with $M^{2+} = Zn^{2+}$. The stability constant for ML^- is obtained by combination of the determined equilibrium constant K_{III} with the constant for equilibrium IV together with the protonation constants for L^{3-} . For Cu^{2+} ,



the 1 : 1 NTA complex is very stable with respect to the 1 : 1 TREN complex and reaction III takes place at quite high pH. With the introduction of a second metal ion M^{*2+} , which forms

$$\frac{[ML]}{[M][L]} = \frac{[H]^3 [M(TREN)]}{[H_3TREN][M]} \frac{[HL]}{[H][L]} \frac{1}{K_{III}}$$

complexes only with NTA, the exchange reaction V occurs in a suitable pH range such that



an accurate value of the equilibrium constant can be obtained. In this last case the stability constant of M^*L^- must also be known. Note that the equilibrium constants for the TREN complexes can be obtained by the usual pH method. Because all the pK values of H_3TREN^{3+} are quite high (8.56; 9.59 and 10.29), it is possible to evaluate stability constants up to 10^{20} in this way, instead of the 10^9 limit when only NTA is present. Using similar equilibria Schwarzenbach and Freitag (51 S) obtained the stability constants for the 1 : 1 NTA complexes with Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and La^{3+} . The values for the complexes of the first two cations have also been obtained using the standard pH method ($K_1 < 10^9$!) and are reported in the same work. The higher value was obtained for $FeNTA^-$ with $\log K_1 = 8.82$. For millimolar solutions of the ferrous ion and of the monoprotonated ligand HL^{2-} , the ligand number \bar{n} before any base addition will already be 0.271 therefore a lower precision of K_1 with respect to that for weaker complexes would be expected. In spite of the above limitation for the direct pH method, the literature contains papers using this method to determine stability constants $> 10^{10}$ with NTA as ligand. The decrease in precision of the K values due to the increased ligand number in acidic solutions can be followed in the graphical representation of the $\log K_1$ values. These correspond to the pH values of the solutions with

millimolar concentrations of the components ($[M]_t = [L]_t = 10^{-3}M$) at half neutralization of HL^{2-} with strong base (Fig.2). For $\log K_1$ values between 3 and 9 a linear dependence with the

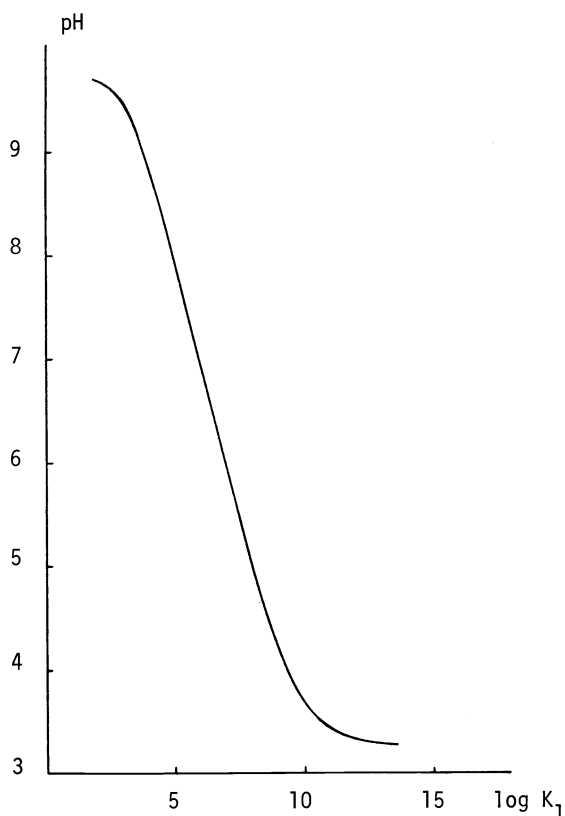


Fig. 2. pH values at half neutralization of HL^{2-} for millimolar solutions of the components versus $\log K_1$

pH value is observed with $d \log K_1 / d \text{pH} = -1$. This corresponds to the range for which the constant K_1 can be obtained with higher precision and an error $\sigma(\text{pH})$ of 0.01 in pH is reflected by a numerically equal error in $\log K_1$. At $\log K_1 = 10$ the error is already $3 \sigma(\text{pH})$, for $\log K_1 = 12$ it is $30 \sigma(\text{pH})$ and for $\log K_1 = 13$ it is $66 \sigma(\text{pH})$. Further it is necessary to consider other sources of error, such as those in the analytical total concentrations of the components: metal ion, ligand and strong base. These errors are equal in magnitude and in sign for all points of a curve and are therefore systematic errors. The % error in K_1 is calculated for the values of K_1 and half neutralization of HL^{2-} in Fig. 3 using the partial derivatives of K_1 with respect to the variables $[M]_t$, $[L]_t$, $[\text{OH}]_t$ and $[\text{H}]$ and the law of propagation of errors. It appears that the error due to $[L]_t$ can be especially relevant and have more influence than those due to $[\text{OH}]_t$ and to $[M]_t$. The experimental values for the standard deviations for the different quantities are:

$$\sigma([M]_t) = 0.00005 \text{ M}, \sigma([L]_t) = 0.00005 \text{ M}, \sigma([\text{OH}]_t) = 0.00005 \text{ M} \text{ and } \sigma([\text{H}]) = 0.003 [\text{H}] \ln(10).$$

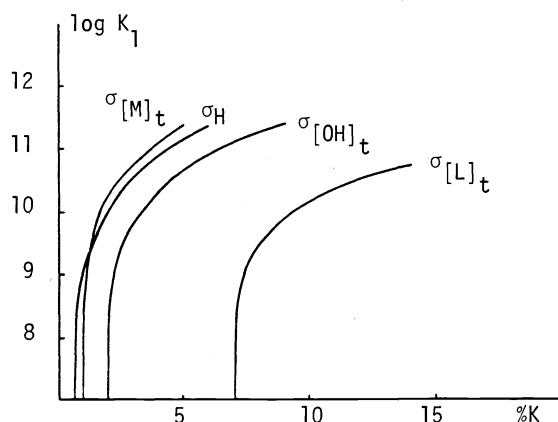
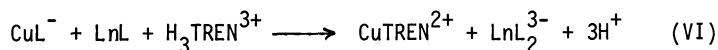


Fig. 3. The % error in $\log K_1$ from the single experimental quantities

A reduction in the errors of the total concentrations can be partially achieved by repeating the calculation of the constants after variation of the total concentrations. The best values for these analytical concentrations are those which yield the lowest standard deviations for the required constants. The treatment of the error in $[H]$ as a systematic error in the standardization of the cell is generally not meaningful because this procedure can be applied in different ways to give different final results with the same precision (79 A, 80 A).

In calculating the error of a stability constant only the errors involved in the investigated equilibrium are normally considered, whereas the values for any other (protonation equilibrium or stability) constants used in the calculation are usually arbitrarily assumed to be known exactly. For instance, in the case under discussion, the error given by Schwarzenbach (for the constants of the NTA complexes obtained with the TREN exchange equilibrium) is identical to that for the corresponding reactions of type III or IV, respectively. The figures given do not correspond to the standard deviation but to the largest deviation of $\log K_1$ after elimination of some values (51 S) which deviate in an unexpected manner in the opinion of the author. By comparison of similar results one can estimate that the error given corresponds to between 1.5 and 2 σ (σ = standard deviation of the equilibrium constant). The inclusion of errors for other constants (which are normally not included) is done by using the law of error propagation: $\sqrt{\sum_{r=1}^R \sigma_r^2}$ where σ_r is the standard deviation of the logarithm of each constant involved and R is the number of constants used in the calculation. In the case of the constants discussed above, the value of σ obtained for the stability constant of $Zn(NTA)^-$ (49 R) from reaction III is obtained by putting $\sigma_1 = 0.03$ for $\log K_{IV}$, $\sigma_2 = 0.02$ for the pK of HL^{2-} and $\sigma_3 = 0.03$ for $\log K_{III}$ given $\sigma = 0.05$, i.e. the value given by Schwarzenbach can be considered to be a good measure of the standard deviation of this stability constant.

The exchange reaction V has been used by Anderegg (60 A) and by Moeller and Ferrus (62 M) in the determination of the stability constants of the 1 : 1 and 1 : 2 NTA complexes of the lanthanide cations. The stepwise constant K_2 from La^{3+} to Gd^{3+} can also be obtained using the direct pH method ($K_2 \leq 10^{9.5}$) (60 A). Moeller and Ferrus have obtained values of K_1 (from V, with $M = Cu$ and $M^* = Ln$) and K_2 (from VI) in the temperature range from 15 to 40 °C at



intervals of 5 °C. In the course of this investigation the pK value of HL^{2-} was also measured; the authors considered the agreement of the value obtained at 20 °C (9.80) with that obtained by Schwarzenbach (9.73) to be excellent (!).

In new investigations, KNO_3 was preferred to KCl as the inert salt because NO_3^- forms much weaker complexes than Cl^- with metal ions. This makes the correction of the stability constants for the presence of chloro complexes as well as for mixed chloro NTA complexes unnecessary. In the presence of KNO_3 it is necessary to use a cell with liquid junction for pH measurements, because the reference electrodes used (calomel or AgCl , Ag) are reversible to chloride ion. This can be a source of error if the potential due to this junction changes with time. The following cells are often used:

| | | | | |
|---|-----------------|---------------------------------------|---|-----------------------------|
| A | Glass electrode | Solution at constant ionic strength I | Solution at the same ionic strength I with partial substitution of the anion with Cl^- , | HgCl , Hg |
| B | Glass electrode | Solution at constant ionic strength I | Saturated KCl solution | HgCl , Hg |

The first cell is preferred because of better constancy of the liquid junction potential due to negligible diffusion between the two solutions. Indeed, if cell B were to be proposed (70 U) for an operational definition of pH, its use should be discouraged for routine measurements of complex formation equilibria because of possible contamination of the solutions in contact.

One of the major causes of error in using buffer solution to calibrate for pH values in the activity scale arises from using buffer solutions having another composition to the solution to be measured. This type of error results from the difference in liquid-junction potential of the two solutions and is named by Bates and co-workers as "residual liquid-junction". Its importance in the measurement of the pH of blood has been discussed recently (78 B) and found to be 0.03 and 0.05 for solutions at $I = 0.1$ and 0.16 , respectively.

It should be emphasized that the determined value of a stability constant will be only exactly valid for the ionic medium (and temperature) used; the influence of the ions has to be taken into consideration in any discussion of values in different inert salts. For this reason inert salts are generally preferred which do not seriously interfere with the investigated equilibria. This should generally be the case for tetramethylammonium or tetraethylammonium perchlorate, but the former is only of low solubility and usually cannot be used. Potassium has only a weak tendency to bind NTA ($\log K_{\text{KL}} = 0.6$ ($I = 0.1$) (67 A)) and is generally used as its nitrate salt.

Hughes and Martell (56 H) determined the thermodynamic pK values for nitrilotriacetic acid as well as the thermodynamic stability constants of the 1 : 1 NTA complexes with Mn(II) , Mg(II)

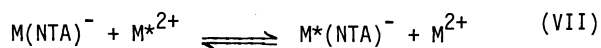
Ca(II) and Ba(II) using KCl as the inert salt and using a cell without liquid junction potential (Pt, H₂, Solution I (KCl), AgCl, Ag) for the temperatures 0, 10, 20 and 30 °C. They used only one solution for the determination of a single constant at I values between 0.02 and 0.08 M. The literature E₀ value for the reference electrode was used directly without separate calibration. The value of α in the Debye-Hückel equation was arbitrarily chosen to give a minimum slope for the extrapolated function. Because of the potassium ion association with NTA, the presence of KCl in the more dilute solutions causes a small pH decrease of 0.03 of a unit.

When investigating the equilibria between certain cations and ligands the field of measurement is very often limited to that covering only the species of interest. For instance, if one has to determine the formation constant for a 1 : 1 complex, one tries to find the experimental conditions for which, besides this species, there is only free metal ion and ligand (initially in a protonated form) present. However, side reactions are possible, especially with H₂O, to yield protonated and/or hydroxo complexes. In the case of the ligand under discussion, species of the latter type are expected. Martell was one of the first to recognize the importance of such species and he gave, for instance, formation constants for Th(OH)₂(NTA)⁻.

Biochemists show preference for mixed constants; i.e. for constants for which H⁺ activity is used for H⁺ and the concentration scale for the other species. Cohen and Wilson (66 C) determined the pK values for HL²⁻ in 1 M NaCl and 1 M NaNO₃ using, for standardization, a Fisher buffer of pH = 7 in a cell with glass and saturated Hg₂Cl₂ electrode. They determined the stability constant of ZnL⁻ using the direct pH method even though the use of this method in this case had already been discouraged by Schwarzenbach (49 S); further, in the calculations the presence of H₂L⁻ was ignored! Koryta and Kössler (50 K) have attempted to use polarographic measurements to investigate the equilibria between NTA and Zn²⁺, Cd²⁺ and Pb²⁺ in KCl solutions with I = 0.1, 0.2 and 0.3 M. They determined, from the height of the wave for the M²⁺ and M(NTA)⁻ reduction, the concentration of these species in acidic solutions containing an excess of ligand. The measured pH value and the concentration of M(NTA)⁻ together with the total concentration of ligand gave the concentration of the free

$$[\text{NTA}]_t = [\text{M(NTA)}] + \sum [\text{H}_p\text{NTA}] = [\text{M(NTA)}] + \sum \kappa_p [\text{H}]^p [\text{NTA}]$$

nitritotriacetate ion. They used for their calculations (for the system at different ionic strengths) the pK values for I = 0.1 of 49 S and no details were given concerning the pH standardization of the cell used. For both these reasons it is difficult to estimate the experimental error. Schwarzenbach has preferred to use the polarographic method to determine [M] and [M(NTA)] for solutions in which an exchange equilibrium VII between two metal ions M²⁺ and M*²⁺ takes place. The equilibrium constant for VII K_{VII} is identical to the ratio



of the stability constants of $M^*(NTA)^-$ and $M(NTA)^-$. To obtain exact values for the constants, it is necessary to know one of these constants exactly. The value of K_1 for $Cu(NTA)^-$ was therefore checked using TREN exchange V and $\log K_1 = 12.96 \pm 0.05$ (56 S) was obtained against 12.68 of 51 S. The stability constants of the 1 : 1 complexes with Zn^{2+} , Ni^{2+} , Pb^{2+} , Co^{2+} , Cd^{2+} and lanthanide cations were obtained using the exchange equilibria VII from the values of $\log K_{VII}$ given in the following scheme:

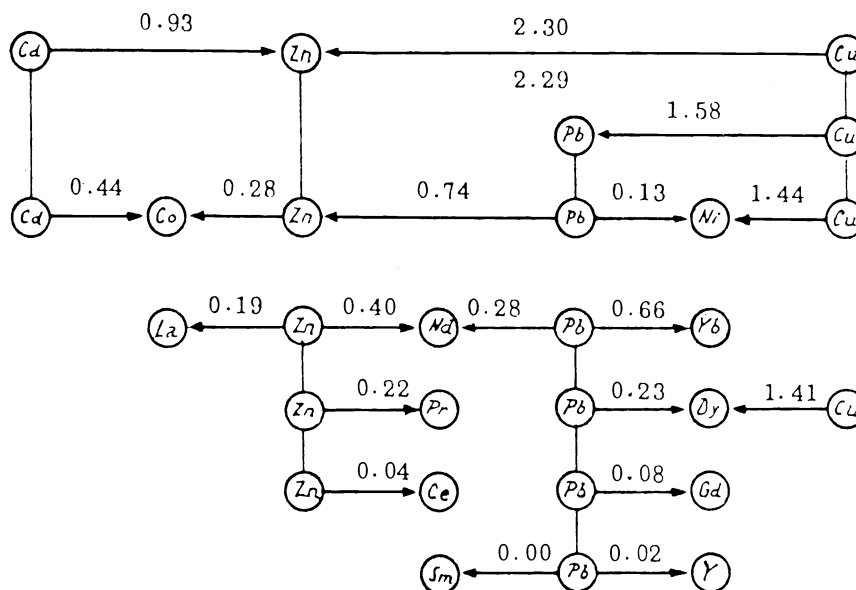


Fig. 4. Schematic representation of polarographic measurements with NTA (55 G).

An arrow ($M \rightarrow M^*$ or $M^* \leftarrow M$) separates each pair of the investigated cations. The mixtures investigated normally contained equimolar amounts of the two metal ions and of the ligand and further, the pH value of the equilibrated solutions was between 5 and 5.6. This implies that the whole concentration of ligand is bound to the metal ions in proportion to the respective stability constants. The absence of protonated species $M(NTA)H$ simplifies calculation of the equilibrium constants. Unfortunately, for some cations, sulphate salts were used to prepare the metal solution (Cd^{2+} , Mn^{2+} and Ce^{3+}) even though the SO_4^{2-} anion can alter the position of the equilibrium by formation of simple sulphato and/or mixed complexes.

A further investigation based on polarographic measurements was performed by Noddack and Oertel (57 N) using reaction VI. They determined the concentration of free Cu^{2+} or Ni^{2+} in the presence of lanthanide cations in solution containing an acetic acid acetate buffer. The stability constants of the copper and nickel 1 : 1 complexes were obtained from polarographic and pH measurements in $10^{-4}M$ solutions of both $HNTA^{2-}$ and the cations while decomposing the complex by decreasing the pH value of the solution. No details of the pH measurements are given. The complex formation with the lanthanide cations has been interpreted postulating the formation of 2 : 3 species $Ln_2(NTA)_3$. These results were

subsequently refuted by Anderegg (60 A) who demonstrated that the results can be interpreted by postulating the formation of only 1 : 1 complexes. The values obtained for the constants are very similar to those of Schwarzenbach and Gut (56 S), even though the effect of acetate ion on the equilibria has been neglected. Instead of measuring the concentration of one species as discussed above, polarography gives, from the displacement of the halfwave potential $\Delta E_{1/2}$ of reduction of a metal ion and the concentration of the free ligand [L], using equation VIII, both the number N of the ligands involved and also β_N . In the case

$$\Delta E_{1/2} = \frac{RT}{nF} \ln(\beta_N [L]^N) \quad (\text{VIII})$$

of Tl^+ the reduction wave is reversible (57 B) and the stability constant for the 1 : 1 complex has been obtained in 1 M KCl with $I = 1.35 - 1.51$ M. The standardization of the cell for pH measurements was made using potassium hydrogen phthalate buffer (pH in activity scale!) and was also used in the determination of the pK value of $HNTA^{2-}$ at $I = 1$ M (!). NTA also forms very strong complexes with Fe^{3+} , which have been investigated by Schwarzenbach and Heller (51 Sa) using pH and redox measurements on solutions of the complex as well as on $FeSO_4$ in the presence of NTA titrated with Br_2 . As the stability of the Fe(II) complexes is known, from the measured potential it is possible to determine that of the Fe^{3+} complex:

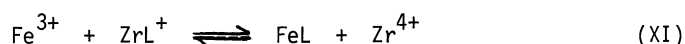
$$E = E_o + \frac{RT}{F} \ln \left(\frac{[Fe(NTA)] K_{Fe(III)NTA}}{[Fe(NTA)^-] K_{Fe(II)NTA}} \right) \quad (\text{IX})$$

Because acetate buffer was used, $Fe^{III}NTA(Ac)^-$ was taken into account but not $Fe^{II}Ac^+$ and $Fe^{II}NTA(Ac)^{2-}$. Further, the required pK values for $Fe^{III}NTA$, as obtained from measurements with solutions of this complex, were used. The stability constants of $Fe^{III}NTA(Ac)^-$, of $Fe(NTA)_2^{3-}$ (K_2) and $E_M = E_o + \frac{RT}{F} \log (K_{Fe(III)NTA} / K_{Fe(II)NTA})$ are obtained from the results of potential measurements in the pH range 3.89 - 5.19. In 1967, Irving and co-workers (67 I) and Anderegg (67 A) independently observed an increase in the solubility of the neutral protonated acid H_3L on addition of strong acid to its solution. They explained this observation in an analogous way to that already postulated for EDTA, namely: formation of H_4L^+ in which all basic groups of the ligand are protonated. The calculation of the protonation constant K_4 is done by means of relation X using pairs of values for the concentration c of the saturated NTA solution at the corresponding pH ($[H^+] = 10^{-pH}$).

$$\begin{aligned} c &= [HL] + [H_2L] + [H_3L] + [H_4L] \\ &= [H_3L] \left(\frac{1}{K_2 K_3 [H]^2} + \frac{1}{K_3 [H]} + 1 + K_4 [H] \right) \end{aligned} \quad (\text{X})$$

Using solutions at $I = 1 \text{ NaClO}_4$ it was possible to determine the protonation constant K_4 without significant change of the ionic medium in the presence of additional HClO_4 .

Spectrophotometry can also be used for determining the concentration of one (or more) species in solution and therefore used to obtain stability constants. Astakhov et al. (61 A) determined the stability constants of the 1 : 1 and 1 : 2 complexes with Pr^{3+} , Sm^{3+} and Nd^{3+} using isomolar solutions ($[\text{L}]_t + [\text{M}]_t$) in dilute solution at 18-20 °C. The spectrophotometric measurements were made at pH = 3 and 4. For the calculation of the concentration of the free NTA, a pK value for HNTA^{2-} of 10.33 (56 H) was used. Because of the variable ionic strength and temperature, only rough values are to be expected! Intorre and Martell (64 I) have investigated the equilibrium XI at pH = 2 in order to estimate the stability



constant of ZrL^+ . It was "assumed that the tetramer species is the only form of the hydrolyzed zirconium present" (!). The order of addition of the reagents was made in different ways in order to insure the achievement of equilibrium. Zhirnova et al. (65 Z) have investigated the equilibrium XII spectrophotometrically using ammonium acetate buffers in the pH range from



2.5 to 3.4 and at an ionic strength fixed "by the concentration of metal and complex ions" (!). Possible hydrolysis of the metal ions was not considered (!). Kornev et al. (66 K) investigated the complex formation in solution of thallium(III) ion in the presence of different quantities of ligand using the same method. The thallium complexes absorb strongly in the UV region. At pH 0.4 the 1 : 1 complex is formed and at pH 1.3-1.7, the 1 : 2 complex is formed. Thallium(III) was introduced as its perchlorate to avoid side reactions. The calculation of the number of protons present in the 1 : 1 and 1 : 2 complexes was carried out after making very restrictive assumptions both concerning the number of species present as well as the concentration of the non-bonded ligand. Since the formation of H_4L^+ was not considered and the ionic strength, which was mainly due to the concentration of perchloric acid (0.025 - 0.5 M), was not maintained constant - the quantitative nature of the results must therefore be considered doubtful. The spectrophotometric method was used by Eberle and coworkers for the determination of the stability constants of the 1 : 1 complexes of NpO_2^+ : $\text{NpO}_2\text{L}^{2-}$, NpO_2HL^- and $\text{NpO}_2(\text{OH})\text{L}^{3-}$ (70 E). As a ligand forming colored complexes with metal ions, 3,4-dihydroxyazobenzene-2'-carboxylic acid was used by Koremann et al. (66 Ka) to measure the stability constant of ZrNTA^+ . The measurements were made in 1 M HCl with a total zirconium concentration of 5×10^{-4} M. The authors expected that under these conditions, Zr^{4+} is present in solution chiefly in monomeric non-hydrolyzed form. The formation of H_4L^+ was not considered.

The distribution ratio of a neutral complex such as an oxinate between an organic and an aqueous phase can be changed by addition to the aqueous phase of a competing ligand such as NTA. The investigation of such two-phase equilibria between aqueous 0.1 M KClO_4 and chloroform was used by Sary (63 S) for the determination of stability constants of NTA complexes with Ag^+ , UO_2^{2+} , Be^{2+} , Co^{2+} , Cu^{2+} , Pb^{2+} , Sc^{3+} , La^{3+} and Ga^{3+} . From the ratio of the metal concentration in the organic and in the aqueous phase in the absence of (q_0) and in the presence of NTA (q) at known pH, the required values of $\beta_{s,t}$ ($= [\text{ML}_s(\text{OH})_t] / ([\text{M}][\text{L}]^s[\text{OH}]^t)$) were obtained. Such measurements were extended to a wide pH range and also involved a wide

$$q_0/q - 1 = \sum_{s=1} \sum_{t=0} \beta_{s,t} [\text{L}^{3-}]^s [\text{OH}^-]^t \quad (\text{XIII})$$

range of total concentrations of the components. The parameters q and q_0 are generally determined using radioisotopes or spectrophotometrically. Possible extraction of other species can give rise to erroneous results. Nevertheless the values of Sary are generally in good agreement with other literature values.

Instead of extracting an uncharged species with a solvent, it is sometimes possible to extract a metal ion using a cation exchange resin and by this method determine the concentration of the metal ion in the aqueous solution. This procedure is especially efficient if a suitable radionuclide is available to allow the concentration of the metal ion to be determined by radiometric tracer analysis. Eberle and Wede (68 E) have determined the stability constants of the 1 : 1 and 1 : 2 NTA complexes with Ce^{3+} , Cm^{3+} , Am^{3+} and Cf^{3+} using equation XIV in which q and q_0 are the distribution ratios of the metal ion between ion

$$1/q = (1 + \beta_1[\text{L}] + \beta_2[\text{L}]^2)/q_0 \quad (\text{XIV})$$

exchanger and solution in the absence and then in the presence of NTA. The ionic strength of the solutions at pH = 2 - 4 was maintained at 0.1 M with NaClO_4 or NH_4ClO_4 . The pK values used for H_3NTA were obtained directly from measurements in solutions with $I = 0.1$ (NaClO_4).

Although there are many possibilities for using a metal electrode to measure directly the concentration of a free metal ion, only a mercury electrode has been used to obtain the stability constants of mercury NTA complexes. The total metal and ligand concentrations were both equal to $2.5 \cdot 10^{-4}$ M; therefore 1 : 2 complexes with mercury(II) which may eventually form cannot be detected. Shorik et al. (67 S) have measured the mercury(II) concentration in the limited pH range 2.6 - 2.85 at $I = 0.1$ (NaClO_4) and 25 °C obtaining $\log K_{\text{HgL}} = 14.60 \pm 0.14$. The pK values for H_3NTA of 51 S valid for 0.1 (KCl) solutions are used. The same authors also used the mercury electrode to determine the stability constants of 1 : 1 complexes with La^{3+} , Sc^{3+} and Th^{4+} (67 Sa) using an exchange reaction of type VII. Corrections were made for hydrolysis of Sc^{3+} and Th^{4+} . The measurement, by proton n.m.r. spectroscopy,

of individual concentrations of metal chelate from the peak heights of the signals for the protons of the respective species (and eventually of the free ligand) in a competitive equilibrium of type VII was used by Merbach et al. (67 M) to determine the ratio of the stability constants of the NTA complexes involved ($\text{Pb}^{2+} - \text{Zn}^{2+}$ or $\text{Mo(VI)} - \text{W(VI)}$). Because of the high total concentration of the components needed, the ionic strength was 1.3 M without further addition of inert salts. Paper electrophoretic mobility measurements can be used to determine approximate stability constants. The electrophoretic mobility at a given free ligand concentration $[\text{L}]$ can be expressed by equation XV, in which u_i is the ionic mobility of ML_i ($u_0 = 1$). In this way Jokl (64 J) has obtained the stability constants for

$$U = u_0 \frac{[\text{M}]}{[\text{M}]_t} + u_1 \frac{[\text{ML}]}{[\text{M}]_t} + u_2 \frac{[\text{ML}_2]}{[\text{M}]_t} + u_3 \frac{[\text{ML}_3]}{[\text{M}]_t} + \dots$$

$$= \frac{\sum_i u_i \beta_i [\text{L}]^i}{\sum_i \beta_i [\text{L}]^i} \quad (\text{XV})$$

the NTA complexes of Mn^{2+} , Co^{2+} and Cu^{2+} .

3. THE STANDARD STATE

Measurements of ionic equilibria are generally made using solutions containing an inert salt which is present to maintain the ionic strength constant as far as possible. Under this condition the activity coefficients of the species investigated in such solutions will be almost constant. Complex formation between an anionic ligand and a cation will cause a change of the ionic strength, but if the concentrations of the complex partners are of the order of magnitude of 1% of the ionic strength this change can be neglected. This is especially so if the exact value of the required ionic strength of the titrated solution is reached at the middle of the buffer region under investigation.

To detect all possible equilibria in a given system large changes in concentration of the investigated components (by a factor 10 or more) are desirable. Because millimolar solutions of the components can be considered to be very near to the limit of lowest concentration for reliable measurements, these changes in concentrations require an ionic strength of at least 1 M. For the measurements with NTA the ionic strength has normally been 0.1 M and therefore only data for simple equilibria (involving formation of mononuclear species) can be considered reliable. Only in more recent papers has an ionic strength of 1 M or more been used. The inert salt is chosen such that its ions will not influence the equilibria present by forming complexes with the metal ion or the ligand under investigation. Potassium nitrate has normally been used as inert salt for NTA studies; the absence of a correction for this salt has been generally reflected by a lowering of the pK value for HNTA^{2-} in comparison with the value obtained in the presence of a cation such as the tetramethylammonium ion (which presum-

ably shows no association tendency towards NTA). In the presence of KCl, a $\log K_1$ value of 0.6 for K^+ and in the presence of $NaClO_4$ a $\log K_1$ of 1.22 for Na^+ has to be considered. This corresponds for $I = 0.1$ M to a decrease of $\log K_1$ of approx. $\log(1 + 0.1 \cdot K_1) = 0.15$ and 0.43, respectively. In the discussion and interpretation of equilibria one has sometimes to include the presence of these weak complexes.

The standard state used is represented by the solution of the inert salt. Therefore the stability constants are normally not corrected for complex formation with the ions of the inert salt. Nevertheless some caution is necessary in reading the literature because in some papers such a correction has been made (64 I). In giving the ionic strength the following two conventions are used:

0.1 (KNO₃); $I = 0.1$ by addition of the inert salt shown in parentheses and

0.1 KNO₃; I undefined but the concentration of KNO₃ is constant at 0.1 M.

However, in some papers there are insufficient details given to distinguish between them.

4. PROTONATION CONSTANTS

By analogy with the practice for metal complex formation, for protonation equilibria one has to consider protonation constants which are formally the inverse of the corresponding acidity constants. The equilibria involved have to be investigated with the same instrumentation, techniques and conditions as those used for the evaluation of stability constants. The evaluation of protonation constants is important also if literature values for the used experimental condition are known. Unverified values can lead to wrong stability constants. A millimolar solution of the uncharged ligand H_3L is quite acidic and corresponds to a protonation degree for NTA of near 1.5. Data from titration procedures allow determination of the protonation (concentration) constants K_1 , K_2 , K_3 and K_4 with concentrations in mol dm^{-3} .

$$K_1 = \frac{[HL]}{[H][L]} ; \quad K_2 = \frac{[H_2L]}{[H][HL]} ; \quad K_3 = \frac{[H_3L]}{[H][H_2L]} ; \quad K_4 = \frac{[H_4L]}{[H][H_3L]}$$

To obtain reliable values of K_4 , the titration of H_3L with a strong acid is usually necessary. The solubility of H_3L in the presence of strong acid is also adequate. Approximately 30 papers refer to independently determined protonation constants of NTA. From these, only two works report protonation constants for $I \rightarrow 0$ (thermodynamic constants). Their comparison reveals large discrepancies in $\log K_p$ values of 0.37 for $p = 1$, of 0.13 for $p = 2$ and of 1.38 for $p = 3$. In relation to the discussion on pages 6,10 and 11, it seems that the data of 56 H are more reliable and are therefore proposed as tentative values with an error which should not exceed ± 0.2 log units.

For $I = 0.1$ with KNO₃ and KCl at 20 °C:

$\log K_1$ lies between 9.73 and 9.69 (49 S, 56 S, 60 B, 66 I, 67 A)

$\log K_2$ lies between 2.49 and 2.57 (49 S, 56 S, 66 I, 67 A)

$\log K_3$ lies between 1.9 and 1.75 (49 S, 56 S, 66 I, 67 A)

The value for $\log K_1$ of Moeller and coworker (62 M) shows a similar error to that of EDTA; namely, too high with respect of the other values. The exact reason of this discrepancy is not clear because the standardization of the cell was carried out by an appropriate procedure. A similar value for $\log K_1$ is given in 75 Va, but in this case the calibration was made in the activity scale and the protonation constants are mixed constants. The values at 0.4 °C of 67 T are to be rejected because $\log K_1$ differs from the expected value by more than 0.8 log unit. For $\log K_4$ at $I = 0.1(\text{KNO}_3)$ and 20 °C only one value is available from the work of Irving and coworkers using solubility measurements. We can therefore propose the following values:

$I = 0.1(\text{KNO}_3)$ or (KCl)

20 °C $\log K_1 = 9.71(\text{R}); \log K_2 = 2.49(\text{R})$

$\log K_3 = 1.86(\text{T}); \log K_4 = 0.8(\text{T})$

For the calculation of $\log K_1$ at the same ionic strength but at other temperatures a linear interpolation of the values of 60 B is proposed. Three values of $\log K_1$ at $I = 0.1 (\text{NaClO}_4)$ or (NaClO_4) or (NaNO_3) and 25 °C have been published 9.75 (73 C), 9.49 (68 E), 9.95 (72 R, 73 Ra), but they differ considerably. The value of 72 R can be immediately discarded (standardization with pH buffers for the H^+ activity scale and "the dissociation constants were calculated from the plot of \bar{n}_H versus pH from the pH values at $\bar{n}_\text{H} = 0.5, 1.5, 2.5$ respectively"). Also the value of 73 Ra (calibration with potassium hydrogen phthalate and with titration of 0.07 M HClO_4 (!)) of the same magnitude is questionable. Because of sodium complex formation, the pK value of HL^{2-} is expected to be lower than the corresponding value in potassium salts at the same temperature. Only the value of 68 E seems to be near to that expected; in comparison with the value for 0.1 (KNO_3), it corresponds to a stability constant for NaL^{2-} of $10^{0.8}$ instead of the $10^{1.22}$ of 63 Ia. For $I = 0.5 (\text{NaClO}_4)$ or (NaNO_3) and 25 °C, three values for $\log K_1$ (9.33 (73 C), 8.94 (76 C), 8.95 (73 M)) were found. Only the first of these shows a marked discrepancy. The value of 9.95 for $\log K_1$ therefore seems appropriate. The difference between this value and that used by Choppin (9.57) (under the same conditions) is quite high. Choppin et al. (77 G) are inclined to interpret the results of measurements of $\log K_1$ in an alkaline medium as reflecting "interference by Na^+ on the electrode at high pH values". "No detectable difference between KNO_3 and NaClO_4 as supporting electrolyte was observed in the determination of the pK values of the simpler ligands". "Moreover, for the polycarboxylate ligands (EDTA, NTA, HEDTA, DCTA and DTPA), measurements of the enthalpies of protonation by titration calorimetry also showed no difference for the two supporting electrolytes". "Accordingly the values for the pK in KNO_3 and NaClO_4 ($I = 0.5$) media were used interchangeably". In view of the above discussion, it appears that Choppin's argument must be refuted. Also the values of $\log K_1$ for $I = 1 (\text{NaClO}_4)$ at 25 °C (8.92) and 20 °C (8.96) are in good agreement (in contrast to $\log K_2$, $\log K_3$ and $\log K_4$). The value given by 66 C in 1 M NaCl (8.70) was obtained using [H] in the activity scale.

TABLE 1. Protonation constants of NTA (see page 2710)

| Type of constants | Medium | t[°C] | log K ₁ ^{b)} | log K ₂ | log K ₃ | log K ₄ | Method ^a | Reference |
|-------------------|--|-------|----------------------------------|--------------------|--------------------|--------------------|---------------------|--------------|
| Thermodynamic | → 0 | 20 | 10.70 | 3.07 | 3.03 | | H | 45 S |
| Concentration | 0.1 KCl | 20 | 9.73 | 2.49 | 1.89 | | H | 49S,51Sa,56S |
| Thermodynamic | → 0(KCl) | 0 | 10.594 | 2.953 | 1.687 | | H | 56 H |
| Thermodynamic | → 0(KCl) | 10 | 10.454 | 2.948 | 1.650 | | H | 56 H |
| Thermodynamic | → 0(KCl) | 20 | 10.334 | 2.940 | 1.650 | | H | 56 H |
| Thermodynamic | → 0(KCl) | 30 | 10.230 | 2.956 | 1.660 | | H | 56 H |
| Thermodynamic | → 0(KCl) | 40 | 10 | 2.978 | 1.686 | | H | 56 H |
| Concentration | 0.1(KNO ₃) | 0.5 | 9.91 | | | | g1 | 60 B |
| Concentration | 0.1(KNO ₃) | 25 | 9.63 | | | | g1 | 60 B |
| Concentration | 0.1(KNO ₃) | 42 | 9.45 | | | | g1 | 60 B |
| Concentration | 0.1(KNO ₃) | 15 | 9.86 | | | | g1 | 62 M |
| Concentration | 0.1(KNO ₃) | 20 | 9.80 | | | | g1 | 62 M |
| Concentration | 0.1(KNO ₃) | 25 | 9.75 | | | | g1 | 62 M |
| Concentration | 0.1(KNO ₃) | 30 | 9.70 | | | | g1 | 62 M |
| Concentration | 0.1(KNO ₃) | 35 | 9.62 | | | | g1 | 62 M |
| Concentration | 0.1(KNO ₃) | 40 | 9.58 | | | | g1 | 62 M |
| Mixed | 1 NaCl | 25 | 8.70 | | | | g1 | 66 C |
| Concentration | 0.1(KCl) | 20 | 9.71(2) | 2.47(2) | 1.75(5) | | g1 | 66 I |
| | | | | 2.50 | 1.88 | | | 66 K |
| | 0.15 | 25 | 9.81(10) | | | | g1 | 66 Kc |
| Concentration | 0.1[(CH ₃) ₄ NC1] | 20 | 9.87 | | | | | 67 A |
| Concentration | 0.1(KNO ₃) | 20 | 9.73 | 2.5 | 1.9 | | g1 | 67 A |
| Concentration | 1[(CH ₃) ₄ NC1] | 20 | 9.67 | 2.4 | 1.7 | | H | 67 A |
| Concentration | 1(NaClO ₄) | 20 | 8.96 | 2.27 | 1.99 | | g1 | 67 A |
| Concentration | 1(NaClO ₄) | 20 | | 2.14 | 1.97 | 1.10 | so1 | 67 A |
| Concentration | 0.1(KCl) | 20 | 9.71(1) | 2.47(1) | 1.71(10) | 0.80(10) | g1,so1 | 67 I |
| Concentration | 0.2(NaClO ₄) | 25 | 9.45 | 2.60 | 1.97 | | g1 | 67 Ba |
| Concentration | 0.1(KNO ₃) | 0.4 | 10.76 | 3.00 | 2.30 | | g1 | 67 T |
| Concentration | 0.1(NaClO ₄) | 25 | 9.49 | 2.67 | 1.68 | | g1 | 68 E |
| Concentration | 0.1(NaNO ₃) | 25 | 9.95 | 2.95 | 2.08 | | g1 | 72 R |
| Concentration | 0.1 NaClO ₄ | 25 | 9.75 | 2.43 | 1.97 | | g1 | 73 C |
| Concentration | 0.5 NaClO ₄ | 25 | 9.33 | 2.43 | 1.97 | | g1 | 73 C |
| Concentration | 0.5(NaClO ₄) | 25 | 8.95(2) | 2.28 | 1.70 | | g1 | 73 M |
| Concentration | 0.1(NaClO ₄) | 25 | 9.95 | 2.38 | 1.98 | | g1 | 73 Ra |
| Concentration | 0.1(KNO ₃) | 25 | 9.58 | 2.88 | | | g1 | 73 S |
| Concentration | 0.1(KNO ₃) | 25 | 9.50 | 2.88 | | | g1 | 73 S |
| Concentration | 3(NaClO ₄) | 25 | 9.17(4) | 2.63(2) | 2.05(5) | 1.27(3) | g1 | 75 L |

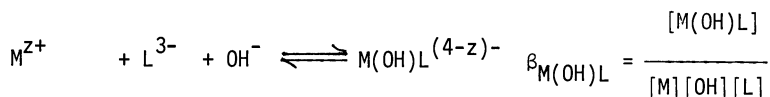
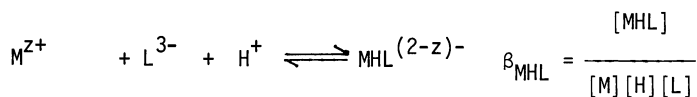
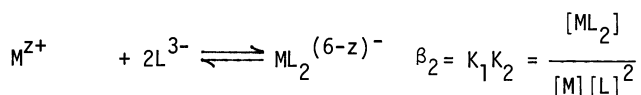
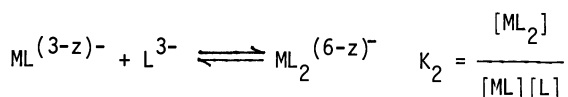
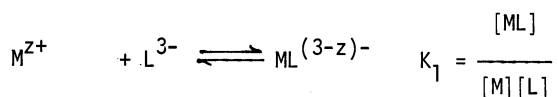
| Type of constants | Medium | t [°C] | log K ₁ ^{b)} | log K ₂ | log K ₃ | log K ₄ | Method ^a | Reference |
|-------------------|--------------------------|--------|----------------------------------|--------------------|--------------------|--------------------|---------------------|-----------|
| Mixed | 0.11(KNO ₃) | 20 | 9.82 | 2.74 | 1.61 | | gl | 75 Va |
| Concentration | 0.5(NaClO ₄) | 25 | 8.94(2) | 2.28(2) | 1.86(2) | 1.6(1) | gl | 76 C |
| Concentration | 0.1(KNO ₃) | 25 | 9.65 | 2.48 | 1.84 | | gl | 76 H |
| Concentration | 1(NaClO ₄) | 25 | 8.92 | 2.41 | 1.81 | 1.39 | gl | 76 Y |
| Concentration | 0.5(KNO ₃) | 25 | 9.57(1) | 2.64(4) | 1.57(6) | | gl | 77 G |

a: H: H electrode; gl: glass electrode; sol: solubility

b: In parentheses the standard deviation of the last digits.

5. METAL COMPLEX FORMATION

The formation of NTA metal complexes is characterised by the following equilibria:



The unit of concentration for the terms in brackets is mol dm⁻³.

The stability constants are given in the same order as that used in the Stability Constants Publications, Inorganic Part, based on the Periodic System. For each group a nearly complete list of all published values is given. They are presented in tables with inclusion of further information in six columns: metal ion, medium, temperature, values of the constants (in parentheses the standard deviation of the last digits), method and reference.

The medium in which the equilibrium constants were measured is normally water, to which a certain quantity of inert salt was added: its concentration or the corresponding ionic strength is given on the basis of the literature in one of the following ways:

| | |
|-----------|--|
| → 0 (KCl) | constant extrapolated to zero ionic strength from measurements in KCl solutions |
| 0.1(KCl) | ionic strength equal 0.1 by addition of KCl |
| 0.1 KCl | constant concentration of KCl equal to 0.1 |
| 0.1 | ionic strength equal to 0.1 mol dm ⁻³ without indication of the inert salt used |

The method used is given by the following symbols:

| | | | |
|-------|---------------------------------|-----|-------------------|
| H | H electrode (pH method) | pol | polarography |
| gl | glass electrode (pH method) | sol | solubility |
| dis | distribution between two phases | tp | electrophoresis |
| nmr | nuclear magnetic resonance | Hg | mercury electrode |
| sp | spectrophotometry | red | redox electrode |
| ix | ion exchanger | M | metal electrode |
| chrom | chromatography (paper) | est | estimated |

If the direct method is not used, the type of equilibrium involved is indicated on the basis of those listed in chapter 2. For instance, pH measurements can be used to obtain the stability constants of complexes of a given metal ion M^{Z+} in the following different ways:

- i) competition between M^{Z+} and H⁺ for L³⁻ (direct pH method)
- ii) competition between M^{Z+}, H⁺ for L³⁻ and an auxiliary ligand (see page 2700, III)
- iii) competition between M^{Z+}, M^{Z*+}, H⁺ for L³⁻ and an auxiliary ligand (see page 2700, v).

For the three cases the method is indicated by:

- i) gl
- ii) gl, III
- iii) gl, V.

On the basis of a critical discussion on the results and on their measure and calculation is selected a list of the more reliable values (75 W).

5.1 Complex formation with alkali ions

As yet, the association with alkali ions has not been investigated sufficiently to yield reliable data. This is due to the fact that the stability constants are small and not easy to obtain accurately. For many purposes they can be neglected. The data should be considered as only tentative for the standard state given. For instance, the values of 63 Ia (Table 2.1) were obtained at I = 0.1(KNO₃) and that of 67 A at 0.1((CH₃)₄NCl). Note that the value for Na⁺ in KNO₃ is four times higher than that for K⁺ in (CH₃)₄NCl. Log K₁ with Na⁺ in this medium is expected to be approximately 1.45. As might be expected from an electrostatic model, the value of K₁ decreases as the radius of the cation increases.

TABLE 2.1 Stability constants of group Ia cations

(For definitions see pages 2713/2714)

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>log K₁</u> | <u>Method</u> | <u>Reference</u> |
|------------------------|--|--------------|--------------------------|---------------|------------------|
| | (see pp. 2713/2714) | | | (see p. 2714) | |
| <u>Li</u> ⁺ | 0.1(KNO ₃) | 20 | 2.51 | gl | 63 Ia |
| <u>Na</u> ⁺ | → 0 | 20 | 2.15 | H | 45 S |
| | 0.1(KNO ₃) | 20 | 1.22(2) | gl | 63 Ia |
| <u>K</u> ⁺ | 0.1(CH ₃) ₄ NC1 | 20 | 0.6 | gl | 67 A |

5.2. Complex formation with alkaline earth cations

For the cations Mg²⁺ to Ba²⁺ we can discuss the results of two different groups determined under the same experimental conditions. Both sets are in good agreement and this permits recommended values of log K₁ to be given in all cases:

| t[°C] | I | Mg ²⁺ | Ca ²⁺ | Sr ²⁺ | Ba ²⁺ |
|-------|----------|------------------|------------------|------------------|------------------|
| 20 | 0.1(KCl) | 5.43 | 6.45 | 5.00 | 4.85 |

The interpolated values of 60 B for 0.1(KNO₃) are 0.08, 0.06, 0.1 and 0.1 lower with respect to the above values. As first found by Schwarzenbach, 1 : 2 complexes M(NTA)₂⁴⁻ are also formed but the stability constant K₂ is low. At I = 0.1(KNO₃) for Ca²⁺, log K₂ = 2.45 (20 °C) and for the other cations the value is < 2. In the case of Be²⁺, the two values are quite different: for 75 Va the inappropriate standardization has already been discussed when treating protonation. The error in pH is almost compensated in the determination of the stability constant because this last quantity depends mainly on the pH difference. The stability constant was obtained using 8 points in the pH range 3.5 - 4.2 giving a value with 7% standard deviation "Turbidity due to beryllium(II) hydroxide appears on increasing the basicity of the solution"; therefore probably hydrolytic products are also present in the pH range investigated. This can lead to a K₁ value which is too high. From distribution measurements of beryllium(II) between a 0.5 M oxine solution in CHCl₃ and an aqueous NTA (0.01 M) solution at 0.1 M (KClO₄), Stary obtained a much lower K₁ (lower by a factor of approximately 3). In this case, because of the large excess of ligand, hydrolytic reactions should not take place. One is therefore tempted to discard the value of 75 Va and to consider the value of 63 S as more reliable. However, there still remain some questions concerning this paper because it would be very difficult to discern the formation of mixed complexes from measurements at only one total ligand concentration. Further, the fact that the maximum amount of beryllium oxinate complex extracted by CHCl₃ represents only 83 and not 100% was not explained. From nephelometric (turbidity) measurements Callis et al. (69 C) have postulated the formation of Ca₂(NTA)⁺ with [Ca₂L]/([Ca][CaL]) = 10^{3.4}. The corresponding equilibrium should be observed by investigation of a mixture in which protonated ligand is in excess: but under these conditions only CaL⁻ was detected (77 A).

TABLE 2.2. Stability constants of group 2a cations

(For definitions see pages 2713/2714)

| <u>Metal</u> | <u>Medium</u> (see pp. 2713/2714) | <u>t</u> [°C] | <u>log K₁</u> | <u>log K₂</u> | <u>Method</u> (see p. 2714) | <u>Reference</u> | |
|-------------------------|--------------------------------------|---------------|--------------------------|--------------------------|--------------------------------|------------------|------|
| <u>Be</u> ²⁺ | 0.1(KClO ₄) | 20 | 7.11(5) | | dis | 63 S | |
| | 0.11(KNO ₃) | 20 ± 1 | 7.64 | | pH | 75 Va | |
| <u>Mg</u> ²⁺ | → 0 | 20 | 7.0 | 3.2 | H | 45 S | |
| | 0.1(KCl) | 20 | 5.41 | | gl | 49 S | |
| | → 0(KCl) | 0 | 6.31 | | H | 56 H | |
| | → 0(KCl) | 10 | 6.39 | | H | 56 H | |
| | → 0(KCl) | 20 | 6.50 | | H | 56 H | |
| | → 0(KCl) | 30 | 6.61 | | H | 56 H | |
| | 0.1(KNO ₃) | 0.5 | 5.33 | | gl | 60 B | |
| | 0.1(KNO ₃) | 25.3 | 5.36 | | gl | 60 B | |
| | 0.1(KNO ₃) | 42.4 | 5.37 | | gl | 60 B | |
| | 0.1(KNO ₃) | 20 | | < 2 | gl | 64 A | |
| | 0.1(KCl) | 20 | 5.46(2) | | gl | 66 I | |
| | 0.1(NH ₄ Cl) | | 6.4 | | chrom | 69 A | |
| | <u>Ca</u> ²⁺ | → 0 | 20 | 8.17 | 3.2 | H | 45 S |
| | | 0.1(KCl) | 20 | 6.41 | | gl | 49 S |
| → 0 | | 0 | 7.70 | | H | 56 H | |
| → 0 | | 10 | 7.652 | | H | 56 H | |
| → 0 | | 20 | 7.608 | | H | 56 H | |
| → 0 | | 30 | 7.595 | | gl | 56 H | |
| 0.1(KNO ₃) | | 0.5 | 6.61 | | gl | 60 B | |
| 0.1(KNO ₃) | | 25.3 | 6.33 | | gl | 60 B | |
| 0.1(KNO ₃) | | 42.4 | 6.35 | | gl | 60 B | |
| 0.1(KNO ₃) | | 15 | 6.59 | | gl | 62 M | |
| 0.1(KNO ₃) | | 20 | 6.56 | | gl | 62 M | |
| 0.1(KNO ₃) | | 25 | 6.57 | | gl | 62 M | |
| 0.1(KNO ₃) | | 30 | 6.57 | | gl | 62 M | |
| 0.1(KNO ₃) | | 35 | 6.53 | | gl | 62 M | |
| 0.1(KNO ₃) | | 40 | 6.53 | | gl | 62 M | |
| 0.1(KNO ₃) | | 20 | | 2.45 | gl | 64 A | |
| 0.1(KCl) | | 20 | 6.46(1) | | gl | 66 I | |
| 0.1(NH ₄ Cl) | | | 6.6 | | chrom | 69 A | |
| 0.1(KNO ₃) | | 20 | 6.50* | | gl | 77 A | |

| <u>Metal</u> | <u>Medium</u> (see pp. 2713/2714) | <u>t[°C]</u> | <u>log K₁</u> | <u>log K₂</u> | <u>Method</u> (see p. 2714) | <u>Reference</u> |
|-------------------------|--------------------------------------|--------------|--------------------------|--------------------------|--------------------------------|------------------|
| <u>Sr</u> ²⁺ | → 0 | 20 | 6.73 | | H | 45 S |
| | 0.1(KCl) | 20 | 4.98 | | gl | 49 S |
| | 0.1(KNO ₃) | 0.5 | 4.90 | | gl | 60 B |
| | 0.1(KNO ₃) | 25.3 | 4.91 | | gl | 60 B |
| | 0.1(KNO ₃) | 42.4 | | | gl | 60 B |
| | 0.1(KNO ₃) | 20 | | < 2 | gl | 64 A |
| | 0.1(KCl) | 20 | 5.01(1) | | gl | 66 I |
| | 0.1(NH ₄ Cl) | | 5.5 | | chrom | 69 A |
| | 0.1 | 20 | 6.42 | | tp | 69 M |
| <u>Ba</u> ²⁺ | → 0 | 20 | 6.41 | | H | 45 S |
| | 0.1(KCl) | 20 | 4.82 | | gl | 49 S |
| | → 0(KCl) | 0 | 5.968 | | H | 56 H |
| | → 0(KCl) | 10 | 5.914 | | H | 56 H |
| | → 0(KCl) | 20 | 5.875 | | H | 56 H |
| | → 0(KCl) | 30 | 5.597 | | H | 56 H |
| | 0.1(KNO ₃) | 0.5 | 4.87 | | gl | 60 B |
| | 0.1(KNO ₃) | 25.3 | 4.72 | | gl | 60 B |
| | 0.1(KNO ₃) | 42.4 | 4.66 | | gl | 60 B |
| | 0.1(KNO ₃) | 20 | | < 2 | gl | 64 A |
| | 0.1(KCl) | 20 | 4.83(3) | | gl | 66 I |

* Formation of Ca₂L⁻ (69 C) cannot be confirmed!

5.3. Complex formation with 3a and 4f cations

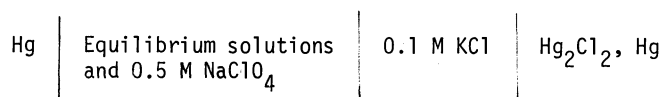
The cations of these groups are, with some exceptions, trivalent and generally show a much greater tendency to form stronger complexes than the cations of groups 1a and 2a. They are able to form 1 : 1 as well as 1 : 2 complexes. In the case of the trivalent rare earth cations, different papers give quantitative results for complex formation for I = 0.1 and 20 °C. Comparison of the results can therefore be made using a plot of log K₁ against atomic number.^a The values of 57 N are also included as calculated for the formation of ML instead of M₂L₃³⁻ as was postulated by Noddack. Indeed, in 60 A, evidence is given for the absence of M₂L₃³⁻ species in these solutions. In some cases and especially from polarographic measurements on exchange equilibria, two close (but different) values are given for the same constant. To avoid confusion only the average of the two results is used here. The plot shows that the values from three papers (56 S, 57 N and 62 M) for the same metal ion can differ by 0.15 and 0.3 log units. This difference is quite considerable and enables only a list of tentative values for the constants to be given. For log K₂ only values from two papers can be considered (62 M, 60 A) and, since their difference is quite low, tentative values can also be given for this constant.

Note a. See Fig. 4

TABLE 2.3. Tentative values at $I = 0.1(\text{KNO}_3)$ and 20°C .

| | <u>La³⁺</u> | <u>Ce³⁺</u> | <u>Pr³⁺</u> | <u>Nd³⁺</u> | <u>Pm³⁺</u> | <u>Sm³⁺</u> | <u>Eu³⁺</u> | <u>Gd³⁺</u> |
|------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| $\log K_1$ | 10.50 | 10.80 | 10.95 | 11.18 | 11 | 11.35 | 11.44 | 11.45 |
| $\log K_2$ | 7.30 | 7.93 | 8.20 | 8.47 | 8.7 | 9.10 | 9.23 | 9.35 |
| | <u>Tb³⁺</u> | <u>Dy³⁺</u> | <u>Ho³⁺</u> | <u>Er³⁺</u> | <u>Tm³⁺</u> | <u>Yb³⁺</u> | <u>Lu³⁺</u> | |
| $\log K_1$ | 11.52 | 11.65 | 11.78 | 11.94 | 12.12 | 12.20 | 12.40 | |
| $\log K_2$ | 9.45 | 9.46 | 9.41 | 9.29 | 9.25 | 9.28 | 9.4 | |

The values of 77 G (for 0.5 NaClO_4) obtained by use of an exchange equilibrium with Hg^{2+} and an Hg electrode appear quite strange because they show a different trend to the other sets of $\log K_1$ values. On alteration of the ionic medium or the temperature, one expects a parallel or at least a monotonic displacement of $\log K_1$. An examination of the dissertation of Gritmon (68 G) suggests that experimental difficulties may be the reason for the results. The cell for the measurements:



can give erroneous EMF values because the solution is almost saturated with KClO_4 of the liquid junction. The solubility of KClO_4 is only 0.11 M. Further, the exchange reaction with mercury(II) in the presence of the metal leads to formation of mercury(I). For solutions with concentrations of Hg_2^{2+} of the same order of magnitude as the rare-earth cations, it is necessary to allow some time to reach equilibrium, because the reduction of Hg^{2+} is not immediate. Other comments about this work are given elsewhere (pp. 2711 and 2734). There exists in the literature some inconsistency in relation to the possible formation of the hydroxo complex $\text{Ln}(\text{NTA})\text{OH}^-$ from $\text{Ln}(\text{NTA})$: i) In the dissertation of Hitz (58 H); supervised by G. Schwarzenbach) it is mentioned that "the titration curves of $\text{Y}(\text{NTA})$, $\text{La}(\text{NTA})$ and $\text{Ce}(\text{NTA})$ with KOH solutions diverge strongly from the theoretical form" expected for simple deprotonation to a hydroxo complex $\text{Ln}(\text{NTA})\text{OH}^-$. ii) In 70 V are given values of the constant $K = [\text{Ln}(\text{NTA})\text{OH}^-]/([\text{Ln}(\text{NTA})][\text{OH}^-])$ with an error of 0.01 log unit.

Further comments:

Sc³⁺: In 57 N the hydrolysis of Sc^{3+} is not considered. The following tentative values are given:

$$0.1 (\text{NaClO}_4), 25^\circ\text{C} \log K_1 \quad 12.68(2) \quad (67 \text{ S})$$

$$0.1 (\text{KClO}_4), 20^\circ\text{C} \log \beta_2 \quad 24.1 \quad (63 \text{ S})$$

The authors of 67 S, with the techniques used for Sc^{3+} (Hg exchange, VII), obtained a stability constant for LaL in a good agreement with other literature values (67 Sa).

Eu²⁺: The values can be proposed as tentative - it seems that a protonated 1 : 1 complex may also be formed.

Ce^{IV}: Ce^{IV} solutions in the presence of sulphate ions ($c = 0.5$ or 1 M) are stable at pH 3.5

and on addition of NTA a change in the spectrum is observed (69 M, 71 P). Measurements of the equilibrium involved in 0.5 and 1 M $(\text{NH}_4)_2\text{SO}_4$ show the formation of a 1 : 1 complex. The authors calculated two values of the stability constant with respect to Ce^{IV} : i) considering the presence of H_3L only (!) and ii) considering "all forms in which NTA is present".

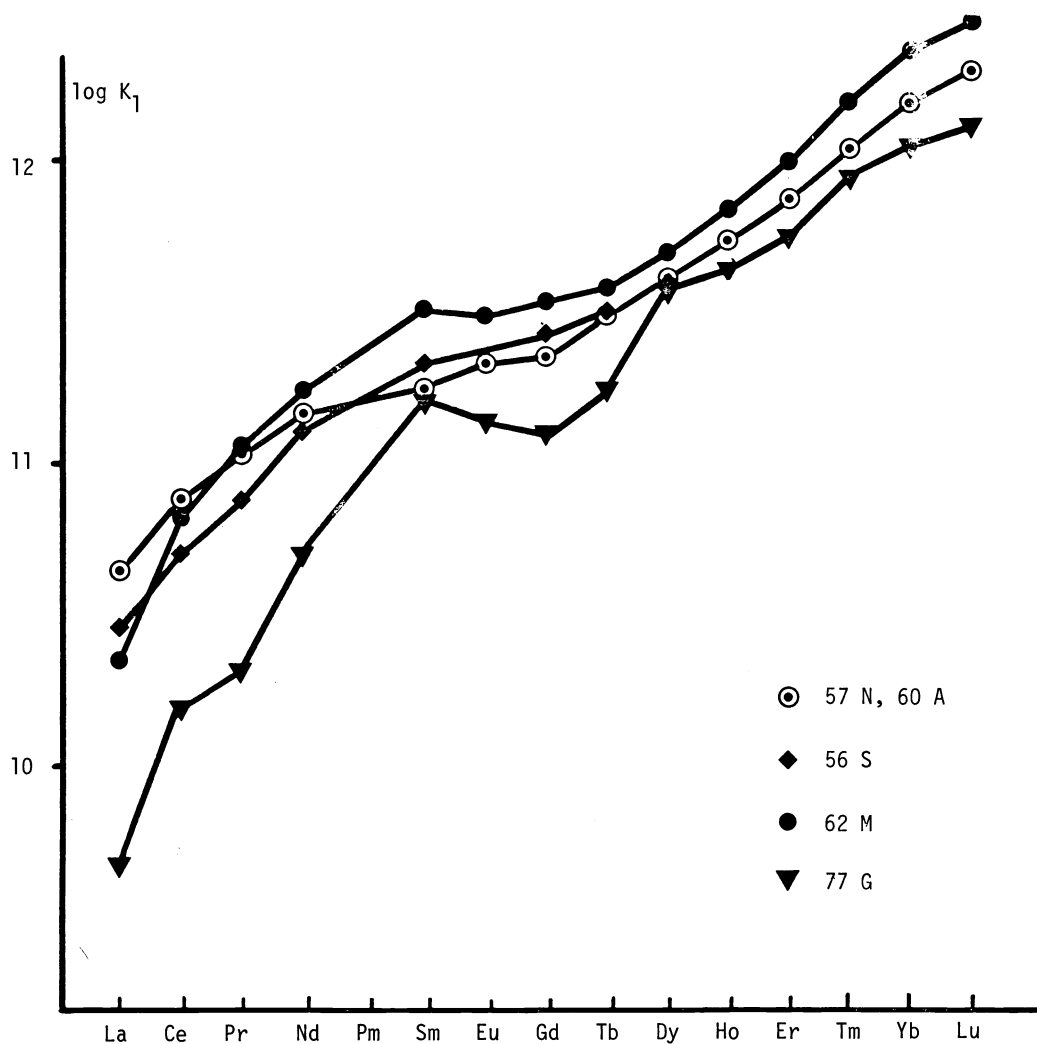


Fig. 5 The logarithm of K_1 for the NTA complexes with trivalent lanthanide cations.

TABLE 2.4. Stability constants of 3a and 4f cations

(For definitions see pages 2713/2714)

| <u>Metal</u> | <u>Medium</u> (see pp. 2713/2714) | <u>t</u> [°C] | <u>log K₁</u> | <u>log K₂</u> | <u>log β₂</u> | <u>Method</u> (see p. 2714) | <u>Reference</u> |
|-------------------------|--------------------------------------|---------------|--------------------------|--------------------------|--------------------------|--------------------------------|------------------|
| <u>Sc</u> ³⁺ | 0.1 (KNO ₃) | 20 | 13.91 | | | pol. VII | 57 N, 60 A |
| | 0.1 (KC1O ₃) | 20 | | | 24.1 | dis | 63 S |
| | 0.1 (NaC1O ₄) | 25 | 12.68(20) | | | Hg, VII | 67 S |
| <u>Y</u> ³⁺ | 0.1 (KNO ₃) | 20 | 11.41 | | | pol. VII | 56 S |
| | 0.1 (KNO ₃) | 20 | 11.30 | | | pol. VIII | 57 N, 60 A |
| | 0.1 (KNO ₃) | 15 | 11.46 | 9.09 | | pH, V, VI | 62 M |
| | 0.1 (KNO ₃) | 20 | 11.46 | 9.09 | | pH, V, VI | 62 M |
| | 0.1 (KNO ₃) | 25 | 11.48 | 9.03 | | pH, V, VI | 62 M |
| | 0.1 (KNO ₃) | 30 | 11.54 | 8.94 | | pH, V, VI | 62 M |
| | 0.1 (KNO ₃) | 35 | 11.56 | 8.84 | | pH, V, VI | 62 M |
| | 0.1 (KNO ₃) | 40 | 11.60 | 8.83 | | pH, V, VI | 62 M |
| | 0.5 NaC1O ₄ | 25 | 11.09(9) | | | Hg, VII | 77 G |
| <u>La</u> ³⁺ | 0.1 (KC1) | 20 | 10.47 | | | pH, V | 51 S |
| | 0.1 (KNO ₃) | 20 | 10.47 | | | pol, VII | 56 S |
| | 0.1 (KNO ₃) | 20 | 10.64 | | | pol, VII | 57 N, 60 A |
| | 0.1 (KC1) | 20 | | 7.37 | | pH | 60 A |
| | 0.1 (KC1O ₃) | 20 | | | 17.15(10) | dis | 63 S |
| | 0.1 (NaC1O ₄) | 25 | 10.5(2) | | | Hg, VII | 67 Sa |
| | 0.1 (NaC1O) | 25 | 10.6(2) | | | sol | 67 Sa |
| | 0.5 NaC1O ₄ | 25 | 9.68(9) | | | Hg, VII | 77 G |
| | 0.1 (KNO ₃) | 15 | 10.38 | 7.34 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 20 | 10.37 | 7.25 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 25 | 10.36 | 7.24 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 30 | 10.43 | 7.25 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 35 | 10.43 | 7.17 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 40 | 10.49 | 7.16 | | gl, V, VI | 62 M |
| | <u>Ce</u> ³⁺ | 0.001 | | | 8.1 | | gl |
| 0.1 (KNO ₃) | | 20 | 10.71 | | | pol. VII | 56 S |
| 0.1 (KNO ₃) | | 20 | 10.88 | | | pol. VII | 57 N, 60 A |
| 0.1 (KC1) | | 20 | | 7.98 | | gl | 60 A |
| 0.1 (KNO ₃) | | 15 | 10.85 | 7.94 | | gl, V, VI | 62 M |
| 0.1 (KNO ₃) | | 20 | 10.83 | 7.88 | | gl, V, VI | 62 M |
| 0.1 (KNO ₃) | | 25 | 10.83 | 7.84 | | gl, V, VI | 62 M |
| 0.1 (KNO ₃) | | 30 | 10.87 | 7.85 | | gl, V, VI | 62 M |
| 0.1 (KNO ₃) | | 35 | 10.86 | 7.76 | | gl, V, VI | 62 M |
| 0.1 (KNO ₃) | | 40 | 10.91 | 7.73 | | gl, V, VI | 62 M |
| 0.1 | | 18-20 | 10.97(5) | | 20.85(7) | ix | 65 V |

| <u>Metal</u> | <u>Medium</u> (see pp. 2713/2714) | <u>t[°C]</u> | <u>log K₁</u> | <u>log K₂</u> | <u>log β₂</u> | <u>Method</u> (see p. 2714) | <u>Reference</u> |
|------------------------------------|--|--------------|--------------------------|--------------------------|--------------------------|--------------------------------|------------------|
| <u>Ce³⁺</u> | 0.1(NaClO ₄) | 25 | 10.60(1) | | 17.90(9) | ix | 68 E |
| | 0.1 | 20 | 8.45 | | | tp | 68 M |
| | 0.1 | 20 | 10.98 ^a | | 18.43 | tp | 71 S |
| <u>Ce^{IV}</u> | 1(NH ₄) ₂ SO ₄ | 20 | 17.9(1) | | | sp | 69 M |
| | 1(NH ₄) ₂ SO ₄ | 20 | 18.68 | | | sp | 69 M |
| | 0.5(NH ₄) ₂ SO ₄ | 20 | 18.64 | | | sp | 71 P |
| | 1(NH ₄) ₂ SO ₄ | 20 | 18.47 | | | sp | 71 P |
| <u>Pr³⁺</u> | 0.1(KNO ₃) | 20 | 10.88 | | | pol, VII | 56 S |
| | 0.1(KNO ₃) | 20 | 11.02 | | | pol, VII | 57 N, 60 A |
| | 0.1(KCl) | 20 | | 8.18 | | gl | 60 A |
| | 0.02 | 18-20 | 10.28 | | 19.25 | sp | 61 A |
| | 0.1(KNO ₃) | 15 | 11.11 | 8.31 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 20 | 11.07 | 8.22 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 25 | 11.07 | 8.18 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 30 | 11.12 | 8.15 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 35 | 11.08 | 8.10 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 40 | 11.11 | 8.06 | | gl, V, VI | 62 M |
| 0.5 NaClO ₄ | 25 | 10.31(9) | | | Hg, VII | 77 G | |
| <u>Nd³⁺^b</u> | 0.1(KNO ₃) | 20 | 11.11 | | | pol, VII | 56 S |
| | 0.1(KNO ₃) | 20 | 11.17 | | | pol, VII | 57 N, 60 A |
| | 0.1(KCl) | 20 | | 8.44 | | gl | 60 A |
| | 0.02 | 18-20 | 10.49 | | 19.47 | sp | 61 A |
| | 0.1(KNO ₃) | 15 | 11.28 | 8.59 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 20 | 11.25 | 8.51 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 25 | 11.26 | 8.47 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 30 | 11.30 | 8.45 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 35 | 11.08 | 8.37 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 40 | 11.11 | 8.06 | | gl, V, VI | 62 M |
| | 0.5 NaClO ₄ | 25 | 10.71(9) | | | Hg, VII | 77 G |
| <u>Pm³⁺</u> | 0.1(H,NaClO ₄) | 20 | 11 | | 19.71 | dis | 66 S |
| <u>Sm³⁺</u> | 0.1(KNO ₃) | 20 | 11.33 | | | pol, VII | 56 S |
| | 0.1(KNO ₃) | 20 | 11.25 | | | pol, VII | 57 N, 60 A |
| | 0.1(KCl) | 20 | | 9.15 | | gl | 60 A |
| | 0.2 | 18-20 | 10.78 | | 20.54 | sp | 61 A |
| | 0.1(KNO ₃) | 15 | 11.53 | 9.17 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 20 | 11.51 | 9.05 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 25 | 11.53 | 9.00 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 30 | 11.55 | 8.97 | | gl, V, VI | 62 M |

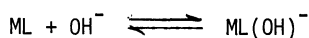
| <u>Metal</u> | <u>Medium</u> (see pp. 2713/2714) | <u>t</u> [°C] | <u>log K₁</u> | <u>log K₂</u> | <u>log β₂</u> | <u>Method</u> (see p. 2714) | <u>Reference</u> |
|-------------------------|--------------------------------------|---------------|--------------------------|--------------------------|--------------------------|--------------------------------|------------------|
| <u>Sm</u> ³⁺ | 0.1 (KNO ₃) | 35 | 11.52 | 8.91 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 40 | 11.54 | 8.87 | | gl, V, VI | 62 M |
| | 0.5 NaClO ₄ | 25 | 11.21(9) | | | Hg, VII | 77 G |
| <u>Eu</u> ²⁺ | 0.5 NaClO ₄ | 25 | 5.55 ^C | | 8.62 | gl | 73 C |
| <u>Eu</u> ³⁺ | 0.1 (KNO ₃) | 20 | 11.33 | | | pol, VII | 57 N, 60 A |
| | 0.1 (KNO ₃) | 15 | 11.52 | 9.36 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 20 | 11.49 | 9.27 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 25 | 11.52 | 9.18 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 30 | 11.54 | 9.18 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 35 | 11.53 | 9.08 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 40 | 11.55 | 9.02 | | gl, V, VI | 62 M |
| | 0.1 (NH ₄ Cl) | 20 | | | 20.42 | dis | 66 Sa |
| | 0.1 | 20 | 9.10 | | | tp | 68 M |
| 0.5 NaClO ₄ | 25 | 11.13(9) | | | Hg, VII | 77 G | |
| <u>Gd</u> ³⁺ | 0.1 (KNO ₃) | 20 | 11.43 | | | pol, VII | 56 S |
| | 0.1 (KNO ₃) | 20 | 11.36 | | | pol, VII | 57 N, 60 A |
| | 0.1 (KCl) | 20 | | 9.36 | | gl, V | 60 A |
| | 0.1 (KNO ₃) | 15 | 11.57 | 9.46 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 20 | 11.54 | 9.34 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 25 | 11.54 | 9.26 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 30 | 11.59 | 9.23 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 35 | 11.57 | 9.12 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 40 | 11.60 | 9.09 | | gl, V, VI | 62 M |
| 0.5 NaClO ₄ | 25 | 11.11(9) | | | Hg, VII | 77 G | |
| <u>Tb</u> ³⁺ | 0.1 (KNO ₃) | 20 | 11.50 | | | pol, VII | 57 N, 60 A |
| | 0.1 (KNO ₃) | 15 | 11.60 | 9.53 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 20 | 11.58 | 9.45 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 25 | 11.59 | 9.38 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 30 | 11.65 | 9.32 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 35 | 11.65 | 9.25 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 40 | 11.67 | 9.20 | | gl, V, VI | 62 M |
| | 0.5 NaClO ₄ | 25 | 11.25(9) | | | Hg, VII | 77 G |
| <u>Dy</u> ³⁺ | 0.1 (KNO ₃) | 20 | 11.59 | | | pol, VII | 56 S |
| | 0.1 (KNO ₃) | 20 | 11.67 | | | pol, VII | 57 N, 60 A |
| | 0.1 (KCl) | 20 | | 9.40 | | gl, V | 60 A |
| | 0.1 (KNO ₃) | 15 | 11.73 | 9.57 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 20 | 11.71 | 9.48 | | gl, V, VI | 62 M |
| | 0.1 (KNO ₃) | 25 | 11.74 | 9.41 | | gl, V, VI | 62 M |

| <u>Metal</u> | <u>Medium</u> (see pp. 2713/2714) | <u>t[°C]</u> | <u>log K₁</u> | <u>log K₂</u> | <u>log β₂</u> | <u>Method</u> (see p. 2714) | <u>Reference</u> |
|------------------------|--------------------------------------|--------------|--------------------------|--------------------------|--------------------------|--------------------------------|------------------|
| <u>Dy³⁺</u> | 0.1(KNO ₃) | 30 | 11.79 | 9.37 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 35 | 11.81 | 9.27 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 40 | 11.84 | 9.21 | | gl, V, VI | 62 M |
| | 0.5 NaClO ₄ | 25 | 11.58(9) | | | Hg, VII | 77 G |
| <u>Ho³⁺</u> | 0.1(KNO ₃) | 20 | 11.75 | | | pol, VII | 57 N, 60 A |
| | 0.1(KNO ₃) | 15 | 11.87 | 9.52 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 20 | 11.85 | 9.41 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 25 | 11.90 | 9.35 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 30 | 11.96 | 9.31 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 35 | 11.95 | 9.21 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 40 | 12.00 | 9.19 | | gl, V, VI | 62 M |
| | 0.5 NaClO ₄ | 25 | 11.65(9) | | | gl, VII | 77 G |
| <u>Er³⁺</u> | 0.1(KNO ₃) | 20 | 11.89 | | | pol, VII | 57 N, 60 A |
| | 0.1(KNO ₃) | 15 | 12.03 | 9.36 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 20 | 12.00 | 9.29 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 25 | 12.03 | 9.26 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 30 | 12.09 | 9.21 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 35 | 12.10 | 9.14 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 40 | 12.15 | 9.11 | | gl, V, VI | 62 M |
| | 0.5 NaClO ₄ | 25 | 11.76(9) | | | Hg, VII | 77 G |
| <u>Tm³⁺</u> | 0.1(KNO ₃) | 20 | 12.05 | | | pol, VII | 57 N, 60 A |
| | 0.1(KNO ₃) | 15 | 12.21 | 9.32 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 20 | 12.20 | 9.25 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 25 | 12.22 | 9.23 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 30 | 12.28 | 9.22 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 35 | 12.27 | 9.17 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 40 | 12.30 | 9.16 | | gl, V, VI | 62 M |
| | 0.5 NaClO ₄ | 25 | 11.95(9) | | | Hg, VII | 77 G |
| <u>Yb³⁺</u> | 0.1(KNO ₃) | 20 | 12.08 | | | pol, VII | 56 S |
| | 0.1(KNO ₃) | 20 | 12.20 | | | pol, VII | 57 N, 60 A |
| | 0.1(KCl) | 20 | | 9.02 | | gl | 60 A |
| | 0.1(KNO ₃) | 15 | 12.39 | 9.36 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 20 | 12.37 | 9.33 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 25 | 12.40 | 9.29 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 30 | 12.45 | 9.28 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 35 | 12.45 | 9.25 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 40 | 12.48 | 9.23 | | gl, V, VI | 62 M |
| | 0.5 NaClO ₄ | 25 | 12.06(9) | | | Hg, VII | 77 G |

| <u>Metal</u> | <u>Medium</u> | <u>t</u> [°C] | <u>log K₁</u> | <u>log K₂</u> | <u>log β₂</u> | <u>Method</u> | <u>Reference</u> |
|-------------------------|------------------------|---------------|--------------------------|--------------------------|--------------------------|---------------|------------------|
| | (see pp. 2713/2714) | | | | | (see p. 2714) | |
| <u>Lu</u> ³⁺ | 0.1(KNO ₃) | 20 | 12.32 | | | po1, VII | 57 N, 60 A |
| | 0.1(KNO ₃) | 15 | 12.48 | 9.49 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 20 | 12.47 | 9.33 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 25 | 12.49 | 9.42 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 30 | 12.55 | 9.44 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 35 | 12.54 | 9.39 | | gl, V, VI | 62 M |
| | 0.1(KNO ₃) | 40 | 12.58 | 9.41 | | gl, V, VI | 62 M |
| | 0.5 NaClO ₄ | 25 | 12.12(9) | | | Hg, VII | 77 G |

- a: $K(\text{Ce}^{3+} + \text{L}^{3-} + \text{HL}^{2-} \rightleftharpoons \text{CeHL}_2) 12.0 (?) (71 \text{ S}),$ see also page 2728.
- b: The value of K_1 given by Vickery (57 V) is of uncertain source and was therefore omitted.
- c: $\text{pK of EuHL} = 7.4 (73 \text{ C}).$

TABLE 2.5. Equilibrium constant for:



valid at $I = 0.2(\text{KNO}_3)$, $t = 20 \pm 1$ °C, obtained by use of the pH method with glass electrode (70 V).

$$K = \frac{[\text{ML OH}]}{[\text{ML}][\text{OH}]} \quad ; \quad \text{concentrations in mol} \cdot \text{dm}^{-3}.$$

| | <u>Sc</u> ³⁺ | <u>Y</u> ³⁺ | <u>La</u> ³⁺ | <u>Ce</u> ³⁺ | <u>Pr</u> ³⁺ | <u>Nd</u> ³⁺ | <u>Sm</u> ³⁺ |
|--------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| log K ^a | 7.44 | 6.83 | 5.07 | 4.72 | 5.99 | 6.08 | 6.17 |
| | <u>Eu</u> ³⁺ | <u>Gd</u> ³⁺ | <u>Tb</u> ³⁺ | <u>Er</u> ³⁺ | <u>Tm</u> ³⁺ | <u>Yb</u> ³⁺ | <u>Lu</u> ³⁺ |
| log K | 6.21 | 6.28 | 6.35 | 6.53 | 6.62 | 6.74 | 6.87 |

a: ± 0.01

5.4. Complex formation with 4a cations

For some cations the quantitative data are scarce and the description of the measurements too inadequate to estimate the reliability of the results obtained. Further, in the calculations, only the formation of 1 : 1 complexes has been considered normally, and there is a lack of knowledge concerning the existence of 1 : 2 species. The measurement of K_1 in the presence of excess ligand can lead to K_1 values which are too large if there is formation of ML_2

species. In only one study involving Zr^{4+} (at pH 2) the formation of $Zr(NTA)_2^{2-}$ is considered! If this species is present in this pH region then, for the tetravalent cations, all data for these cations may require a correction. In another study the formation of $Th(NTA)_2^{2-}$ below pH 4 was mentioned (68 B) but was not investigated.

Zr⁴⁺: In 64 I an exchange of type VI with Fe^{3+} is followed spectrophotometrically at pH = 2. In the calculation of K_1 corrections were made for the different side reactions: i) hydrolysis of Zr^{4+} and Fe^{3+} ; ii) complex formation of Fe^{3+} with Cl^- . The value of K_1 obtained by use of that of 51 Sa for K_1 of FeL is in good agreement with the other values. Consistency of the values of K_1 of ZrL^+ is found in spite of the use of protonation constants of 49 S which are valid for other experimental conditions and neglecting the presence of H_4L^+ in solutions at pH values near 0. Among these papers the work of Prasilova et al. should be mentioned. These authors used a liquid ion exchanger and "at acidity higher than 1.5 M $HClO_4$ the exchange of Zr^{4+} ions from the aqueous phase and the hydrogen ions the organic phase is inversely dependent on the fourth power of the hydrogen ion concentration in the aqueous phase". The values obtained for K_1 are dependent on the ionic strength. In the work of 66 L the formation of 1 : 2 species under the conditions used (pH = 2) for NTA as well as for EDTA is postulated from spectrophotometric measurements. Because this seems quite unexpected for the latter ligand, these results must be questioned.

Th⁴⁺: The results of 58 C are not considered here because they were obtained using the direct pH method for $K_1 > 10$! The value given by Shorik et al. (67 Sa) is doubtful, because $\log K_1$, which was obtained in the pH range 2.47 to 2.60, varies between 12.95 and 13.51. Also the variation of the concentration of the components among the individual mixtures is smaller than the variation of K_1 . There remains only the value of 67 B which was obtained using the exchange equilibrium VII with Fe^{3+} and potentiometric measurements of the equilibrium concentration of Fe^{3+} (at pH = 2). This value of K_1 can be considered as tentative. Since it is corrected for Na^+ complex formation in 0.1($NaClO_4$), it corresponds to the value which should be expected in 0.1($KClO_4$). The value of K_2 for the formation of $Th(NTA)_2^{2-}$ - as well as for the other cations of this group - is not known but is expected to be high. $Th(NTA)_2^{2-}$ is formed at pH 4 but at pH 9, since $Th(NTA)_2(OH)^{3-}$ predominates, at least one coordinated H_2O molecule is still probably present in the 1 : 2 complex!

Selected values:

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>log K₁</u> | <u>Reference</u> | <u>Rank</u> |
|------------------|------------------|--------------|--------------------------|------------------|-------------|
| Zr ⁴⁺ | 0.1(KCl) | 25 | 20.8 | 64 I, 66 E | T |
| Th ⁴⁺ | 0.1($NaClO_4$) | 20 | 16.9 ^a | 67 B | T |

a: corrected for Na^+ complex formation

TABLE 2.6. Stability constants of 4a cations

(For definitions see pages 2713/2714)

| <u>Metal</u> | <u>Medium</u> (see pp. 2713/2714) | <u>t[°C]</u> | <u>log K₁</u> | <u>log β₂</u> | <u>Method</u> (see p. 2714) | <u>Reference</u> |
|-------------------|--------------------------------------|--------------|--------------------------|--------------------------|--------------------------------|------------------|
| Ti ³⁺ | 1.2(KCl) | 20 | a) | | | |
| TiO ²⁺ | 0.1(KClO ₄) | 20 | 12.3(1) | | dis | 63 S |
| Zr ^{4+b} | 0.1 | 25 | 20.8(1) | | sp | 64 I |
| | 0.23 HClO ₄ | | 20.81 | | ix | 66 E |
| | 1 HClO ₄ | | 19.51 | | ix | 66 E |
| | ? (HClO ₄) | | | 7.8(2) | sp | 66 L |
| | 1(HCl) | 18 - 20 | 18.93 | | sp | 66 Ka |
| | 2 HClO ₄ | 19 - 21 | 18.6 | | ix | 70 P |
| Hf ^{4+c} | 0.23 HClO ₄ | | 20.34 | | ix | 66 E |
| Th ^{4+d} | 0.1(KNO ₃) | 25 | 12.4 | | gl | 58 C |
| | 0.1(NaClO ₄) | 20 | 16.9 | | Fe, VII | 67 B |
| | 0.1(NaClO ₄) | 25 | 13.3(2) | | Hg, VII | 67 S |

a: $\log K (\text{Ti}^{3+} + \text{HL}^{2-} \rightleftharpoons \text{TiHL}^+) = 18.7(1)$ at $I = 1.2(\text{KCl})$, 20°C , sp tp (73 Y).

b: $\log K (\text{Zr}^{4+} + \text{H}_3\text{L} \rightleftharpoons \text{ZrL}^+ + 3\text{H}^+) = 5.35(5)$ at $I = 1(\text{HClO}_4)$, $?^\circ\text{C}$, ix (64 E) and $= 4.08(4)$ at $I = 2(\text{HClO}_4)$, $?^\circ\text{C}$, ix (64 E).

c: $\log K (\text{Hf}^{4+} + \text{H}_3\text{L} \rightleftharpoons \text{HfL}^+ + 3\text{H}^+) = 5.05(9)$ at $I = 1 \text{ HClO}_4$, $?^\circ\text{C}$, ix (64 E) and $= 3.83(2)$ at $I = 2 \text{ HClO}_4$, $?^\circ\text{C}$, ix (64 E).

d: pK of ThL^+ : 6.62(1) (68 B), $\log K (\text{Th}(\text{OH})_2\text{L}^- + 2\text{H}^+ \rightleftharpoons \text{ThL}^+) = 8.2$ (58 C).

5.5. Complex formation with 5a cations

Only for vanadium equilibrium data have been obtained for different metal oxidation states. For V^{3+} K_1 is obtained polarographically (exchange VII with Cu^{2+} in presence of an acetic acid-acetate buffer, calculations with $\log K_1 (\text{CuL}^-) = 12.68$ (51 S)) and K_2 by the direct pH method taking into consideration the formation of $\text{V}(\text{OH})\text{L}^-$. The vanadyl ion VO_2^{2+} forms a 1 : 1 complex which is stabilised by formation of two hydroxo complexes. The value of K_1 obtained by the direct pH method is not very reliable because it is $> 10^{10}$. Pervanadyl ion VO_2^+ forms quite stable complexes as compared with other monovalent cations. The K_1 value has been obtained by different authors spectrophotometrically. Tischenko, Pechurova and Spitzin (72 T) have interpreted the complex formation postulating the formation of $\text{VO}_2\text{H}_2\text{L}$ instead of VO_2L^{2-} . The complex VO_2L is decomposed in basic solution: $\text{VO}_2\text{L}^{2-} + 2\text{H}_2\text{O} \rightleftharpoons \text{HVO}_4^{2-} + \text{L}^{3-} + 3\text{H}^+$ ($\log K = -28.3$ at 25°C and in 1 M NaClO_4).

Selected values:

| <u>Metal</u> | <u>Medium</u> | <u>t [°C]</u> | <u>log K₁</u> | <u>log K₂</u> | <u>Reference</u> | <u>Rank</u> |
|------------------------------|--------------------------|---------------|--------------------------|--------------------------|------------------|-------------|
| V ³⁺ | 0.1(NaClO ₄) | 20 | 13.41 | 8.68 | 70 P | T |
| VO ²⁺ | 0.1(KNO ₃) | 25 | 10.82 | | 73 S | T |
| VO ₂ ⁺ | 3(NaClO ₄) | 25 | 13.8 | | 75 L, 78 L | T |

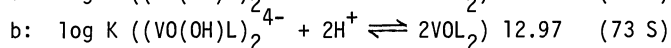
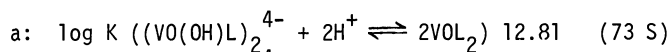
TABLE 2.7. Stability constants of group 5a cations

(For definitions see pages 2713/2714)

| <u>Metal</u> | <u>Medium</u> | <u>t [°C]</u> | <u>log K₁</u> | <u>log K₂</u> | <u>Method</u> | <u>Reference</u> |
|-----------------------------------|--------------------------|---------------|--------------------------|--------------------------|---------------|------------------|
| | (see pp. 2713/2714) | | | | (see p. 2714) | |
| <u>V³⁺</u> | 0.1(NaClO ₄) | 20 | 13.41 | 8.68(2) | pl | 70 P |
| <u>VO²⁺</u> | 0.1(KNO ₃) | 25 | 10.82 | | gl | 73 S |
| | 0.1(KNO ₃) | 30 | 10.70 | | gl | 73 S |
| <u>VO₂⁺</u> | 3 NaClO ₄ | 25 | 13.78 | | gl | 75 L |
| | 1(NaClO ₄) | | 13.8(4) | | sp | 76 Y |
| | 3 NaClO ₄ | 25 | 13.8(2) | | sp, gl | 78 L |

TABLE 2.8. pK values of 1 : 1 complexes

| <u>Metal</u> | <u>Medium</u> | <u>t [°C]</u> | <u>Complex</u> | <u>pK₁</u> | <u>Method</u> | <u>Reference</u> |
|------------------------|--------------------------|---------------|------------------|-----------------------|---------------|------------------|
| | (see pp. 2713/2714) | | | | (see p. 2714) | |
| <u>VO²⁺</u> | 0.1(NaClO ₄) | 25 | VOL ⁻ | 7.38(5) | gl | 66 Kb |
| | 0.1(KNO ₃) | 25 | VOL ⁻ | 7.23 ^a | gl | 73 S |
| | 0.1(KNO ₃) | 30 | VOL ⁻ | 7.17 ^b | gl | 73 S |



5.6. Complex formation with 6a and 5f cations

With the exception of the actinides, the group contains cations with generally high charge, which is often neutralized by coordination of O²⁻ and OH⁻ to yield either cations with low charge or anions. The oxo species MO_x^{z-2x} with z - 2x ≤ 0 can form complexes with NTA. MoO₃L

and WO_3L are stable between pH 3 and 7. Decomposition takes place with formation of MoO_4^{2-} and WO_4^{2-} , respectively. For Np^{4+} only small amounts of hydrolytic products are present between pH 0 and 1 (75 M), i.e. the conditions under which the 1 : 1 and the 1 : 2 complexes are formed. It is noted that the stability constants K_1 and K_2 are estimated to be of similar order of magnitude. The trivalent cations of the actinides show a similar tendency to form 1 : 1 and 1 : 2 complexes as the lanthanides. Some doubt surrounds the results of Moskvin and Shalinetz in which protonated species of type MHL_2 are considered. Such a species was postulated for $M^{3+} = Am^{3+}, Cm^{3+}$ and Ce^{3+} , although other authors such as Sary, Anderegg and Moeller and Ferrus did not observe them. Simple calculation using the data of the Russian authors show that the pK of this species lies between 3 and 4 and therefore they should be detectable by the above authors. Moskvin (71 Ma) postulated the presence of MHL_2 to explain the deviation of K_1 which results on increased acidity of the solution; a better explanation seems to be to assume the presence of MHL^+ .

Selected values:

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>log K₁</u> | <u>log K₂</u> | <u>log β₂</u> | <u>Reference</u> | <u>Rank</u> |
|--------------|--|--------------|--------------------------|--------------------------|--------------------------|------------------|-------------|
| UO_2^{2+} | 0.1(NaClO ₄) | 20 | 9.56 | | | 61 S | T |
| Np^{4+} | 1(H,Na)ClO ₄ | 25 | 17.28 | | 32.06 | 71 E | T |
| NpO_2^+ | 0.1(NH ₄ ClO ₄) | 25 | 6.80 | | | 70 E | T |
| PuO_2^+ | 0.1(NaClO ₄) | 25 | 6.91 | | | 70 E | T |
| Am^{3+} | 0.1(NaClO ₄) | 25 | 12.00 | 9.11 | | 72 E | T |
| Cm^{3+} | 0.1(NH ₄ ClO ₄) | 25 | 11.80 | | 20.58 | 68 E | T |
| Cf^{3+} | 0.1(NaClO ₄) | 25 | 11.92 | | 21.21 | 68 E | T |

TABLE 2.9. Stability constants of 6a and 5f cations

(For definitions see pages 2713/2714)

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>log K₁</u> | <u>log K₂</u> | <u>log β₂</u> | <u>Method</u> | <u>Reference</u> |
|--------------|-----------------------------------|--------------|--------------------------|--------------------------|--------------------------|---------------|------------------|
| | (see pp. 2713/2714) | | | | | (see p. 2714) | |
| Cr^{3+} | 0.1 KCl | 20 | > 10 | | | gl | 48 S |
| U^{3+} | | | 12.4 | | | est | 69 Ma |
| UO_2^{2+} | 0.1(NaClO ₄) | 20 | 9.56(3) | | | dis, ix | 61 S |
| | 0.1 | 20 | 7.88 | | | tp | 68 M |
| Np^{3+} | | | 12.7 | | | | 69 Ma |
| Np^{4+} | 1(ClO ₄ ⁻) | 25 | 17.28 | | 32.06 | sp | 70 P |
| | 1(H,Na)ClO ₄ | 25 | 17.28 | | 32.06 | sp | 71 E |

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>log K₁</u> | <u>log K₂</u> | <u>log β₂</u> | <u>Method</u> | <u>Reference</u> |
|------------------------------------|--|--------------|--------------------------|--------------------------|--------------------------|---------------|------------------|
| | (see pp. 2713/2714) | | | | | (see p. 2714) | |
| <u>NpO₂⁺</u> | 0.1(NH ₄ ClO ₄) | 25 | 6.80(10) | | | sp | 70 E |
| | 1(ClO ₄ ⁻) | 25 | 5.85 | | 6.77 | sp | 78 Pa |
| <u>Pu³⁺</u> | | | 10.60 | | | ? | 69 Ma |
| <u>PuO₂⁺</u> | 0.1(NaClO ₄) | 25 | 6.91(4) | | | ix | 70 E |
| <u>Am^{3+a}</u> | 0.1(NaClO ₄) | 25 | 11.52(1) | | 20.24(3) | ix | 68 E |
| | 0.1(NaClO ₄) | 15 | 11.90 | 9.13 | | | 72 E |
| | 0.1(NaClO ₄) | 25 | 11.99 | 9.11 | | | 72 E |
| | 0.1(NaClO ₄) | 50 | 11.71 | 8.68 | | | 72 E |
| | 0.1(NH ₄ Cl) | 20 | ~11 | | 19.74 | dis | 66 S |
| | | | | 13.46 | | | est |
| | 1(NH ₄ Cl) | 19-21 | 10.87(5) | | | ix | 71 Ma |
| | 0.1 | 20 | 11.55 | | 19.52 | tp | 71 S |
| <u>Cm^{3+a}</u> | 0.1(NH ₄ Cl) | 20 | | | 20.13 | dis | 66 Sa |
| | 0.1(NH ₄ ClO ₄) | 25 | 11.80(1) | | 20.58(3) | ix | 68 E |
| | | | 13.53 | | | | 69 Ma |
| | 0.1 | 20 | 11.52 | | 19.57 | tp | 71 S |
| <u>Cf³⁺</u> | 0.1(NaClO ₄) | 25 | 11.92(3) | | 21.21(2) | ix | 68 E |

a: Values for $\log K(M^{3+} + L^{3-} + HL^{2-} \rightleftharpoons MHL_2^{2-})$: Cm³⁺ 13.7 (I = 1(NH₄Cl), 20 ± 1 °C, ix, 71 Ma); Cm³⁺ 13.72 (I = 0., 20 °C, tp, 71 S); Am³⁺ 13.65 (I = 0.1 1(NH₄Cl), 20 ± 1 °C, 71 Ma); Am³⁺ 13.56 (I = 0., 20 °C, tp, 71 S)

TABLE 2.10. pK values of M(NTA) complexes

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>Complex</u> | <u>pK₁</u> | <u>pK₂</u> | <u>pK₃</u> | <u>Method</u> | <u>Reference</u> |
|------------------------------------|----------------------|--------------|---------------------|-----------------------|-----------------------|-----------------------|---------------|------------------|
| <u>Cr³⁺</u> | 0.001 | 20 | CrL | 6.5 | 7.3 | | gl | 48 S |
| | 0.1 KNO ₃ | 22 | CrL | 5.87 | 8.74 | 11.8 | sp | 72 I |
| <u>NpO₂⁺</u> | 0.1 | 25 | NpO ₂ HL | 1.77(37) | 11.46(11) | | sp | 70 E |

TABLE 2.11. Equilibria involving Mo^{VI} and W^{VI}

| <u>Metal</u> | <u>Medium</u> (see pp. 2713/2714) | <u>t[°C]</u> | <u>Logarithm of Equilibrium Constant</u> | <u>Method</u> (see. p. 2714) | <u>Ref.</u> |
|------------------------|--------------------------------------|--------------|---|---------------------------------|-------------|
| <u>Mo^{VI}</u> | 1.3 | 28 | $K(\text{MoO}_4^{2-} + \text{WO}_3\text{L}^{3-} \rightleftharpoons \text{MoOL}^{3-} + \text{WO}_4^{2-})$ 0.15 | nmr | 67 M |
| | 0.5(NaClO ₄) | 25 | $K(\text{MoO}_4^{2-} + \text{L}^{3-} + 2\text{H}^+ \rightleftharpoons \text{MoO}_3\text{L}^{3-})$ 17.90(3) | gl | 76 C |
| | 0.15(KNO ₃) | 25 | $K(\text{MoO}_4^{2-} + \text{L}^{3-} + 2\text{H}^+ \rightleftharpoons \text{MoO}_3\text{L}^{3-})$ 18.94(3) | gl | 66 K |
| | 1 - 2.5 | 35 | $K(\text{MoO}_4^{2-} + \text{L}^{3-} + 2\text{H}^+ \rightleftharpoons \text{MoO}_3\text{L}^{3-})$ 18.90(8) | nmr | 66 K |
| <u>W^{VI}</u> | 0.15 | 25 | $K(\text{WO}_4^{2-} + \text{L}^{3-} + 2\text{H}^+ \rightleftharpoons \text{WO}_3\text{L}^{3-})$ 18.86(5) | gl | 66 K |
| | 1 - 2.5 | 35 | $K(\text{WO}_4^{2-} + \text{L}^{3-} + 2\text{H}^+ \rightleftharpoons \text{WO}_3\text{L}^{3-})$ 19.1(2) | nmr | 66 K |
| | 0.5(NaClO ₄) | 25 | $K(\text{WO}_4^{2-} + \text{L}^{3-} + 2\text{H}^+ \rightleftharpoons \text{WO}_3\text{L}^{3-})$ 17.75(3) | gl | 76 C |

5.7. Complex formation with 7a cations

Mn²⁺ forms 1 : 1 and 1 : 2 complexes with NTA, which have usually been investigated by use of the direct pH method. Complexes of Mn³⁺ were investigated (71 B) using the pyrophosphate complex as a starting product. The spectrophotometric measurements were made at pH 3.5 because at this pH the solutions of the NTA complex do not contain hydroxo species and the rate of reduction of Mn^{III} is relatively slow. The calculation of the stability constant is performed taking into account the stability of the pyrophosphate complex. The value of Gorski et al. for Tc^{IV} cannot be considered reliable, because of the expected and little known hydrolysis of Tc^{IV} under the conditions used.

Selected values:

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>log K₁</u> | <u>log K₂</u> | <u>Reference</u> | <u>Rank</u> |
|------------------|------------------------|--------------|--------------------------|--------------------------|------------------|-------------|
| Mn ²⁺ | 0.1(KNO ₃) | 20 | 7.44 | 3.55 | 51 S, 60 A | T |

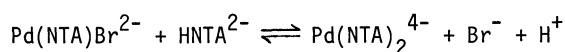
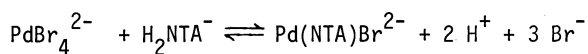
TABLE 2.12. Equilibrium constants of group 7a cations

| <u>Cation</u> | <u>Medium</u> (see pp. 2713/2714) | <u>t[°C]</u> | <u>log K₁</u> | <u>log K₂</u> | <u>Method</u> (see. p. 2714) | <u>Reference</u> |
|----------------------------|--------------------------------------|--------------|--------------------------|--------------------------|---------------------------------|------------------|
| <u>Mn²⁺</u> | → 0 | 20 | 10 ^a | | gl | 48 S |
| | 0.1(KCl) | 20 | 7.44 | | gl | 51 S |
| | → 0(KCl) | 0 | 8.525 | | gl | 56 H |
| | → 0(KCl) | 10 | 8.534 | | gl | 56 H |
| | → 0(KCl) | 20 | 8.573 | | gl | 56 H |
| | → 0(KCl) | 30 | 8.644 | | gl | 56 H |
| | 0.1(KNO ₃) | 20 | | 3.55 | gl | 60 A |
| | 0.03 | 25 | | 3.02(2) | nmr | 78 S |
| <u>Mn³⁺</u> | 1(NaClO ₄) | | 20.25 | | sp | 71 B |
| <u>TcO(OH)⁺</u> | 0.1(NaClO ₄) | | 13.8(2) | | ix | 70 G |

a: pK value of MnL: 12 (47 S)

5.8. Complex formation with 8a cations

Equilibrium data are known for some divalent and one trivalent cation of this group. In all cases only tentative values can be given because of the scarcity of numerical results. Equilibria involving Fe^{3+} have received the attention of different authors but two of them used the direct pH method for the determination of K_1 in spite of its inadequacy. Indeed, the 1 : 1 complex (with $\log K_1 \geq 16$) is completely formed in the solution of the protonated ligand and metal ion before addition of any strong base. One has to consider not relevant and purely fortuitous the value obtained with this method by 73 M (which is very near to the tentative value). The 1 : 1 complex behaves as an acid with $\text{pK} = 4$; this stabilises the 1 : 1 complex and results in only limited formation of the 1 : 2 complex. Using a metal/ligand ratio of 1 : 2 and millimolar solutions of the components the complex FeL_2^{3-} is 50% decomposed in FeLOH^- and HL^{2-} in neutral solution. Some results of 71 Ba obtained from polarographic measurements of the formation of Fe(II)HL are not discussed here because of uncertainty about them in the opinion of the original authors. The results of a rapid titration of a solution of the 1 : 1 complex FeL were used by Schwarzenbach and Heller (51 Sa) to obtain two pK values which had low standard deviations. This contrasts with the results of Gustafson and Martell who observed a slow equilibration and "upon standing for 2 to 3 months precipitation, probably of ferric hydroxide, was observed in all the solutions employed in these measurements". The low pK value of 51 Sa compared with that of 63 G could signify that some dimeric species are already formed in the corresponding solutions. In this case the low standard deviation of the pK of FeL is unexpected. These inconsistencies can only be mentioned here with a warning for caution when using these constants. There are also some doubts concerning the value of K_2 of 51 Sa because the complex Fe(OH)L^- is always present in comparable amount to that of FeL_2^{3-} in the pH range for its formation. On the other hand distribution measurements in presence of 8-hydroxyquinoline (69 S) give values of K_1 and K_2 which are in good agreement with those of 51 Sa. When comparing the reliability of the values of K_1 of FeL of 51 Sa and of 67 B one has to consider that in the former case the literature value of the standard potential $\text{Fe}^{3+}/\text{Fe}^{2+}$ is used, but in the second case the calibration and the determination of K_1 is made using data from the same titration. The stability constants for the palladium(II) complexes were obtained by combination of spectrophotometric as well as of pH measurements for the following equilibria:



Selected values:

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>log K₁</u> | <u>log K₂</u> | <u>Reference</u> | <u>Rank</u> |
|------------------|------------------------|--------------|--------------------------|--------------------------|------------------------|-------------|
| Fe^{2+} | 0.1 KCl | 20 | 8.83 | | 51 S, 51 Sa, 53 S | T |
| Fe^{3+} | 0.1(KCl) | 20 | 16.26 | 8.5 | 67 B | T |
| Co^{2+} | 0.1(KNO ₃) | 20 | 10.4 | 4.01 | 55 S, 56 S, 64 A | T |
| Ni^{2+} | 0.1(KNO ₃) | 20 | 11.54 | 4.88 | 55 S, 56 S, 63 S, 64 A | R |
| Pd^{2+} | 1(NaClO ₄) | 20 | 17.1 | 6.6 | 76 A | T |

TABLE 2.13. Stability constants of group 8a cations

(For definitions see pages 2713/2714)

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>log K₁</u> | <u>log K₂</u> | <u>log β₂</u> | <u>Method</u> | <u>Reference</u> |
|-------------------------------------|--------------------------|--------------|--------------------------|--------------------------|--------------------------|---------------|------------------|
| | (see pp. 2713/2714) | | | | | (see p. 2714) | |
| <u>Fe²⁺</u> ^a | 0.1(KCl) | 20 | 8.84 | | | gl, III | 51 S |
| | 0.1(KCl) | 20 | 8.82 | | | gl, III | 51 Sa |
| | 0.1(KCl) | 20 | 8.83 | | | gl, III | 53 S |
| <u>Fe³⁺</u> | ~ 0.001 | 20 | > 10 | | | gl | 48 S |
| | 0.1(KCl) | 20 | 15.87(20) | 8.45(40) | | | 51 Sa |
| | 0.1(KClO ₄) | 20 | 15.91(3) | | 24.61(5) | dis | 63 S |
| | 0.1(NaClO ₄) | 20 | 16.26 | | | red | 67 B |
| | 0.5(NaNO ₃) | 25 | 16.33 ^b | | | gl | 73 M |
| | 0.1(NaClO ₄) | 25 | 11.70 | 8.14 | | gl | 73 Ra |
| <u>Co²⁺</u> | ~ 0.001 | 20 | | 3.9 | | gl | 48 S |
| | 0.1 KCl | 20 | 10.6 | | | gl, V | 51 S |
| | 0.1(KNO ₃) | 20 | 10.38 | | | pol, VII | 55 S |
| | 0.1(KNO ₃) | 20 | 10.4 | | | pol, VIII | 56 S |
| | 0.1(KClO ₄) | 20 | 10.81(3) | | 14.28(5) | dis | 63 S |
| | 0.1(KNO ₃) | 20 | | 4.01 | | gl | 64 A |
| | 0.1(KNO ₃) | 20 | 10.0 | 3.9 | | chrom | 64 J |
| <u>Ni²⁺</u> | 0.001 | 20 | 10 | 4.7 | | gl | 48 S |
| | 0.1 KCl | 20 | 11.26 | | | gl, V | 51 S |
| | 0.1(KNO ₃) | 20 | 11.53 | | | pol, VII | 55 S |
| | 0.1(KNO ₃) | 20 | 11.54 | | | pol, VII | 56 S |
| | 0.1(KNO ₃) | 20 | | 4.88 | | gl | 64 A |
| | 0.1(KClO ₄) | 20 | 11.54(8) | | | dis | 63 S |
| <u>Pd²⁺</u> | 1(NaClO ₄) | 20 | 17.1 | 6.6 | | gl, sp | 76 A |

a: $\log K (\text{Fe}^{2+} + \text{HL}^{2-} \rightleftharpoons \text{FeHL})$ 1.0 (I = 0.2, 20 °C, pol, 71 Ba)

b: $\log K (\text{Fe}^{3+} + \text{L}^{3-} \rightleftharpoons \text{Fe(OH)L}^- + \text{H}^+)$ 12.35 (I = 0.5(NaNO₃), 25 °C, gl, 73 M)

TABLE 2.14 pK values of ML⁻

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>pK₁</u> | <u>pK₂</u> | <u>Method</u> | <u>Reference</u> |
|------------------------|------------------------|--------------|-----------------------|-----------------------|---------------|------------------|
| | (see pp. 2713/2714) | | | | (see p. 2714) | |
| <u>Fe²⁺</u> | 0.1(KCl) | 20 | 10.6 | | gl | 51 Sa |
| <u>Fe³⁺</u> | ~ 0.001 | 20 | 4 | 9 | gl | 48 S |
| | 0.1(KCl) | 20 | 4.08 | 7.77 | gl | 51 Sa |
| | 1(KCl) | 25 | 5.0 ^a | | gl | 63 G |
| <u>Co²⁺</u> | ~ 0.001 | 20 | 12 | | gl | 48 S |
| <u>Pd²⁺</u> | 1(NaClO ₄) | 20 | 7.82 | | gl | 76 A |

a: $\log K(2\text{FeLOH}^- \rightleftharpoons \text{Fe}_2(\text{OH})_2\text{L}_2^{2-})$ 4.0 (I = 1(KCl); 25 °C; gl; 63 G)

5.9. Complex formation with lb cations

The stability constant of CuL⁻ cannot be obtained from the direct pH method (see pages 2698 and 2701) and the values of 56W and 67 T are discarded. In 73 Ra the formation of CuHL is postulated but some inconsistencies are shown to be present by 73 Ma.

Selected values:

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>log K₁</u> | <u>log K₂</u> | <u>Reference</u> | <u>Rank</u> |
|------------------------|-------------------------|--------------|--------------------------|--------------------------|--------------------------------------|-------------|
| <u>Cu²⁺</u> | 0.1(KNO ₃) | 20 | 12.96 | 4.3 | 56 S, 63 S, 62 M, 60 A and this work | T |
| <u>Ag⁺</u> | 0.1(KClO ₄) | 20 | 5.16 | | 63 S | T |

TABLE 2.15 Stability constants of lb group cations

(For definitions see pages 2713/2714)

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>log K₁</u> | <u>log K₂</u> | <u>Method</u> | <u>Reference</u> |
|------------------------|------------------------|--------------|--------------------------|--------------------------|---------------|------------------|
| | (see pp. 2713/2714) | | | | (see p. 2714) | |
| <u>Cu²⁺</u> | 0.1 KCl | 20 | 12.68 | | gl, V | 51 S |
| | 0.1(KNO ₃) | 20 | 12.96 | | gl, V | 55 S |
| | 0.1(KNO ₃) | 20 | 12.7 | | gl | 56 W |
| | 0.1(KNO ₃) | 20 | | 4.47 | gl | 64 A |
| | 0.1(KNO ₃) | 15 | 13.21 | | gl, V | 62 M |
| | 0.1(KNO ₃) | 20 | 13.16 | | gl, V | 62 M |
| | 0.1(KNO ₃) | 25 | 13.10 | | gl, V | 62 M |
| | 0.1(KNO ₃) | 30 | 13.15 | | gl, V | 62 M |
| | 0.1(KNO ₃) | 35 | 13.10 | | gl, V | 62 M |
| | 0.1(KNO ₃) | 40 | 13.13 | | gl, V | 62 M |

| <u>Metal</u> | <u>Medium</u> | <u>t</u> [°C] | <u>log K₁</u> | <u>log K₂</u> | <u>Method</u> | <u>Reference</u> |
|------------------------|-------------------------|---------------|--------------------------|--------------------------|---------------|------------------|
| | (see pp. 2713/2714) | | | | (see p. 2714) | |
| <u>Cu²⁺</u> | 0.1(KClO ₄) | 20 | 13.05(1) | | gl, V | 63 S |
| | 0.1(KNO ₃) | 20 | 11.5 | 3.3 | | 64 J |
| | 0.1 | 25 | 13.3 | | Cu | 73 H |
| <u>Ag⁺</u> | 0.1(KClO ₄) | 20 | 5.16(5) | | dis | 63 S |

a: At I = 0.07; 25 °C, $K(\text{CuL}^- + \text{OH}^- \rightleftharpoons \text{CuLOH}^{2-})$ 4.39(1), (68 H).

TABLE 2.16. pK values of CuL^-

| <u>Metal</u> | <u>Medium</u> | <u>t</u> [°C] | <u>pK</u> | <u>Method</u> | <u>Reference</u> |
|------------------------|--------------------------|---------------|-----------|---------------|------------------|
| <u>Cu²⁺</u> | 0.1(NaClO ₄) | 25 | 9.14(2) | gl | 68 Ib |
| | 0.1(KNO ₃) | 25 | 9.14 | gl | 68 Ia |

5.10. Complex formation with 2b cations

Zn²⁺: The values of 66 C and 66 I for K_1 are obtained by the direct pH method. In consideration of the inadequacy of this method for this system, these values are discarded. There then remain the values of 55 S and 56 S for $\log K_1$ and of 60 A for $\log K_2$.

Cd²⁺: The value of $\log K_1$ is slightly lower than 10 but it was preferably obtained by use of exchange reactions. Because of complex formation with Cl^- , only the values obtained in presence of NO_3^- and ClO_4^- are considered accurate. Only tentative values can be given.

Hg²⁺: In 67 S a very limited pH and concentration range is used (see p. 2708) in the determination of K_1 . The spectrophotometric investigation done by Chernova et al. (69 C) relies on a greater absorbance from HgL^- with respect to Hg^{2+} and of the protonated ligand. Using some assumptions, complex formation was predicted to take place by loss of 2H^+ at $\text{pH} < 0.7$ and 3H^+ at $\text{pH} > 0.7$. Treatment of the data yielded values for the formation constants of HgHL and HgL^- which were too large and it was considered that H_3L is the stable form of the ligand over the whole pH range (!). The ionic strength was produced by the metal and ligand ions as well as by the strong acid added and therefore was not constant. Further the formation of H_4L^+ was not considered. For these reasons the values of the constants must be considered doubtful. The results of 77 G seem questionable for the following reasons:

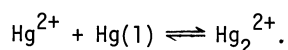
- i) use of the value of Schwarzenbach and Anderegg (54 S) for the ratio $q = [\text{Hg}_2^{2+}]/[\text{Hg}^{2+}]$ for KNO_3 solutions for the calculation of the equilibrium concentration of Hg_2^{2+} and Hg^{2+} .
- ii) the following relationship was used for the calculation of the concentrations of the above species:

$$C_{\text{Hg}} = [\text{Hg}^{2+}] + 2[\text{Hg}_2^{2+}]$$

instead of:

$$C_{\text{Hg}} = [\text{Hg}^{2+}] + [\text{Hg}_2^{2+}]$$

which takes into consideration that Hg_2^{2+} is obtained from Hg^{2+} and $\text{Hg}(1)$ in the following manner:



Use of the value of Sillén et al. (47 S) for the conditions maintained in 77 G one obtains a difference in E^0 of 4.3 mV! iii) at the contact between the 0.5 M NaClO_4 and the 0.1 M KNO_3 solutions, insoluble KClO_4 is formed leading to the possibility of unstable potential values. On the basis of these arguments the value of 67 S is considered more reliable.

Selected values:

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>log K₁</u> | <u>log K₂</u> | <u>Reference</u> | <u>Rank</u> |
|------------------|--------------------------|--------------|--------------------------|--------------------------|------------------|-------------|
| Zn ²⁺ | 0.1(KNO ₃) | 20 | 10.66 | 3.62 | 56 S, 55 S, 60 A | T |
| Cd ²⁺ | 0.1(KNO ₃) | 20 | 9.80 | 4.48 | 56 S, 60 A | T |
| Hg ²⁺ | 0.1(NaClO ₄) | 25 | 14.6 | | 67 S | T |

TABLE 2.17. Stability constants of group 2b cations

(For definitions see pages 2713/2714)

| <u>Metal</u> | <u>Medium</u> (see pp. 2713/2714) | <u>t[°C]</u> | <u>log K₁</u> | <u>log K₂</u> | <u>log β₂</u> | <u>Method</u> (see p. 2714) | <u>Reference</u> |
|------------------------|--------------------------------------|--------------|--------------------------|--------------------------|--------------------------|--------------------------------|------------------|
| <u>Zn²⁺</u> | 0.001 | 20 | > 10 | ~ 3 | | gl | 48 S |
| | 0.1 KCl | 20 | 10.49 | | | gl, III | 49 S |
| | 0.1 KCl | 20 | 10.45 | | | gl, V | 51 S |
| | 0.1(KNO ₃) | 20 | 10.67 | | | gl | 55 S |
| | 0.1 KCl | 20 | 10.35 | | | pol | 55 K |
| | 0.1(KNO ₃) | 20 | 10.66 | | | pol, VII | 56 S |
| | 0.1(KNO ₃) | 20 | | 3.62 | | gl | 64 A |
| | 1(NaCl or NaNO ₃ ?) | 25 | 9.18(6) | | | gl | 66 C |
| | 0.1(KCl) | 20 | 10.44(3) | | | gl | 66 I |
| <u>Cd²⁺</u> | 0.001 | 20 | > 10 | 5.7 | | gl | 48 S |
| | 0.1 KCl | 20 | 9.16 | | | pol | 50 K |
| | 0.2 KCl | 20 | 8.85 | | | pol | 50 K |
| | 0.3 KCl | 20 | 8.61 | | | pol | 50 K |
| | 0.1 KCl | 20 | 9.54 | | | pH | 51 S |
| | 0.1(KNO ₃) | 20 | 9.83 | | | pol | 55 S |
| | 0.1(KNO ₃) | 20 | 9.80 | | | pol | 56 S |
| | 0.1(KNO ₃) | 20 | | 4.78 | | gl | 64 A |
| | 0.1(KClO ₄) | 20 | | | 15.45(4) | dis | 63 S |
| | 0.1(KNO ₃) | 20 | 10.0 | 4.6 | | tp | 64 J |
| | 1.0(NaClO ₄) | 30 | 9.2(2) | | | dis | 65 H |
| | 1 - 2 | 25 | 9.4 | 4.9 | | nmr | 69 R |

| <u>Metal</u> | <u>Medium</u> | <u>t [°C]</u> | <u>log K₁</u> | <u>log K₂</u> | <u>log β₂</u> | <u>Method</u> | <u>Reference</u> |
|------------------------|--------------------------|---------------|--------------------------|--------------------------|--------------------------|---------------|------------------|
| | (see pp. 2713/2714) | | | | | (see p. 2714) | |
| <u>Hg²⁺</u> | 0.1(NaClO ₄) | 25 | 14.6(1) | | | Hg | 67 S |
| | | 18 - 22 | 16.39 | | | sp | 69 C |
| | 0.5 NaClO ₄ | 25 | 13.48(9) | | | Hg | 77 G |

TABLE 2.18. pK values of complexes

| <u>Metal</u> | <u>Medium</u> | <u>t [°C]</u> | <u>complex</u> | <u>pK₁</u> | <u>Method</u> | <u>Reference</u> |
|-------------------------------------|------------------------|---------------|------------------|-----------------------|---------------|------------------|
| <u>Zn²⁺</u> ^a | 0.001 | 20 | ZnL ⁻ | ~ 10 | gl | 48 S |
| | 0.1(KNO ₃) | 25 | ZnL ⁻ | 10.06 | gl | 71 Ia |
| <u>Cd²⁺</u> | 0.001 | 20 | CdL ⁻ | ~ 12 | gl | 48 S |
| | 0.1 KNO ₃ | 25 | CdL ⁻ | 11.25 | gl | 71 Ia |

a: $\log K [\text{ZnL}^- + \text{OH}^- \rightleftharpoons \text{ZnL}(\text{OH})^{2-}]$ 3.55 (I = 0.07 - 0.08; 25 °C; gl (68 H) and 4.01 (I = 0.4 - 0.6; 25 °C; nmr (73 R)).

5.11. Complex formation with 3b cations

For Al³⁺: A complete set of values of equilibrium constants for AlL and its hydrolytic species is given by 67 Ba. The protonation constants of the ligand obtained by the same authors are of the expected magnitude. Further the calibration was done with the appropriate procedure and experimental conditions. The stability constant K₁ was obtained spectrophotometrically in the pH range 3.5 - 4 by use of an exchange reaction with Co²⁺, for which the value K₁ = 10^{10.44} was obtained spectrophotometrically. The hydrolysis of Al³⁺ was taken into consideration with pK of Al³⁺ = 4.85. The difference between the value of K₁ determined by 67 Ba and 63 S is remarkably high and the tentative value must be considered quite uncertain.

For Ga³⁺: Polarographic measurements involving exchange with Cu²⁺ have been used by 68 Z with solutions at pH 2.5. The value obtained is similar to that of 67 B but in very poor agreement with that of 76 H. The reason for this discrepancy is not clear. In this latter study the same exchange reaction VII with Cu²⁺ was used, but the concentration of CuL⁻ was obtained spectrophotometrically. However, the absorbtivity of the complex is only approximately four times that of the aquated copper(II) ion. On the other hand, the value obtained by exchange VII with Hg²⁺ (69 C) is not very accurate as already explained under Hg²⁺ due to the inconstancy of the ionic strength and the uncertain value of K₁ for HgL⁻.

For In³⁺: The exchange of type VII with Fe³⁺ was investigated using ammonium acetate as a buffer at variable ionic strengths and pH = 2.5 - 3.4 (65 Z). The hydrolysis of Fe³⁺ and In³⁺ was not considered. The distribution of In¹¹⁴ between aqueous solution and ion exchanger was investigated in 0.1 to 0.5 M HClO₄ without consideration of H₄L⁺ (63 R).

For Tl⁺: Two values of K₁ determined under the same experimental conditions agree very well.

For Tl³⁺: Information on the complexes of Tl³⁺ was first published by Koch and Pfrepper (61 K), who from the absorbtion of Tl³⁺ ions on a cation exchanger in the presence of NTA, suggested

the possible formation of complexes $Tl(HL)_n^{-2n+3}$. Kul'ba and Makasov (65 K) using redox and spectrophotometric measurements investigated the complex formation with $TlCl_3$ as a starting material. They postulated the formation of $Tl(H_2L)_3$ and Kornev et al. (66 K) showed by spectrophotometric studies that the formation of a 1 : 1 complex was complete at $pH \sim 0.4$ and that at $pH 2$ a 1 : 2 complex is formed. The determination of the protons displaced by complex formation leads to the postulation that the species TlH_2L^{2+} and TlH_3L_2 are formed (provided it is assumed that from $pH 0.3$ to 1.3 the ligand is present in solution mainly as H_3L). The value of K_1 was obtained by Anderegg from redox measurements at $pH = 0$; it was assumed that the complex was not protonated. K_2 was obtained by the same method from measurements between $pH 2$ and 4 where eventually protonated species can be detected.

Selected values:

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>log K₁</u> | <u>log K₂</u> | <u>Reference</u> | <u>Rank</u> |
|------------------------|---------------------------|--------------|--------------------------|--------------------------|------------------|-------------|
| <u>Al³⁺</u> | 0.1(KClO ₄) | 20 | 9.5 | | 63 S | T |
| <u>Ga³⁺</u> | 0.1(KNO ₃) | 20 | 13.7 | | 67 B, 68 Z | T |
| <u>In³⁺</u> | 0.1(KNO ₃) | 20 | 16.9 | 7.4 | 63 S, 67 B | T |
| <u>Tl⁺</u> | 0.1(KNO ₃) | 20 | 4.74 | | 63 Ia, 67 Aa | R |
| <u>Tl³⁺</u> | 1(Na, HClO ₄) | 20 | 20.9 | 11.6 | 67 Aa | T |

TABLE 2.19. Stability constants of group 3b cations

(For definitions see pages 2713/2714)

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>log K₁</u> | <u>log K₂</u> | <u>log β₂</u> | <u>Method</u> | <u>Reference</u> |
|------------------------|--------------------------|--------------|--------------------------|--------------------------|--------------------------|---------------|------------------|
| | (see pp. 2713/2714) | | | | | (see p. 2714) | |
| <u>Al³⁺</u> | 0.001 | 20 | > 10 | | | gl | 48 S |
| | 0.1(KClO ₄) | 20 | 9.5 | | | dis | 63 D |
| | 0.2(NaClO ₄) | 20 | 11.37 | | | sp, gl | 67 Ba |
| <u>Ga³⁺</u> | 0.1(KClO ₄) | 20 | | | 25.81(4) | | 63 S |
| | 0.1(NaClO ₄) | 20 | 13.6 | | | red, VII | 76 H |
| | 0.1(KNO ₃) | 22 | 13.95 | | | pol | 68 Z |
| | | 18 - 22 | 17.7(2) | | | sp | 69 C |
| | 0.1 | 25 | 16.2 | | | sp | 76 H |
| <u>In³⁺</u> | 0.5 | | 14.88(9) | | | ix | 63 R |
| | 0.1(KClO ₄) | 20 | | | 24.4 | dis | 63 S |
| | | 20 - 22 | 15.88 | | | | 65 Z |
| | 0.1(NaClO ₄) | 20 | 16.9 | | | red. VII | 67 B |

| <u>Metal</u> | <u>Medium</u> | <u>t</u> [°C] | <u>log K₁</u> | <u>log K₂</u> | <u>log β₂</u> | <u>Method</u> | <u>Reference</u> |
|------------------------|---------------------------|---------------|--------------------------|--------------------------|--------------------------|---------------|------------------|
| | (see pp. 2713/2714) | | | | | (see p. 2714) | |
| <u>Tl⁺</u> | 1 KCl | 25 | 3.44(3) | | | pol | 57 B |
| | 0.1(KNO ₃) | 20 | 4.74(1) | | | pH | 63 Ia |
| | 0.1(KNO ₃) | 20 | 4.75 | | | pH | 67 Aa |
| | 0.15(NaClO ₄) | 25 | 4.42(4) | | | sp, gl | 71 M |
| | | | 5.00 | | | ix | 69 K |
| <u>Tl³⁺</u> | 1(HNO ₃) | 25 | 18 | | | gl | 65 K |
| | | 20 | | | | sp | 66 K |
| | 1(H,NaClO ₄) | 20 | 20.9 | | 32.5 | red | 67 Aa |

TABLE 2.20. pK values of complexes

| <u>Metal</u> | <u>Medium</u> | <u>t</u> [°C] | <u>complex</u> | <u>pK₁</u> | <u>pK₂</u> | <u>Method</u> | <u>Reference</u> |
|------------------------|--------------------------|---------------|----------------|-----------------------|-----------------------|---------------|------------------|
| | (see pp. 2713/2714) | | | | | (see p. 2714) | |
| <u>Al³⁺</u> | 0.001 | 20 | AlL | 5.8 | | gl | 48 S |
| | 0.2(NaClO ₄) | 25 | AlL | 5.09 | 8.28 | gl | 67 Ba |
| | 0.2(NaClO ₄) | 25 | AlHL | 1.90 | | gl | 67 Ba |
| <u>Ga³⁺</u> | 0.1 | 25 | GaL | 4.27(2) | 7.64(3) | sp | 76 H |

5.12. Complex formation with 4b cations

Pb²⁺ forms 1 : 1 and 1 : 2 (?) complexes with NTA. The stability constants obtained by use of spectrophotometric measurements (70 K) are normally less reliable.

As^{III} from polarographic and redox potential measurements Elenkova et al. (73 E) postulated the formation of As(OH)₂HL. The species should be detectable by pH titrations of mixtures containing H₃AsO₃ and protonated NTA with strong base.

Bi³⁺: The values of K₁ and K₂ in 70 K are given as tentative values.

Selected values:

| <u>Metal</u> | <u>Medium</u> | <u>t</u> [°C] | <u>log K₁</u> | <u>log K₂</u> | <u>Reference</u> | <u>Rank</u> |
|------------------------|------------------------|---------------|--------------------------|--------------------------|---------------------|-------------|
| <u>Pb²⁺</u> | 0.1(KNO ₃) | 20 | 11.4 | | 55 S, 56 S, 63 S | R |
| | | | | 1.4 | 60 A | T |
| <u>Bi³⁺</u> | 1 NaClO ₄ | | 17.54 | 9.01 | 70 K | T |

TABLE 2.21 Stability constants of group 4b cations

(For definitions see pages 2713/2714)

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>log K₁</u> | <u>log β₂</u> | <u>Method</u> | <u>Reference</u> |
|------------------------|--------------------------|--------------|--------------------------|--------------------------|---------------|------------------|
| | (see pp. 2713/2714) | | | | (see p. 2714) | |
| <u>Pb²⁺</u> | 0.2 KCl | | 10.68 | | pol | 50 K |
| | 0.1(KNO ₃) | 20 | 11.39 | | pol | 55 S |
| | 0.1 KCl | 20 | 11.8 | | gl, VII | 51 S |
| | 0.1(KNO ₃) | 20 | 11.39 | | | 56 S |
| | 0.1(KClO ₄) | 20 | 11.47(4) | | dis | 63 S |
| | 0.1(NaClO ₄) | 25 | 12.40(10) | | pol | 69 V |
| | 0.1 NaClO ₄ | 20 | 11.83 ^a | | sp | 70 Ka |
| | 1 NaClO ₄ | 20 | 10.64 ^b | | sp | 70 Ka |
| <u>Bi³⁺</u> | 1 NaClO ₄ | | 17.54 | 26.55 | sp | 70 K |

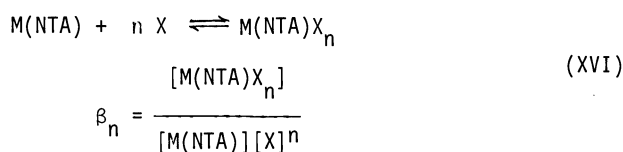
a: $\log K (\text{Pb}^{2+} + \text{HL}^{2-} \rightleftharpoons \text{PbHL}) = 3.99$ (I = 0.1 NaClO₄) = 3.60 (I = 1 NaClO₄)
(70 K)

TABLE 2.22. Equilibrium constants involving NTA and cations of this group

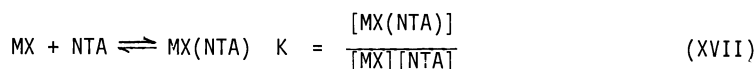
| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>Logarithm of the Constant</u> | <u>Method</u> | <u>Ref.</u> |
|-------------------------|---------------------------------------|--------------|---|---------------|-------------|
| | (see pp. 2713/2714) | | | (see p. 2714) | |
| <u>As^{III}</u> | 0.1(Na ₂ SO ₄) | 24 | $K(\text{As}(\text{OH})_2^+ + \text{H}^+ + \text{L}^{2-} \rightleftharpoons \text{As}(\text{OH})_2\text{HL}^-)$ 15.33(15) | gl | 73 E |
| | 0.1(Na ₂ SO ₄) | 25 | $K(\text{As}(\text{OH})_2^+ + \text{H}^+ + \text{L}^{2-} \rightleftharpoons \text{As}(\text{OH})_2\text{HL}^-)$ 15.58(20) | pol | 73 E |
| <u>Po^{IV}</u> | 1.0(NaClO ₄) | 22 | $K(\text{Po}(\text{OH})_2^{2+} + 2 \text{HL}^{2-} \rightleftharpoons \text{Po}(\text{OH})_2(\text{HL})_2^{2-})$ 8.18 | dis | 66 K |
| | 0.4 | 25 | $K(\text{Po}(\text{OH})_2^{2+} + 2 \text{HL}^{2-} \rightleftharpoons \text{Po}(\text{OH})_2(\text{HL})_2^{2-})$ 5.18 | ix | 66 K |

6. MIXED COMPLEXES

For complexes of the type $M(\text{NTA})X_n$ the constants of the equilibrium XVI are given in Table 3.1.



If X forms more stable 1 : 1 complexes than NTA, then the equilibrium XVII is appropriate. The corresponding data are given in Table 3.4. and refer to equilibria



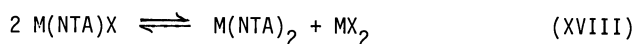
with X = EDTA.

The methods used for determining these equilibrium constants are:

1) the direct pH method (= pH). This is possible because the corresponding equilibria normally occur in a convenient pH range. NTA (and EDTA) forms quite stable complexes and the formation of $\text{M}(\text{NTA})X_n$ (and $\text{MX}(\text{NTA})$) are separately detectable; the calculation of the equilibrium constants is straightforward. Some cation is necessary because of the possible formation of hydroxo complexes $\text{M}(\text{NTA})\text{OH}$ (and $\text{M}(\text{EDTA})\text{OH}$) and $\text{M}(\text{NTA})_2$.

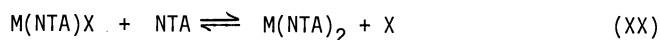
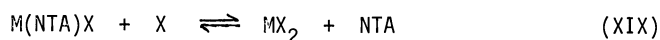
2) spectrophotometric measurements (= sp) are also possible if the absorption of $\text{M}(\text{NTA})$, $\text{M}(\text{NTA})X_n$ and $\text{M}(\text{NTA})\text{OH}$ are very different, but the precision of the constants is generally not comparable to that from method 1). Values of the overall constants may be calculated by combination of the constants given above with the stability constants of MNTA and MEDTA.

The auxiliary ligands X (see Table 3.1) generally form much weaker complexes with M than does NTA and therefore a proportionation of the type (XVIII) does not take place.



This can be considered to be the case if the constant of this last equilibrium is $< 10^{-4}$.

In some cases the following side reactions are possible. MX_2 and $\text{M}(\text{NTA})_2$ can only be neglected if the equilibrium constants



are $\leq 10^{-5}$. The use of mixtures with total concentration ratios $\text{M}:\text{NTA}:\text{X} = 1:1:1$ and $1:1:n$ allows the determination of the equilibrium constants for formation of mixed complexes of type XVI and XVII without the above complications (68 I, 68 IC, 68 H, 75 I, 74 Ia, 74 Ib ...). Mixed complex formation involving EDTA and NTA is also of interest but the decomposition in 1 : 1 : 1 millimolar solutions of complexes of type $\text{Ln}(\text{EDTA})\text{NTA}^{4-}$ ranges from about 4% (La^{3+}) to about 30% (Lu^{3+}). This decomposition was calculated using the known values of the stability constants of the species involved.

TABLE 3.1. Stability constant β_1 of equilibrium XVI for mixed NTA complexes

| <u>Metal</u> | <u>Medium</u> (see pp. 2713/2714) | <u>t[°C]</u> | <u>Mixed complex</u> | <u>log β_1</u> | <u>Method</u> (see p. 2714) | <u>Reference</u> |
|---------------------------|--------------------------------------|--------------|----------------------|---------------------------------|--------------------------------|------------------|
| <u>Acetic acid</u> | | | | | | |
| Fe ³⁺ | 0.1(KCl) | 20 | Fe(NTA)X | 2.3 | pH | 51 Sa |
| <u>Malonic Acid</u> | | | | | | |
| Zn ²⁺ | 0.4 - 0.6 | 25 | Zn(NTA)X | 1.34(1) | nmr | 73 R |
| <u>Oxalic acid</u> | | | | | | |
| Ni ²⁺ | 0.5(KNO ₃) | 25 | Ni(NTA)X | 2.17(4) | sp | 67 J |
| Ga ³⁺ | 1(NaClO ₄) | 20 | Ga(NTA)X | 4.38 | sp | 77 S |
| <u>Citric acid</u> | | | | | | |
| La ³⁺ | 0.1(KNO ₃) | 25 | La(NTA)X | 3 | pH | 74 Tb |
| Pr ³⁺ | 0.1(KNO ₃) | 25 | Pr(NTA)X | 3 | pH | 74 Tb |
| Nd ³⁺ | 0.1(KNO ₃) | 25 | Nd(NTA)X | 3.4 | pH | 74Ta, 74Tb |
| Sm ³⁺ | 0.1(KNO ₃) | 25 | Sm(NTA)X | 3 | pH | 74 Tb |
| Eu ³⁺ | 0.1(KNO ₃) | 25 | Eu(NTA)X | 3.4 | pH | 75 T |
| Gd ³⁺ | 0.1(KNO ₃) | 25 | Gd(NTA)X | 2.5 | pH | 75 T |
| Tb ³⁺ | 0.1(KNO ₃) | 25 | Tb(NTA)X | 3.4 | pH | 75 T |
| Dy ³⁺ | 0.1(KNO ₃) | 25 | Dy(NTA)X | 4.25 | pH | 75 T |
| Ho ³⁺ | 0.1(KNO ₃) | 25 | Ho(NTA)X | 4.5 | pH | 75 T |
| Er ³⁺ | 0.1(KNO ₃) | 25 | Er(NTA)X | 3.6 | pH | 75 T |
| Tm ³⁺ | 0.1(KNO ₃) | 25 | Tm(NTA)X | 3.6 | pH | 75 T |
| Yb ³⁺ | 0.1(KNO ₃) | 25 | Yb(NTA)X | 3.6 | pH | 75 T |
| Lu ³⁺ | 0.1(KNO ₃) | 25 | Lu(NTA)X | 2.9 | pH | 75 T |
| Y ³⁺ | 0.1(KNO ₃) | 25 | Y(NTA)X | 3.3 | pH | 74 T |
| Cu ²⁺ | 0.1(NaClO ₄) | 25 | Cu(NTA)X | 4.57 | pH | 72 Ra |
| <u>Ammonia</u> | | | | | | |
| Ni ²⁺ | 0.5(KCl) | 25 | Ni(NTA)X | 2.54(4) | sp | 70 F, 67 J |
| Zn ²⁺ | 1.5 | 25 | Zn(NTA)X | 2.33 | pH | 70 F |
| <u>d,l-Tartaric acid</u> | | | | | | |
| Cu ²⁺ | 0.1(NaClO ₄) | 25 | Cu(NTA)X | 5.17 | pH ^a | 72 Ra |
| <u>meso-Tartaric acid</u> | | | | | | |
| Cu ²⁺ | 0.1(NaClO ₄) | 25 | Cu(NTA)X | 5.12 | pH ^a | 72 Ra |
| <u>Salicylic acid</u> | | | | | | |
| Ni ²⁺ | 0.5(NaClO ₄) | ? | Ni(NTA)X | 3.03 | pH | 63 I |
| Cu ²⁺ | 0.5(NaClO ₄) | ? | Cu(NTA)X | 5.32 | pH | 63 I |
| | 0.1(KNO ₃) | 24 - 26 | Cu(NTA)X | 7.20(6) | pH | 70 S |
| | 0.1(NaClO ₄) | 25 | Cu(NTA)X | 7.35 | pH | 72 Ra |

| <u>Metal</u> | <u>Medium</u> | <u>t [°C]</u> | <u>Mixed complex</u> | <u>log β_1</u> | <u>Method</u> | <u>Reference</u> |
|------------------------------------|------------------------------|---------------|----------------------|---------------------------------|---------------|------------------|
| (see pp. 2713/2714) | | | | | (see p. 2714) | |
| <u>Sulfosalicylic acid</u> | | | | | | |
| Ni ²⁺ | 0.1(KNO ₃) | 24 - 26 | Ni(NTA)X | 3.92(6) | pH | 70 S |
| Cu ²⁺ | 0.1(KNO ₃) | 24 - 26 | Cu(NTA)X | 5.62(5) | pH | 70 S |
| Zn ²⁺ | 0.1(KNO ₃) | 24 - 26 | Zn(NTA)X | 4.23(9) | pH | 70 S |
| <u>Glycine</u> | | | | | | |
| Mn ²⁺ | 0.07-0.08(KNO ₃) | 25 | Mn(NTA)X | 2.24(1) | pH | 68 H |
| | 0.1(KNO ₃) | 25 | Mn(NTA)X | 1.80(10) | pH | 71 Ib |
| Co ²⁺ | 0.07-0.08(KNO ₃) | 25 | Co(NTA)X | 3.65 | pH | 68 H |
| | 0.1(KNO ₃) | 25 | Co(NTA)X | 3.38 | pH | 71 Ib |
| Ni ²⁺ | 0.5(KNO ₃) | ? | Ni(NTA)X | 4.41 | pH | 71 Ib |
| | 0.5(NaCl) | 25 | Ni(NTA)X | 4.89(4) | pH | 67 I |
| | 0.07-0.08(KNO ₃) | 25 | Ni(NTA)X | 4.95 | pH | 68 H |
| | 0.1(NaClO ₄) | 25 | Ni(NTA)X | 4.41(1) | pH | 68 Ia |
| | 0.1(KNO ₃) | 25 | Ni(NTA)X | 4.41(4) | pH | 71 Ib |
| | 0.1(NaClO ₄) | 25 | Ni(NTA)X | 4.55(5) | | 75 V |
| Cu ²⁺ | 0.07-0.08(KNO ₃) | 25 | Cu(NTA)X | 5.44(1) | pH | 68 H |
| | 0.1(NaClO ₄) | 25 | Cu(NTA)X | 5.44 | pH | 68 Ia |
| | 0.1(KNO ₃) | 25 | Cu(NTA)X | 5.26(2) | pH | 71 Ib |
| | 0.1(NaClO ₄) | 25 | Cu(NTA)X | 5.26(2) | pH | 75 V |
| Zn ²⁺ | 0.07-0.08(KNO ₃) | 25 | Zn(NTA)X | 3.64 | pH | 68 H |
| | 0.1(KNO ₃) | 25 | Zn(NTA)X | 5.59 | pH | 71 Ib |
| | 0.1(KNO ₃) | 25 | Zn(NTA)X | 3.76 | pH | 71 T |
| | 0.4 - 0.6 | 25 | Zn(NTA)X | 3.62(4) | nmr | 73 R |
| Cd ²⁺ | | 25 | Cd(NTA)X | 2.93(17) | nmr | 73 R |
| Pb ²⁺ | 0.07-0.08(KNO ₃) | 25 | Pb(NTA)X | 1.93 | pH | 68 H |
| <u>α-Alanine</u> | | | | | | |
| Ni ²⁺ | 0.1(KNO ₃) | 25 | Ni(NTA)X | 4.25(2) | pH | 71 T |
| | 0.1(NaClO ₄) | 25 | Ni(NTA)X | 4.31(3) | pH | 75 V |
| Cu ²⁺ | 0.07-0.08(KNO ₃) | 25 | Cu(NTA)X | 5.42 | pH | 68 H |
| | 0.1(KNO ₃) | 25 | Cu(NTA)X | 5.36(3) | pH | 71 T |
| | 0.1(NaClO ₄) | 25 | Cu(NTA)X | 5.18(7) | pH | 75 V |
| Zn ²⁺ | 0.1(KNO ₃) | 25 | Zn(NTA)X | 3.36(3) | pH | 71 T |
| Cd ²⁺ | 0.1(KNO ₃) | 25 | Cd(NTA)X | 2.80(5) | pH | 71 T |
| <u>β-Alanine</u> | | | | | | |
| Cu ²⁺ | 0.07-0.08(KNO ₃) | 25 | Cu(NTA)X | 4.56 | pH | 68 H |
| <u>Glycine methylester</u> | | | | | | |
| Cu ²⁺ | 0.07-0.08(KNO ₃) | 25 | Cu(NTA)X | 3.06 | pH | 68 H |

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>Mixed complex</u> | <u>log β_1</u> | <u>Method</u> | <u>Reference</u> |
|---------------------------|------------------------------|--------------|----------------------|---------------------------------|---------------|------------------|
| | (see pp. 2713/2714) | | | | (see p. 2714) | |
| <u>Sarcosine</u> | | | | | | |
| Co ²⁺ | 0.1(KNO ₃) | 25 | Co(NTA)X | 3.13 ^b | pH | 71 Id |
| Ni ²⁺ | 0.1(KNO ₃) | 25 | Ni(NTA)X | 4.23 ^b | pH | 71 Id |
| Cu ²⁺ | 0.1(KNO ₃) | 25 | Cu(NTA)X | 5.15 ^b | pH | 71 Id |
| Zn ²⁺ | 0.1(KNO ₃) | 25 | Zn(NTA)X | 3.22 ^b | pH | 71 Id |
| Cd ²⁺ | 0.1(KNO ₃) | 25 | Cd(NTA)X | 2.64 ^b | pH | 71 Id |
| Co ²⁺ | 0.1(NaClO ₄) | 25 | Co(NTA)X | 3.18(3) | pH | 68 Ia |
| Ni ²⁺ | 0.1(NaClO ₄) | 25 | Ni(NTA)X | 4.14(2) | pH | 68 Ia |
| Cu ²⁺ | 0.1(NaClO ₄) | 25 | Cu(NTA)X | 5.01(2) | pH | 68 Ia |
| Zn ²⁺ | 0.1(NaClO ₄) | 25 | Zn(NTA)X | 3.18(3) | pH | 68 Ia |
| <u>Aspartic acid</u> | | | | | | |
| Mn ²⁺ | 0.1(NaClO ₄) | 25 | Mn(NTA)X | 2.08(4) | pH | 68 I |
| Ni ²⁺ | 0.1(NaClO ₄) | 25 | Ni(NTA)X | 4.20(3) | pH | 68 I |
| Cu ²⁺ | 0.1(NaClO ₄) | 25 | Cu(NTA)X | 5.31(2) | pH | 68 I |
| Zn ²⁺ | 0.1(NaClO ₄) | 25 | Zn(NTA)X | 3.24(3) | pH | 68 I |
| Cd ²⁺ | 0.1(KNO ₃) | 25 | Cd(NTA)X | 2.96(5) | pH | 71 T |
| <u>Iminodiacetic acid</u> | | | | | | |
| Zn ²⁺ | 0.4 - 0.6 | 25 | Zn(NTA)X | 3.61(11) | nmr | 73 R |
| Cd ²⁺ | ? | 25 | Cd(NTA)X | 4.01(5) | pH | 73 R |
| <u>Glycylglycine</u> | | | | | | |
| Mn ²⁺ | 0.1(NaClO ₄) | 25 | Mn(NTA)X | 2.08(8) | pH | 68 Ib |
| Co ²⁺ | 0.1(NaClO ₄) | 25 | Co(NTA)X | 2.08(3) | pH | 68 Ib |
| Ni ²⁺ | 0.1(NaClO ₄) | 25 | Ni(NTA)X | 3.04(4) | pH | 68 Ib |
| Cu ²⁺ | 0.1(NaClO ₄) | 25 | Cu(NTA)X | 3.43(6) | pH | 68 Ib |
| Zn ²⁺ | 0.1(NaClO ₄) | 25 | Zn(NTA)X | 2.28(5) | pH | 68 Ib |
| <u>Glycine ethylester</u> | | | | | | |
| Cu ²⁺ | 0.07-0.08(KNO ₃) | 25 | Cu(NTA)X | 3.15 | pH | 68 H |
| <u>Dimethylglycine</u> | | | | | | |
| Co ²⁺ | 0.1(KNO ₃) | 25 | Co(NTA)X | 3.30 ^b | pH | 71 Id |
| Cu ²⁺ | 0.1(KNO ₃) | 25 | Cu(NTA)X | 5.34 ^b | pH | 71 Id |
| Zn ²⁺ | 0.1(KNO ₃) | 25 | Zn(NTA)X | 3.28 ^b | pH | 71 Id |
| Cd ²⁺ | 0.1(KNO ₃) | 25 | Cd(NTA)X | 2.70 ^b | pH | 71 Id |

| <u>Metal</u> | <u>Medium</u> | <u>t</u> [°C] | <u>Mixed complex</u> | <u>log β_1</u> | <u>Method</u> | <u>Reference</u> |
|---|------------------------------|---------------|----------------------|---------------------------------|---------------|------------------|
| (see pp. 2713/2714) | | | | | (see p. 2714) | |
| <u>Histamine</u> | | | | | | |
| Co ²⁺ | 0.1(NaClO ₄) | 25 | Co(NTA)X | 3.76(8) | pH | 69 B |
| Ni ²⁺ | 0.1(NaClO ₄) | 25 | Ni(NTA)X | 4.89(4) | pH | 69 B |
| Cu ²⁺ | 0.1(NaClO ₄) | 25 | Cu(NTA)X | 6.11(4) | pH | 69 B |
| Zn ²⁺ | 0.1(NaClO ₄) | 25 | Zn(NTA)X | 3.61(8) | pH | 69 B |
| <u>Proline</u> | | | | | | |
| Co ²⁺ | 0.1(KNO ₃) | 25 | Co(NTA)X | 3.85(5) ^b | pH | 71 Ib |
| Ni ²⁺ | 0.1(KNO ₃) | 25 | Ni(NTA)X | 4.99(4) ^b | pH | 71 Ib |
| Cu ²⁺ | 0.1(KNO ₃) | 25 | Cu(NTA)X | 6.24(2) ^b | pH | 71 Ib |
| Zn ²⁺ | 0.1(KNO ₃) | 25 | Zn(NTA)X | 3.98(5) ^b | pH | 71 Ib |
| Cd ²⁺ | 0.1(KNO ₃) | 25 | Cd(NTA)X | 3.05(5) ^b | pH | 71 Ib |
| <u>Glutamic acid</u> | | | | | | |
| Mn ²⁺ | 0.1(NaClO ₄) | 25 | Mn(NTA)X | 2.22(4) | pH | 68 I |
| Co ²⁺ | 0.1(NaClO ₄) | 25 | Co(NTA)X | 2.96(3) | pH | 68 I |
| Ni ²⁺ | 0.1(NaClO ₄) | 25 | Ni(NTA)X | 4.04(3) | pH | 68 I |
| Cu ²⁺ | 0.1(NaClO ₄) | 25 | Cu(NTA)X | 5.10(3) | pH | 68 I |
| Zn ²⁺ | 0.1(NaClO ₄) | 25 | Zn(NTA)X | 2.96(4) | pH | 68 I |
| <u>Valine</u> | | | | | | |
| Cu ²⁺ | 0.07-0.08(KNO ₃) | 25 | Cu(NTA)X | 5.10 | pH | 68 H |
| <u>Ethyl β-alanine</u> | | | | | | |
| Cu ²⁺ | 0.07-0.08(KNO ₃) | 25 | Cu(NTA)X | 3.65 | pH | 68 H |
| <u>Pyridyl carbaldoxime</u> | | | | | | |
| Ni ²⁺ | 0.5(NaNO ₃) | ? | Ni(NTA)X | 5.18 | pH | 63 I |
| Cu ²⁺ | 0.5(NaNO ₃) | ? | Cu(NTA)X | 6.20 | pH | 63 I |
| <u>Histidine</u> | | | | | | |
| Mn ²⁺ | 0.1(NaClO ₄) | 25 | Mn(NTA)X | 2.49(5) | pH | 68 Ia |
| Co ²⁺ | 0.1(NaClO ₄) | 25 | Co(NTA)X | 3.94(3) | pH | 68 Ia |
| Ni ²⁺ | 0.1(NaClO ₄) | 25 | Ni(NTA)X | 5.03(3) | pH | 68 Ia |
| Cu ²⁺ | 0.07-0.08(KNO ₃) | 25 | Cu(NTA)X | 5.73 | pH | 68 H |
| Cu ²⁺ | 0.1(NaClO ₄) | 25 | Cu(NTA)X | 4.52(4) | pH | 68 Ia |
| Zn ²⁺ | 0.1(NaClO ₄) | 25 | Zn(NTA)X | 3.95(3) | pH | 68 Ia |
| Pb ²⁺ | 0.1(NaClO ₄) | 25 | Pb(NTA)X | 1.50(6) | pH | 68 Ia |

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>Mixed complex</u> | <u>log β_1</u> | <u>Method</u> | <u>Reference</u> |
|---|------------------------------|--------------|----------------------|---------------------------------|---------------|------------------|
| (see pp. 2713/2714) | | | | | (see p. 2714) | |
| <u>1-Aminocyclopentanecarboxylic acid</u> | | | | | | |
| Co ²⁺ | 0.1(KNO ₃) | 25 | Co(NTA)X | 3.10 ^b | pH | 71 Ia |
| Ni ²⁺ | 0.1(KNO ₃) | 25 | Ni(NTA)X | 4.03 ^b | pH | 71 Ia |
| Cu ²⁺ | 0.1(KNO ₃) | 25 | Cu(NTA)X | 5.29 ^b | pH | 71 Ia |
| Zn ²⁺ | 0.1(KNO ₃) | 25 | Zn(NTA)X | 3.28 ^b | pH | 71 Ia |
| Cd ²⁺ | 0.1(KNO ₃) | 25 | Cd(NTA)X | 2.5 ^b | pH | 71 Ia |
| <u>Piperidine carboxylic acid</u> | | | | | | |
| Co ²⁺ | 0.1(KNO ₃) | 25 | Co(NTA)X | 3.30(2) ^b | pH | 71 Ic |
| Ni ²⁺ | 0.1(KNO ₃) | 25 | Ni(NTA)X | 4.12(2) ^b | pH | 71 Ic |
| Cu ²⁺ | 0.1(KNO ₃) | 25 | Cu(NTA)X | 5.33(1) ^b | pH | 71 Ic |
| Cd ²⁺ | 0.1(KNO ₃) | 25 | Cd(NTA)X | 2.44(5) ^b | pH | 71 Ic |
| <u>Leucine</u> | | | | | | |
| Cu ²⁺ | 0.07-0.08(KNO ₃) | 25 | Cu(NTA)X | 5.35 | pH | 68 H |
| <u>Buthylglycine</u> | | | | | | |
| Cu ²⁺ | 0.07-0.08(KNO ₃) | 25 | Cu(NTA)X | 3.33 | pH | 68 H |
| <u>Ethylvaline</u> | | | | | | |
| Mn ²⁺ | 0.07-0.08(KNO ₃) | 25 | Mn(NTA)X | 2.39 | pH | 68 H |
| Co ²⁺ | 0.07-0.08(KNO ₃) | 25 | Co(NTA)X | 2.88 | pH | 68 H |
| Ni ²⁺ | 0.07-0.08(KNO ₃) | 25 | Ni(NTA)X | 2.03(1) | pH | 68 H |
| Cu ²⁺ | 0.07-0.08(KNO ₃) | 25 | Cu(NTA)X | 2.88 | pH | 68 H |
| Zn ²⁺ | 0.07-0.08(KNO ₃) | 25 | Zn(NTA)X | 1.58(8) | pH | 68 H |
| Pb ²⁺ | 0.07-0.08(KNO ₃) | 25 | Pb(NTA)X | 1.55(10) | pH | 68 H |
| <u>Arginine</u> | | | | | | |
| Mn ²⁺ | 0.1(NaClO ₄) | 25 | Mn(NTA)X | 1.94(4) | pH | 68 Ia |
| Co ²⁺ | 0.1(NaClO ₄) | 25 | Co(NTA)X | 3.13(3) | pH | 68 Ia |
| Ni ²⁺ | 0.1(NaClO ₄) | 25 | Ni(NTA)X | 4.20(2) | pH | 68 Ia |
| Cu ²⁺ | 0.1(NaClO ₄) | 25 | Cu(NTA)X | 5.22(3) | pH | 68 Ia |
| Zn ²⁺ | 0.1(NaClO ₄) | 25 | Zn(NTA)X | 3.28(3) | pH | 68 Ia |
| Pb ²⁺ | 0.1(NaClO ₄) | 25 | Pb(NTA)X | 1.58(7) | pH | 68 Ia |
| <u>Methylhistidine</u> | | | | | | |
| Cu ²⁺ | 0.07-0.08(KNO ₃) | 25 | Cu(NTA)X | 4.90 | pH | 68 H |
| <u>Ethylleucine</u> | | | | | | |
| Cu ²⁺ | 0.07-0.08(KNO ₃) | 25 | Cu(NTA)X | 2.79 | pH | 68 H |

| <u>Metal</u> | <u>Medium</u> | <u>t [°C]</u> | <u>Mixed complex</u> | <u>log β_1</u> | <u>Method</u> | <u>Reference</u> |
|---------------------------|---------------------------------------|---------------|----------------------------|---------------------------------|---------------|------------------|
| | (see pp. 2713/2714) | | | | (see p. 2714) | |
| <u>Phenylalanine</u> | | | | | | |
| Cu ²⁺ | 0.07-0.08(KNO ₃) | 25 | Cu(NTA)X | 4.99 | pH | 68 H |
| <u>Tryptophan</u> | | | | | | |
| Co ²⁺ | 0.1(NaClO ₄) | 25 | Co(NTA)X | 3.08(5) | pH | 69 Aa |
| Ni ²⁺ | 0.1(NaClO ₄) | 25 | Ni(NTA)X | 4.12(4) | pH | 69 Aa |
| Cu ²⁺ | 0.1(NaClO ₄) | 25 | Cu(NTA)X | 5.06(2) | pH | 69 Aa |
| Zn ²⁺ | 0.1(NaClO ₄) | 25 | Zn(NTA)X | 3.02(4) | pH | 69 Aa |
| <u>Ethylphenylalanine</u> | | | | | | |
| Cu ²⁺ | 0.07-0.08(KNO ₃) | 25 | Cu(NTA)X | 2.77 | pH | 68 H |
| <u>Thioglycollic acid</u> | | | | | | |
| Zn ²⁺ | 0.2(NaClO ₄) | 35 | Zn(NTA)X | 5.17(2) | pH | 27 P |
| <u>Thiolactic acid</u> | | | | | | |
| Zn ²⁺ | 0.2(NaClO ₄) | 35 | Zn(NTA)X | 5.21(3) | pH | 72 P |
| <u>Thiomalic acid</u> | | | | | | |
| Zn ²⁺ | 0.2(NaClO ₄) | 35 | Zn(NTA)X | 5.13(2) | pH | 72 P |
| <u>Ethylenediamine</u> | | | | | | |
| Ni ²⁺ | 0.5(NaClO ₄) | 25 | Ni(NTA)X | 7.20(6) | sp | 67 J |
| Zn ²⁺ | 0.4 - 0.6 | 25 | Zn(NTA)X | 5.00(7) | nmr | 73 R |
| Cd ²⁺ | ? | 25 | Cd(NTA)X | 5.05(5) | nmr | 73 R |
| <u>Pyridine</u> | | | | | | |
| Ni ²⁺ | 1.5(NH ₄ NO ₃) | 25 | Ni(NTA)X | 1.21 | pH | 69 F |
| Zn ²⁺ | 1.5(NH ₄ NO ₃) | 25 | Zn(NTA)X | 0.76 | pH | 70 F |
| <u>Phenol</u> | | | | | | |
| Fe ³⁺ | 0.1(KNO ₃) | rt | Fe(NTA)(OH)X | 5 | sp | 76 K |
| | 0.1(KNO ₃) | rt | Fe(NTA)(OH) ₂ X | 2.3 | sp | 76 K |
| <u>Catechol</u> | | | | | | |
| La ³⁺ | 0.1(KNO ₃) | 25 | La(NTA)X | 7.99(8) | pH | 78 T |
| Pr ³⁺ | 0.1(KNO ₃) | 25 | Pr(NTA)X | 7.43(13) | pH | 78 T |
| Nd ³⁺ | 0.1(KNO ₃) | 25 | Nd(NTA)X | 7.63(14) | pH | 78 T |

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>Mixed complex</u> | <u>log β_1</u> | <u>Method</u> | <u>Reference</u> |
|--------------------------|------------------------|--------------|----------------------|---------------------------------|---------------|------------------|
| (see pp. 2713/2714) | | | | | (see p. 2714) | |
| <u>Tiron</u> | | | | | | |
| Ni ²⁺ | 0.1(KNO ₃) | 24 - 26 | Ni(NTA)X | 6.76(5) | pH | 70 S |
| Fe ³⁺ | 0.1(KCl) | 20 | Fe(NTA)X | 15.7 | sp | 51 H (75 C) |
| Cu ²⁺ | 0.1(KNO ₃) | 24 - 26 | Cu(NTA)X | 9.51(8) | pH | 70 S |
| Zn ²⁺ | 0.1(KNO ₃) | 24 - 26 | Zn(NTA)X | 7.07(7) | pH | 70 S |
| <u>Chromotropic acid</u> | | | | | | |
| Fe ³⁺ | 0.1(KCl) | 20 | Fe(NTA)X | 17.0 | pH, sp | 51 H (75 C) |

a: A Cu solid electrode was also used.

b: K values also for 15, 50 and 70 °C.

TABLE 3.2. Formation of protonated complex ($K_1 = \frac{[M(NTA)HX]}{[M(NTA)X][H]}$)

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>Mixed complex</u> | <u>log K_1</u> | <u>Method</u> | <u>Reference</u> |
|------------------------|------------------------------|--------------|----------------------|-----------------------------|---------------|------------------|
| (see pp. 2713/2714) | | | | | (see p. 2714) | |
| <u>Histidine</u> | | | | | | |
| Cu ²⁺ | 0.07-0.08(KNO ₃) | 25 | Cu(NTA)HX | 4.16 | pH | 68 H |
| <u>Methylhistidine</u> | | | | | | |
| Cu ²⁺ | 0.07-0.08(KNO ₃) | 25 | Cu(NTA)HX | 3.98 | pH | 68 H |

TABLE 3.3. pK values of M(NTA)X ($K_1 = \frac{[M(NTA)X(OH)][H]}{[M(NTA)X]}$)

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>Complex</u> | <u>pK₁</u> | <u>Method</u> | <u>Reference</u> |
|----------------------|--------------------------|--------------|----------------|-----------------------|---------------|------------------|
| (see pp. 2713/2714) | | | | | (see p. 2714) | |
| <u>Glycylglycine</u> | | | | | | |
| Co ²⁺ | 0.1(NaClO ₄) | 25 | Co(NTA)X | 10.80(10) | pH | 68 Ib |
| Ni ²⁺ | 0.1(NaClO ₄) | 25 | Ni(NTA)X | 11.30(10) | pH | 68 Ib |
| Cu ²⁺ | 0.1(NaClO ₄) | 25 | Cu(NTA)X | 9.79(3) | pH | 68 Ib |
| <u>Histamine</u> | | | | | | |
| Co ²⁺ | 0.1(NaClO ₄) | 25 | Co(NTA)HX | 7.93(4) | pH | 69 B |
| Ni ²⁺ | 0.1(NaClO ₄) | 25 | Ni(NTA)HX | 7.38(9) | pH | 69 B |
| Cu ²⁺ | 0.1(NaClO ₄) | 25 | Cu(NTA)HX | 7.58(8) | pH | 69 B |
| Zn ²⁺ | 0.1(NaClO ₄) | 25 | Zn(NTA)HX | 8.41(12) | pH | 69 B |

TABLE 3.4. Stability constants of M(EDTA)NTA from equilibrium XVII

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>Mixed complex</u> | <u>log K</u> | <u>Method</u> | <u>Reference</u> |
|---------------------|------------------------|--------------|----------------------|--------------|---------------|------------------|
| (see pp. 2713/2714) | | | | | (see p. 2714) | |
| La ³⁺ | 0.1(KNO ₃) | 20 | La(EDTA)NTA | 4.79 | pH | 71 G |
| | ? | 25 | La(EDTA)NTA | | | 71 K |
| Ce ³⁺ | 0.1(KNO ₃) | 20 | Ce(EDTA)NTA | 4.72 | pH | 71 G |
| Pr ³⁺ | 0.1(KNO ₃) | 20 | Pr(EDTA)NTA | 4.67 | pH | 71 G |
| Nd ³⁺ | 0.1(KNO ₃) | 20 | Nd(EDTA)NTA | 4.77 | pH | 71 G |
| Sm ³⁺ | 0.1(KNO ₃) | 20 | Sm(EDTA)NTA | 5.00 | pH | 71 G |
| Eu ³⁺ | 0.1(KNO ₃) | 20 | Eu(EDTA)NTA | 5.03 | pH | 71 G |
| | 1.0 | ? | Eu(EDTA)NTA | 5.13(5) | sp | 72 T |
| Gd ³⁺ | 0.1(KNO ₃) | 20 | Gd(EDTA)NTA | 4.86 | pH | 71 G |
| Tb ³⁺ | 0.1(KNO ₃) | 20 | Tb(EDTA)NTA | 4.65 | pH | 71 G |
| Dy ³⁺ | 0.1(KNO ₃) | 20 | Dy(EDTA)NTA | 4.28 | pH | 71 G |
| Ho ³⁺ | 0.1(KNO ₃) | 20 | Ho(EDTA)NTA | 3.95 | pH | 71 G |
| Er ³⁺ | 0.1(KNO ₃) | 20 | Er(EDTA)NTA | 3.52 | pH | 71 G |
| Tm ³⁺ | 0.1(KNO ₃) | 20 | Tm(EDTA)NTA | 3.13 | pH | 71 G |
| Yb ³⁺ | 0.1(KNO ₃) | 20 | Yb(EDTA)NTA | 2.85 | pH | 71 G |
| Lu ³⁺ | 0.1(KNO ₃) | 20 | Lu(EDTA)NTA | 2.81 | pH | 71 G |
| | ? | 25 | Lu(EDTA)NTA | 2.3 | nmr | 71 K |

7. THERMODYNAMIC DATA

Enthalpies and entropies of complex formation are compiled in Tables 4.1-4 in the units given in the original work together with the SI units: ΔH and ΔS in kJ mol^{-1} and $\text{J mol}^{-1} \text{K}^{-1}$, respectively. In all cases the values refer to the i th stepwise equilibrium:

7.1. Determination of the enthalpy of complex formation

The enthalpy change on formation of a ligand-proton or a ligand-metal complex can be obtained using a calorimeter. The heat evolved or absorbed on mixing a solution of the cation or strong acid with a solution of the ligand is measured. The amount of heat on mixing will be the sum of the molar enthalpies of formation of the different species multiplied by the number of moles of each formed. Corrections are sometimes necessary for dilution. Normally, the enthalpies of protonation are obtained first and their values are used in the calculations involving metal complexation. By use of different concentrations of the components it is possible to cover the whole range of complex formation (protonation). The concentration of the species formed can be calculated if the equilibrium constants of all species for the chosen conditions are known. Linear equations in the unknown enthalpies are obtained each of the n steps of association. From m ($\geq n$) measurements it is possible to calculate each molar enthalpy. If $m \gg n$, least squares methods can be used and the standard deviations of the enthalpy values as well as of the measured heat can be obtained. The entropy of association can then be calculated using the following relationship:

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{\Delta H + RT \ln K}{T}$$

Under some restricted conditions calorimetric measurements give both formation constants and enthalpies of the single association reactions; however in several such studies the accuracy of the results have been somewhat over-estimated (73 Ha, 73 P). From the equilibrium constants at different temperatures, the enthalpy of the reaction can be calculated by use of the van't Hoff equation

$$\frac{d \log K}{dT} = \frac{\Delta H}{2.3 R T^2}$$

This method was extensively used in the period before the necessary instrumentation for calorimetric measurements was readily available. It is still used but is generally of low accuracy. For instance, at $I = 0.1(\text{KNO}_3)$ the following ΔH_1 values in kcal mol^{-1} were found:

| Mg^{2+} | Ca^{2+} | Ba^{2+} | Sr^{2+} | |
|------------------|------------------|------------------|------------------|--------|
| 3 | -2 | -2 | 0 | (60 B) |
| | -0.81 | -1 | | (62 M) |

These values should be compared with those of Table 4.1. Other difficulties can arise: for instance, in systems in which 1 : 1 and 1 : 2 complexes are formed, it is often impossible to determine ΔH alone, especially if the pH of the solution and the composition have not been chosen very carefully. This was found to be the case in the attempted measurements by 64 Ea of the enthalpies of formation of the 1 : 1 complexes for the lanthanide cations. The 10% excess of the cation over the required amount for 1 : 1 ratio does not ensure the formation only of ML. Because the final concentration of the complex was 0.01 M, for a ratio $K_1/K_2 = 100$, one obtains 10% ML_2 and for $K_1/K_2 = 1000$, 1% ML_2 . Because ΔH_1 and ΔH_2 may be different in sign and magnitude, the error in ΔH_1 can be quite large. This is especially so because the ΔH_1 values are low in magnitude. From the approximate values of 62 M one obtains, for instance, a correction of $0.5 \text{ kcal mol}^{-1}$ for Tb^{3+} , Dy^{3+} and $0.03 \text{ kcal mol}^{-1}$ for La^{3+} . The thermodynamic data of Table 4.1 - 5 were obtained by direct calorimetric measurements.

TABLE 4.1. Values for group 1a and 2a NTA complexes (see XXI)

| <u>Cation</u> | <u>Medium</u> | <u>t</u> [$^{\circ}C$] | <u>ΔH_1</u> ^a | <u>ΔS_1</u> ^b | <u>ΔH_1</u> ^c | <u>ΔS_1</u> ^d | <u>Reference</u> |
|------------------------|------------------------|--------------------------|---|---|---|---|------------------|
| <u>H⁺</u> | 0.1(KNO ₃) | 20 | -4.73 | 28.4 | -19.8 | 118.8 | 64 A |
| | 0.1(KNO ₃) | 20 | -4.57 | | -19.1 | | 64 H |
| <u>Mg²⁺</u> | 0.1(KNO ₃) | 20 | 4.44 | 39.8 | 18.6 | 166.5 | 64 A |
| | 0.1(KNO ₃) | 20 | 4.07 | | 17.0 | | 64 Ea |
| <u>Ca²⁺</u> | 0.1(KNO ₃) | 20 | -1.36 | 24.2 | -5.69 | 101.3 | 64 A |
| | 0.1(KNO ₃) | 20 | -1.36 | 24.7 | -5.69 | 103.3 | 64 H |
| <u>Sr²⁺</u> | 0.1(KNO ₃) | 20 | -0.53 | 17.5 | -2.22 | 73.2 | 64 A |
| | 0.1(KNO ₃) | 20 | -0.54 | 20.9 | -2.25 | 87.4 | 64 H |
| <u>Ba²⁺</u> | 0.1(KNO ₃) | 20 | -1.44 | 17.1 | -6.02 | 71.5 | 64 A |

a: kcal mol⁻¹b: cal mol⁻¹K⁻¹c: kJ mol⁻¹d: J mol⁻¹K⁻¹

TABLE 4.2. Values for cations of the group 3a and 4f (see XXI)

| Metal | Medium | t[°C] | ΔH_1^a | ΔS_1^b | ΔH_1^c | ΔS_1^d | Reference |
|------------------|------------------------|-------|----------------|----------------|----------------|----------------|-----------|
| Y ³⁺ | 0.1(KNO ₃) | 20 | 1.027 | 56 | 4.297 | 234 | 64 Ea |
| La ³⁺ | 0.1(KNO ₃) | 20 | 0.32 | 48.8 | 1.34 | 204 | 64 Ea |
| Ce ³⁺ | 0.1(KNO ₃) | 20 | -0.215 | 48.8 | -0.90 | 204 | 64 Ea |
| Pr ³⁺ | 0.1(KNO ₃) | 20 | -0.502 | 48.8 | -2.10 | 204 | 64 Ea |
| Nd ³⁺ | 0.1(KNO ₃) | 20 | -0.803 | 48.8 | -3.36 | 204 | 64 Ea |
| Sm ³⁺ | 0.1(KNO ₃) | 20 | -1.047 | 49.1 | -4.38 | 205 | 64 Ea |
| Eu ³⁺ | 0.1(KNO ₃) | 20 | -1.029 | 49.1 | -4.31 | 205 | 64 Ea |
| Gd ³⁺ | 0.1(KNO ₃) | 20 | -0.626 | 50.7 | -2.62 | 212 | 64 Ea |
| Tb ³⁺ | 0.1(KNO ₃) | 20 | -0.061 | 52.8 | -0.255 | 221 | 64 Ea |
| Dy ³⁺ | 0.1(KNO ₃) | 20 | 0.35 | 54.8 | 1.46 | 229 | 64 Ea |
| Ho ³⁺ | 0.1(KNO ₃) | 20 | 0.543 | 56.1 | 2.27 | 235 | 64 Ea |
| Er ³⁺ | 0.1(KNO ₃) | 20 | 0.593 | 56.9 | 2.48 | 238 | 64 Ea |
| Tm ³⁺ | 0.1(KNO ₃) | 20 | 0.585 | 57.8 | 2.45 | 242 | 64 Ea |
| Yb ³⁺ | 0.1(KNO ₃) | 20 | 0.4 | 58.0 | 1.7 | 243 | 64 Ea |
| Lu ³⁺ | 0.1(KNO ₃) | 20 | 0.18 | 57.7 | 0.75 | 241 | 64 Ea |

a: kcal mol⁻¹b: cal mol⁻¹K⁻¹c: kJ mol⁻¹d: J mol⁻¹K⁻¹

Table 4.3. Values for cations of the groups 7a, 8a, 1b, 2b, 4b (see XXI)

| Metal | Medium | t[°C] | ΔH_1^a | ΔS_1^b | ΔH_2^a | ΔS_2^b | ΔH_1^c | ΔS_1^d | ΔH_2^c | ΔS_2^d | Reference |
|------------------|------------------------|-------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-----------|
| Mn ²⁺ | 0.1(KNO ₃) | 20 | 1.44 | 38.9 | -5.58 | -1.7 | 6.0 | 163 | -23.3 | -7.1 | 64 A |
| | 0.1(KNO ₃) | 20 | 1.14 | 37.9 | | | 4.8 | 158 | | | 64 H |
| Fe ³⁺ | 0.1(KNO ₃) | 20 | 3.2 | 83.6 | | | 13.4 | 350 | | | 64 A |
| Co ²⁺ | 0.1(KNO ₃) | 20 | -0.07 | 47.2 | -4.76 | 2.1 | -0.3 | 197 | -19.9 | 8.8 | 64 A |
| | 0.1(KNO ₃) | 20 | -0.15 | 47.1 | | | -0.6 | 197 | | | 64 H |
| Ni ²⁺ | 0.1(KNO ₃) | 20 | -2.56 | 47.2 | -5.57 | 7 | -10.7 | 197 | -23.3 | 29.3 | 64 A |
| | 0.1(KNO ₃) | 20 | -2.53 | 47.1 | | | -10.6 | 197 | | | 64 H |
| Cu ²⁺ | 0.1(KNO ₃) | 20 | -1.87 | 52.8 | -7.03 | -3.5 | -7.8 | 221 | -29.4 | -14.6 | 64 A |
| | 0.1(KNO ₃) | 20 | -1.84 | 53.0 | -6.46 | | -7.7 | 222 | -27.0 | | 64 H |
| Zn ²⁺ | 0.1(KNO ₃) | 20 | -0.87 | 45.5 | -2.75 | 7.2 | -3.6 | 190 | -11.5 | 30.1 | 64 A |
| | 0.1(KNO ₃) | 20 | -0.84 | 46.0 | | | -3.5 | 192 | | | 64 H |
| Cd ²⁺ | 0.1(KNO ₃) | 20 | -3.97 | 31.3 | -5.08 | 4.7 | -16.6 | 131 | -21.3 | 19.7 | 64 A |
| Pb ²⁺ | 0.1(KNO ₃) | 20 | -3.81 | 39.1 | | | -15.9 | 164 | | | 64 A |

a: kcal mol⁻¹b: cal mol⁻¹K⁻¹c: kJ mol⁻¹d: J mol⁻¹K⁻¹

In TABLE 4.4. are listed thermodynamic data for mixed complex formation of type:



It should be noted that in this case the concentrations of the components are not such so as to ensure the exclusive formation of the mixed complex $\text{Ln}(\text{EDTA})\text{NTA}^{4-}$. Because of the presence of excess NTA the formation of $\text{Ln}(\text{NTA})_2^{3-}$ is also favoured. This is true even though some measurements with Gd^{3+} showed that increasing the ratio $[\text{NTA}]/[\text{Gd}(\text{EDTA})]$ from 1.4 to 4 the enthalpy of $\text{Gd}(\text{EDTA})\text{NTA}^{4-}$ calculated without considering $\text{Gd}(\text{NTA})_2^{3-}$, remained constant. This may simply signify that the enthalpies of formation of $\text{Ln}(\text{EDTA})\text{NTA}^{4-}$ and $\text{Ln}(\text{NTA})_2^{3-}$ from $\text{Ln}(\text{EDTA})^-$ are probably similar in magnitude.

TABLE 4.4. Thermodynamic data for equilibrium XXII

| <u>Metal</u> | <u>Medium</u> | <u>t</u> [°C] | <u>ΔH</u> ^a | <u>ΔS</u> ^b | <u>ΔH</u> ^c | <u>ΔS</u> ^d | <u>Reference</u> |
|------------------|------------------------|---------------|------------------------|------------------------|------------------------|------------------------|------------------|
| Y ³⁺ | 0.1(KNO ₃) | 20 | -7.00 | -6.8 | -29.3 | -28.5 | 71 G |
| La ³⁺ | 0.1(KNO ₃) | 20 | -6.08 | 1.2 | -25.4 | 5.0 | 71 G |
| Ce ³⁺ | 0.1(KNO ₃) | 20 | -5.72 | 2.1 | -23.9 | 8.8 | 71 G |
| Pr ³⁺ | 0.1(KNO ₃) | 20 | -4.65 | 5.5 | -19.5 | 23.0 | 71 G |
| Nd ³⁺ | 0.1(KNO ₃) | 20 | -4.15 | 7.7 | -17.4 | 32.2 | 71 G |
| Sm ³⁺ | 0.1(KNO ₃) | 20 | -6.23 | 1.6 | -26.1 | 6.7 | 71 G |
| Eu ³⁺ | 0.1(KNO ₃) | 20 | -7.18 | -1.5 | -30.0 | -6.3 | 71 G |
| Gd ³⁺ | 0.1(KNO ₃) | 20 | -7.92 | -4.7 | -33.1 | -19.7 | 71 G |
| Tb ³⁺ | 0.1(KNO ₃) | 20 | -8.49 | -7.7 | -35.5 | -32.2 | 71 G |
| Dy ³⁺ | 0.1(KNO ₃) | 20 | -8.45 | -9.2 | -35.4 | -38.5 | 71 G |
| Ho ³⁺ | 0.1(KNO ₃) | 20 | -8.06 | -9.4 | -33.7 | -39.3 | 71 G |
| Er ³⁺ | 0.1(KNO ₃) | 20 | -7.23 | -8.5 | -30.3 | -35.6 | 71 G |
| Tm ³⁺ | 0.1(KNO ₃) | 20 | -6.75 | -8.7 | -28.2 | -36.4 | 71 G |
| Yb ³⁺ | 0.1(KNO ₃) | 20 | -5.25 | -4.9 | -22.0 | -20.5 | 71 G |
| Lu ³⁺ | 0.1(KNO ₃) | 20 | -3.60 | 0.6 | -15.1 | 2.5 | 71 G |

a: kcal mol⁻¹

c: kJ mol⁻¹

b: cal mol⁻¹K⁻¹

d: J mol⁻¹K⁻¹

Acknowledgment.

The compiler wish to thank Dr. Leonard F. Lindoy for revising English of the first draft.

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LIST OF SELECTED STABILITY CONSTANTS

| <u>Metal</u> | <u>Medium</u> | <u>t</u> [°C] | <u>log K₁</u> | <u>log K₂</u> | <u>log β₂</u> | <u>Rank</u> |
|-----------------------------|--|---------------|--------------------------|--------------------------|--------------------------|-------------|
| Ag ⁺ | 0.1(KClO ₄) | 20 | 5.16 | | | T |
| Al ³⁺ | 0.1(KClO ₄) | 20 | 9.5 | | | T |
| Am ³⁺ | 0.1(NaClO ₄) | 25 | 12.00 | 9.11 | | T |
| Ba ²⁺ | 0.1(KNO ₃) | 20 | 4.85 | | | R |
| Be ²⁺ | 0.1(KNO ₃) | 20 | 7.5 | | | D |
| Bi ³⁺ | 1(NaClO ₄) | 20 | 17.54 | | 26.56 | T |
| Ca ²⁺ | 0.1(KNO ₃) | 20 | 6.45 | | | R |
| Ce ³⁺ | 0.1(KNO ₃) | 20 | 10.80 | 7.93 | | T |
| Cd ²⁺ | 0.1(KNO ₃) | 20 | 9.80 | 4.48 | | T |
| Cf ³⁺ | 0.1(NaClO ₄) | 25 | 11.92 | | 21.21 | T |
| Cm ³⁺ | 0.1(NH ₄ ClO ₄) | 25 | 11.80 | | 20.58 | T |
| Co ²⁺ | 0.1(KNO ₃) | 20 | 10.4 | 4.01 | | T |
| Cu ²⁺ | 0.1(KNO ₃) | 20 | 12.96 | 4.3 | | T |
| Dy ³⁺ | 0.1(KNO ₃) | 20 | 11.65 | 9.45 | | T |
| Er ³⁺ | 0.1(KNO ₃) | 20 | 11.94 | 9.29 | | T |
| Eu ²⁺ | 0.5 NaClO ₄ | 25 | 5.55 | | 8.62 | T |
| Eu ³⁺ | 0.1(KNO ₃) | 20 | 11.44 | 9.23 | | T |
| Fe ²⁺ | 0.1 KCl | 20 | 8.83 | | | T |
| Fe ³⁺ | 0.1(KCl) | 20 | 16.26 | 8.5 | | T |
| Ga ³⁺ | 0.1(KNO ₃) | 20 | 13.7 | | | T |
| Gd ³⁺ | 0.1(KNO ₃) | 20 | 11.45 | 9.35 | | T |
| H ⁺ ^a | 0.1(KNO ₃ /KCl) | 20 | 9.71 | | | R |
| Hg ²⁺ | 0.1(NaClO ₄) | 25 | 14.5 | | | T |
| Ho ³⁺ | 0.1(KNO ₃) | 20 | 11.78 | 9.41 | | T |
| In ³⁺ | 0.1(KNO ₃) | 20 | 16.9 | 7.4 | | T |
| K ⁺ | 0.1((CH ₃) ₄ NCl) | 20 | 0.6 | | | T |
| La ³⁺ | 0.1(KNO ₃) | 20 | 10.51 | 7.30 | | T |
| Li ⁺ | 0.1(KNO ₃) | 20 | 2.51 | | | T |
| Lu ³⁺ | 0.1(KNO ₃) | 20 | 9.4 | | | T |

| <u>Metal</u> | <u>Medium</u> | <u>t[°C]</u> | <u>log K₁</u> | <u>log K₂</u> | <u>log β₂</u> | <u>Rank</u> |
|-------------------------------|--|--------------|--------------------------|--------------------------|--------------------------|-------------|
| Mg ²⁺ | 0.1(KCl) | 20 | 5.43 | | | R |
| Mn ²⁺ | 0.1(KNO ₃) | 20 | 7.44 | 3.55 | | T |
| Na ⁺ | 0.1(KNO ₃) | 20 | 1.22 | | | T |
| Nd ³⁺ | 0.1(KNO ₃) | 20 | 11.18 | 8.47 | | T |
| Ni ²⁺ | 0.1(KNO ₃) | 20 | 11.54 | 4.88 | | T |
| NpO ₂ ⁺ | 0.1(NH ₄ ClO ₄) | 20 | 6.80 | | | T |
| Np ⁴⁺ | 1(NaClO ₄) | 25 | 17.28 | | 32.06 | T |
| Pb ²⁺ | 0.1(KNO ₃) | 20 | 11.4 (R) | 1.4 (T) | | |
| Pd ²⁺ | 1(NaClO ₄) | 20 | 17.1 | 6.6 | | T |
| Pm ³⁺ | 0.1(KNO ₃) | 20 | 11. | 8.7 | | |
| Pr ³⁺ | 0.1(KNO ₃) | 20 | 10.95 | 8.20 | | T |
| PuO ₂ ⁺ | 0.1(NaClO ₄) | 25 | 6.91 | | | T |
| Sc ³⁺ | 0.1(NaClO ₄) | 25 | 12.68 | | | T |
| | 0.1(KClO ₄) | 20 | | | 24.1 | T |
| Sm ³⁺ | 0.1(KNO ₃) | 20 | 11.35 | 9.10 | | T |
| Sr ²⁺ | 0.1(KCl) | 20 | 5.00 | | | R |
| Tb ³⁺ | 0.1(KNO ₃) | 20 | 11.52 | 9.45 | | T |
| Th ⁴⁺ | 0.1(NaClO ₄) | 20 | 16.9 | | | T |
| Tl ⁺ | 0.1(KNO ₃) | 20 | 4.74 | | | R |
| Tl ³⁺ | 1(NaClO ₄) | 20 | 20.9 | 11.6 | | T |
| Tm ³⁺ | 0.1(KNO ₃) | 20 | 12.12 | 9.25 | | T |
| UO ₂ ²⁺ | 0.1(NaClO ₄) | 20 | 9.56 | | | T |
| V ³⁺ | 0.1(NaClO ₄) | 20 | 13.41 | 8.68 | | T |
| VO ²⁺ | 0.1(KNO ₃) | 25 | 10.82 | | | T |
| VO ₂ ⁺ | 3(NaClO ₄) | 25 | 13.8 | | | T |
| Yb ³⁺ | 0.1(KNO ₃) | 20 | 12.20 | 9.28 | | T |
| Zn ²⁺ | 0.1(KNO ₃) | 20 | 10.66 | 3.62 | | T |

$$a: \log ([H_2L]/([HL][H])) = 2.49 (R);$$

$$\log ([H_3L]/([H_2L][H])) = 1.86 (T);$$

$$\log ([H_4L]/([H_3L][H])) = 0.8 (T).$$