

Thermodynamics of Metal Complex Formation in Aqueous Solution. I. A Potentiometric Study of Fluoride Complexes of Hydrogen, Uranium(VI), and Vanadium(IV)

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The formation of fluoride complexes of hydrogen, uranyl(VI), and vanadyl(IV) ions has been studied in an aqueous medium of unit ionic strength with sodium perchlorate as supplementary electrolyte, at 25.0°C. Two methods, both potentiometric, have been used, *viz.* acidity measurements by the quinhydrone electrode, and direct measurements of the concentrations of free fluoride ions by the fluoride membrane electrode (FME).

The systems are all mononuclear. The stability constants for the complexes have been evaluated both graphically and by a computer method. The values found are more precise than any determined before for these systems. Within the limits of error, however, they agree quite well with those determined previously under the same conditions.

The stabilities of complexes are governed by both enthalpy and entropy changes according to

$$\Delta G_i^\circ = \Delta H_i^\circ - T\Delta S_i^\circ \quad (1)$$

where the changes in free energy, ΔG_i° , are related to the stability constants by

$$-\Delta G_i^\circ = RT \ln K_i \quad (2)$$

Strong complexes, characterized by large negative values of ΔG_i° , are formed if the value of ΔH_i° is strongly negative, and/or the value of ΔS_i° strongly positive. In aqueous solutions, strong complexes are as a rule the result of either a large gain of entropy or a large decrease of enthalpy, while the other term is of little importance or even counteracting.¹ The former case occurs when the bonds formed are mainly electrostatic, while the latter case indicates a marked covalent contribution to the bonding. Essential information may thus be gained from a knowledge of both ΔH_i° and ΔS_i° for the formation of a certain system of complexes. These are obtained by an experi-

mental determination of both the stability constants and the enthalpy changes for the complexes in question. We decided to perform such an investigation of the fluoride complexes of the uranyl(VI) and vanadyl(IV) ions as the thermodynamic data known for these systems are rather meagre.

This paper describes the determination of the stability constants. In a following paper² the determination of the enthalpy changes will be described.

The stabilities of these complexes have been studied previously in this laboratory^{3,4} at 20°C and in a perchlorate medium of ionic strength 1 M. The method used was acidity measurements in fluoride buffers, by means of a quinhydrone electrode. From the values of the hydrogen ion concentration, the concentrations of free fluoride were determined, and hence the stability constants.

Recently, however, the fluoride membrane electrode, denoted FME, has opened a path to the direct determination of the free fluoride concentration.⁵ This electrode has been successfully used by Norén⁶ for the investigation of the fluoride complexes of thorium(IV) and uranium(IV). It seemed therefore attractive to use this new tool also for the investigation of the present systems.

The solutions have to be acid in order to suppress the hydrolysis of the uranyl(VI) and vanadyl(IV) ions. Part of the fluoride will therefore be present as hydrogen fluoride complexes, and this part has to be determined. For this purpose, it is necessary to know the stability constants of the fluoride system, as well as the actual hydrogen ion concentration in each solution. This concentration is determined simultaneously with the fluoride ion concentration, by a quinhydrone electrode. The constants for the hydrogen fluoride system are determined in a preliminary, separate investigation.

All measurements refer to a medium of ionic strength 1.00 M, with sodium perchlorate as the supplementary salt, and to a temperature of 25.0°C.

DERIVATION OF STABILITY CONSTANTS FROM THE EMF MEASUREMENTS

Notation. The notation agrees with that used in Ref. 7, when not otherwise stated. For convenience, the most important definitions and formulas are collected below.

C_M, C_H, C_L = total concentrations of metal, hydrogen, and fluoride ions.

$[M], h, [L]$ = free concentrations of metal, hydrogen, and fluoride ions.

$\beta_j = [ML_j]/[M][L]^j$ = overall stability constant of the j :th mononuclear complex.

$\bar{K}_j = [ML_j]/[ML_{j-1}][L]$ = stepwise stability constant of the j :th mononuclear complex.

$\beta_j = \prod_j K_j$

$\delta_j = [HL_j]/h[L]^j$ = overall stability constant of the j :th proton complex.

$$X = 1 + \sum_{j=1}^N \beta_j [L]^j \quad (3)$$

$$X_j = (X_{j-1} - \beta_{j-1})/[L] \quad (4)$$

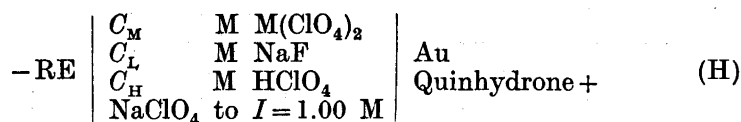
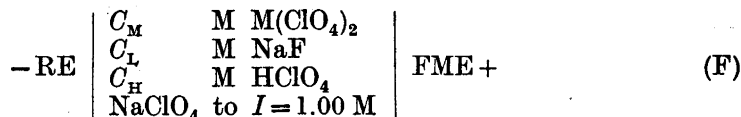
$(X_0 = X; \beta_0 = 1)$

\bar{n} = ligand number (average number of ligands bound per central atom).

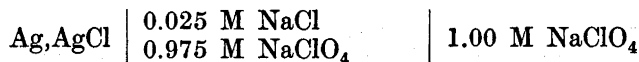
$$\bar{n} = \sum_{j=1}^N j\beta_j[L]^j/X \quad (5)$$

$$\ln X([L]_i) = \int_0^{[L]_i} (\bar{n}/[L]) d[L] \quad (6)$$

Cells measured. The concentrations $[L]$ and h are determined by means of the following cells



where RE is the reference half-cell



The measured E_F and E_H of the cells (F) and (H) are given (in mV), at 25°C by

$$E_F = E_F^\circ - 59.15 \log[L] + E_j \quad (7)$$

$$E_H = E_H^\circ + 59.15 \log h + E_j \quad (8)$$

where the concentrations $[L]$ and h are expressed in molarity units. E_F° and E_H° are cell constants. From measurements of E_F and E_H for known values of $[L]$ and h in the right-hand half-cells, E_F° and E_H° can easily be found (*cf.* p. 3462). E_j is the liquid junction potential between the solution in the right half-cell and 1.00 M NaClO₄ solution. E_j depends almost only upon h and can therefore be determined in separate experiments (*cf.* p. 3462).

From eqns. (7) and (8) we get

$$E_F' = E_F - E_F^\circ - E_j = -59.15 \log[L] \quad (9)$$

$$E_H' = E_H - E_H^\circ - E_j = 59.15 \log h \quad (10)$$

Hence by measuring E_F and E_H it is possible to calculate $[L]$ and h from eqns. (9) and (10), respectively.

Calculation of δ_1 and δ_2 . In a solution containing C_L mM NaF and C_H mM HClO₄ the following equations are valid if the only proton fluoride complexes present are HF and HF₂⁻, which is certainly true in the present concentration range.^{3-5,8}

$$C_L = [L] + [\text{HL}] + 2[\text{HL}_2] \quad (11)$$

$$C_H = h + [\text{HL}] + [\text{HL}_2] \quad (12)$$

$[\text{HL}]$ and $[\text{HL}_2]$ can be expressed by means of the stability constants and $[\text{L}]$ and h according to

$$[\text{HL}] = \delta_1 h [\text{L}] \quad (13)$$

$$[\text{HL}_2] = \delta_2 h [\text{L}]^2 \quad (14)$$

From eqns. (11)–(14) we arrive at

$$(C_L - [\text{L}])/h[\text{L}] = \delta_1 + 2\delta_2[\text{L}] \quad (15)$$

and

$$(C_H - h)/h[\text{L}] = \delta_1 + \delta_2[\text{L}] \quad (16)$$

As both $[\text{L}]$ and h are measured in each solution both $(C_L - [\text{L}])/h[\text{L}]$ and $(C_H - h)/h[\text{L}]$ can be calculated for every measured point. By plotting either of these functions *versus* $[\text{L}]$, it is possible to obtain δ_1 by extrapolation to $[\text{L}] = 0$ and δ_2 from the slopes of the lines. The difference $(C_L - [\text{L}])$ is most accurately determined at small $[\text{L}]$ -values, while the difference $(C_H - h)$ is most accurately measured at small h -values, *i.e.* at high $[\text{L}]$ -values. Consequently, the constant δ_1 , referring to the formation of HF , is best obtained from an extrapolation of $(C_L - [\text{L}])/h[\text{L}]$, while δ_2 , referring to the formation of HF_2 , is best obtained from the slope of $(C_H - h)/h[\text{L}]$.

If on the other hand H_2F_2 or other proton fluoride complexes containing more than one proton exist, both the functions mentioned will be dependent on h and thus on C_H . Hence the presence of such complexes will be revealed if titrations are carried out at different C_H .

Calculation of \bar{n} . From the definition of the ligand number \bar{n} , the following expression is obtained

$$\bar{n} = (C_L - [\text{L}] - [\text{HL}] - 2[\text{HL}_2])/C_M \quad (17)$$

Inserting eqns. (13) and (14) in (17) yields

$$\bar{n} = (C_L - [\text{L}] - \delta_1 h [\text{L}] - 2\delta_2 h [\text{L}]^2)/C_M \quad (18)$$

Hence \bar{n} can be immediately calculated once δ_1 and δ_2 are known, and $[\text{L}]$ and h measured.

It is also possible to determine \bar{n} from measurements of h only. Combination of eqns. (12), (13), and (14) yields

$$C_H = h(1 + \delta_1[\text{L}] + \delta_2[\text{L}]^2) \quad (19)$$

From the measured value of E_H , h is calculated by eqn. (10) and then eqn. (19) is solved for $[\text{L}]$. All the terms on the right-hand side of eqn. (18) are then known and thus \bar{n} . The values of \bar{n} calculated in this way are denoted \bar{n}' , in order to differentiate them from those found from the direct determination of $[\text{L}]$ by the FME.

Once corresponding values of \bar{n} and $[\text{L}]$ are known, the quantity X can be evaluated from a graphical integration of $\bar{n}/[\text{L}]$ plotted against $[\text{L}]$ (*cf.* eqn. (6)), and from corresponding values of X and $[\text{L}]$, the stability constants are then obtained graphically⁷ by plotting the functions $X_j = (X_{j-1} - \beta_{j-1})/[\text{L}]$ *versus* $[\text{L}]$.

The stability constants obtained in this way have been refined by using the data program "Letagrop vrid".⁹

The graphical representation of the fluoride systems. From the constants β_j , the compositions of the systems can be computed for any value of [L]. Provided that only mononuclear complexes are formed, the mole ratios of the various species are computed according to

$$\alpha_0 = \frac{[M]}{C_M} = \frac{1}{X} \quad (20)$$

$$\alpha_j = \frac{[ML_j]}{C_M} = \frac{\beta_j [L]^j}{X}; j \geq 1 \quad (21)$$

The ligand number, \bar{n} , for mononuclear complexes is calculated from eqn. (5).

EXPERIMENTAL

Chemicals. All chemicals used were of *pro analysi* grade.

Uranyl perchlorate was prepared as before.¹⁰ The exact concentration of the stock solution ($C_M = 884$ mM) was determined cerimetrically using ferroin as indicator. In order to avoid hydrolysis an excess of perchloric acid was added to the stock solution. The concentration of the free acid ($C_H = 782$ mM) was determined potentiometrically.³

Vanadium(IV) perchlorate was prepared from vanadium(IV) sulphate (Merck's *p.a.*) following the procedure used by Rossoti.¹¹ The stock solution had a vanadium(IV) concentration of 494 mM. The analysis was carried out by a cerimetric titration,¹² with potentiometric indication of the end-point. A slight oxidation to vanadium(V) occurred during the preparation of the perchlorate solution. The extent of this oxidation was also calculated from the potentiometric titration. The emf-difference between the initial solution before any Ce(IV) had been added and the half-oxidized solution will namely give the ratio between V(V) and V(IV) in the stock solution. The amount of vanadium present as pentavalent was found to be $\approx 0.3\%$ of the total. This contamination is insignificant for our measurements. In order to prevent hydrolysis of the vanadyl(IV) ion,¹¹ an excess of perchloric acid was added to the stock solution. The concentration of free acid ($C_H = 206$ mM) was determined in the same way as for the uranyl perchlorate.

Sodium perchlorate was prepared by neutralizing perchloric acid with sodium carbonate (Merck's *p.a.*). From the neutral, filtered solution crystals were formed between 135°C and 80°C. These were dried at 140°C. The solutions were analyzed both by cation exchange and by weighing a dried sample. The results of the two methods agreed.

Sodium fluoride. A solution of $C_L = 400$ mM, in a perchlorate medium of $I = 1.00$ M, was prepared from sodium fluoride (Merck's *p.a.*) and sodium perchlorate. In order to determine the small amount of foreign basic impurity usually found in fluoride solutions,³ some perchloric acid was added to a sample of the stock solution which was then titrated with alkali. The concentration of this impurity was estimated to about 0.2 % of the total fluoride. The foreign base was suppressed by adjusting the pH value of the solution from originally 9.0 to about 6.3. At this lower pH the basic impurity is mostly converted into the corresponding acid while the fluoride ions are still practically unaffected.

Apparatus. The fluoride membrane electrode used (Orion Research Inc.) consists of a single crystal of lanthanum fluoride doped with europium(II) ions. The crystal is cemented into a plastic tube containing an internal reference solution of sodium chloride and sodium fluoride. A detailed description of the electrode and its function is given in Refs. 5, 6.

To check if the electrode gives Nernstian response to fluoride ion concentrations, values of E_F (for the galvanic cell F on p. 3459) were measured for solutions with known [L]-values in the right-hand half-cell. For this, test solutions containing [L] in the range from 10^{-5} to 0.2 M have been used. Most of the solutions were prepared from the sodium

fluoride stock solution and sodium perchlorate. Thus the free fluoride ion concentration for these solutions could easily be computed. However, the solutions having $[L] < 10^{-3}$ M were prepared as fluoride buffers from the sodium fluoride stock solution, perchloric acid and sodium perchlorate in order not to have too low C_L in the solutions. In these cases the exact $[L]$ -values were calculated using the δ_j -values reported by Farrer *et al.*⁸ In the range investigated, the slope of the Nernst equation was found to be (59.0 ± 0.1) mV which is very close to the theoretical value of 59.15 mV for $RTF^{-1} \ln 10$ at 25°C.

The Ag,AgCl electrodes were prepared according to Brown.¹³ During the measurements two electrodes were used simultaneously in the reference half-cells. They gave the same potential within 0.1 mV. The vessels used for the right-hand half-cells written on p. 3459 were made of methacrylate plastic ("plexiglas"). The burette tips and other parts which might come into contact with the solutions in the reaction vessel were also made of plastic. A teflon-coated magnetic bar was used for stirring. All solutions containing fluoride were stored in polythene bottles. At the measurements the neutral fluoride solutions had to be added from a glass burette. During the 3 h needed for a titration, no perceptible increase of pH occurred, however.

The emfs were measured by a Radiometer PHM 4 valve potentiometer.

Procedure. The solutions in the right-hand half-cell were prepared by adding small amounts of a solution T from a burette to a known volume of a solution S. These solutions were prepared from the stock solutions of metal perchlorate, sodium fluoride, sodium perchlorate, and perchloric acid; their compositions are given in Tables 2-4. For the determination of δ_1 and δ_2 titrations were performed with $C_M = 0$.

Determinations of the cell constant, E_F° in eqn. (9), were performed immediately before and after each titration series. These were carried out by means of a standard fluoride solution in the right-hand half-cell. The standard solution was prepared from the sodium fluoride stock solution and sodium perchlorate and had a known value of $[L]$ (4.000 mM). The E_F° value was found to change slowly⁸ but usually not more than 0.2 mV during a titration series. At the emf measurements performed using the quinhydrone electrode, E_H° was determined for each titration series. At the beginning of the titration the right-hand half-cell contained a metal ion solution having a known value of h , see Tables 2-4. From the measured emf value E_H° was calculated according to eqn. (10). The value of E_H° was remeasured at the end of each titration series by means of a perchloric acid solution with $h = 10.00$ mM and $I = 1.00$ M. In all cases the two E_H° values agreed within 0.2 mV.

The E_F potentials attained their final values within 5 min and were in general reproducible within 0.2 mV. The E_H potentials attained equilibrium practically at once and could usually be reproduced within 0.1 mV. Every titration series was repeated at least once.

MEASUREMENTS AND RESULTS

Determination of liquid junction potentials. The solutions are so acid that perceptible liquid junction potentials exist. Approximately, these depend only on h . They may therefore be determined by measuring the emf's produced by perchloric acid solutions in a 1.00 M perchlorate medium. By plotting $(E_H - 59.15 \log h)$ against h , E_H° has been obtained from the intercept on the ordinate axis. The differences between $(E_H - 59.15 \log h)$ and E_H° are considered to be the liquid junction potentials, assuming the activity coefficients to be constant. Table 1 shows corresponding values of the liquid junction potential E_j and h .

Table 1. The liquid junction potential E_j as a function of h .

$-E_j/\text{mV}$	0.3	0.6	1.0	1.3	1.6	1.9	2.3	2.6
h/mM	5	10	15	20	25	30	35	40

The hydrogen fluoride system. The titration data are collected in Table 1. Titrations were performed for three different values of C_H in order to determine if H_2F_2 exists within the concentration range used. The functions $(C_L - [L])/h[L]$ and $(C_H - h)/h[L]$ are presented in Figs. 1 and 2. Obviously both the

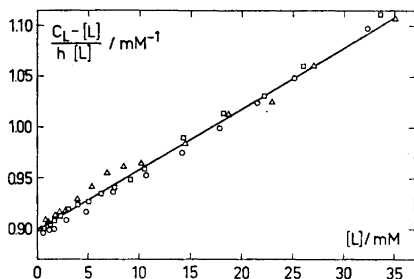


Fig. 1. Evaluation of δ_1 for the hydrogen fluoride system, cf. Table 2.

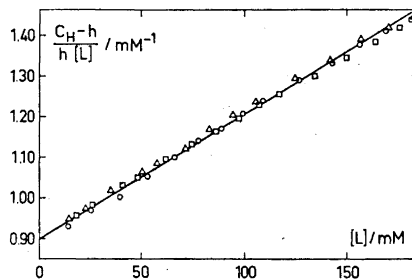


Fig. 2. Evaluation of δ_2 for the hydrogen fluoride system, cf. Table 2.

functions are independent of C_H implying that H_2F_2 is not formed. Moreover both the functions are approximately linear indicating that only the first two mononuclear complexes are present. The intercept on the ordinate axis in Fig. 1 yields the best value of δ_1 and the slope of the line in Fig. 2 the best value of δ_2 , as shown above. The values were then refined by a least squares program in the series "Letagrop vrid".⁹ The following result was obtained:

$$\begin{aligned}\delta_1 &= (899 \pm 5) \text{ M}^{-1} \\ \delta_2 &= (3000 \pm 100) \text{ M}^{-2}\end{aligned}$$

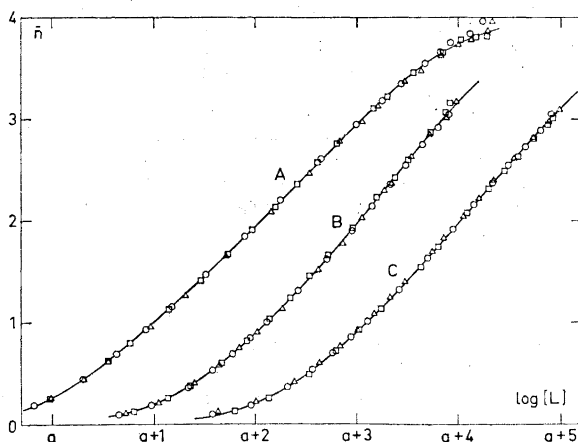


Fig. 3. The complex formation functions of the fluoride systems of uranyl(VI) (A) and vanadyl(IV) (B and C). The curves B and C refer to \bar{n} and \bar{n}' , respectively. For the curves A and B (both referring to \bar{n}), $a = -5$, for the curve C, $a = -6$. Only half of the experimental points of Tables 3 and 4, chosen at random, have been plotted.

Table 2. Experimental potentiometric data for the hydrogen fluoride titrations. The symbols refer to Figs. 1 and 2.

- a) ○ S: $C_H = 30.00$ mM, $C_{NaClO_4} = 970$ mM.
T: $C_{NaF} = 400$ mM, $C_{NaClO_4} = 600$ mM.

C_H /mM, C_L /mM, E_F /mV, $-E_H$ /mV:

29.85, 1.990, 242.7, 92.1; 29.70, 3.960, 223.8, 94.0; 29.56, 5.911, 211.7, 96.0; 29.41, 7.843, 202.3, 98.2; 29.27, 9.756, 194.5, 100.5; 28.99, 13.53, 181.3, 105.6; 28.57, 19.05, 164.0, 114.9; 28.24, 23.53, 150.3, 124.4; 27.91, 27.91, 137.3, 134.7; 27.59, 32.18, 126.0, 144.8; 27.27, 36.36, 116.7, 153.6; 26.97, 40.45, 109.4, 160.9; 26.67, 44.44, 103.5, 167.1; 26.37; 48.35, 98.7, 172.3; 26.09, 52.17, 94.7, 176.7; 25.53, 59.57, 88.3, 184.2; 25.00, 66.67, 83.1, 190.3; 24.49, 73.47, 79.0, 195.5; 24.00, 80.00, 75.5, 199.9; 23.08, 92.3, 69.9, 207.2; 22.22, 103.7, 65.7, 213.3; 21.43, 114.3, 62.2, 218.3; 20.69, 124.1, 59.4, 222.8; 20.00, 133.3, 57.0, 226.7; 18.75, 150.0, 53.1, 233.3; 17.65, 164.7, 50.0, 238.7; 16.67, 177.8, 47.7, 243.3; 15.79, 189.5, 45.7, 247.3; 15.00, 200.0, 43.9, 250.9;

- b) □ S: $C_H = 20.00$ mM, $C_{NaClO_4} = 980$ mM.
T: $C_{NaF} = 400$ mM, $C_{NaClO_4} = 600$ mM.

C_H /mM, C_L /mM, E_F /mV, $-E_H$ /mV:

19.90, 1.990, 232.1, 103.4; 19.80, 3.960, 212.1, 106.2; 19.70, 5.911, 199.1, 109.4; 19.61, 7.843, 188.7, 112.8; 19.51, 9.756, 179.6, 116.8; 19.42, 11.65, 171.3, 120.9; 19.32, 13.53, 163.5, 125.6; 19.23, 15.39, 156.0, 130.5; 19.14, 17.23, 148.9, 135.8; 19.05, 19.05, 142.2, 140.9; 18.96, 20.85, 136.0, 146.1; 18.87, 22.64, 130.4, 150.9; 18.78, 24.41, 125.4, 155.5; 18.69, 26.17, 121.0, 159.5; 18.60, 27.91, 117.1, 163.4; 18.39, 32.18, 109.2, 171.3; 18.18, 36.36, 103.0, 177.8; 17.98, 40.45, 97.9, 183.1; 17.78, 44.44, 93.8, 187.8; 17.39, 52.17, 87.2, 195.3; 17.02, 59.57, 82.1, 201.5; 16.67, 66.67, 77.9, 206.5; 16.00, 80.00, 71.6, 214.9; 15.38, 92.31, 66.8, 221.4; 14.82, 103.7, 63.0, 226.9; 14.29, 114.3, 59.9, 231.5; 13.79, 124.1, 57.4, 235.7; 13.33, 133.3, 55.2, 239.2; 12.50, 150.0, 51.6, 245.4; 11.77, 164.7, 48.8, 250.5; 11.11, 177.8, 46.5, 255.1; 10.53, 189.5, 44.7, 258.8; 10.00, 200.0, 43.1, 262.3;

- c) △ S: $C_H = 10.00$ mM, $C_{NaClO_4} = 990$ mM.
T: $C_{NaF} = 400$ mM, $C_{NaClO_4} = 600$ mM.

C_H /mM, C_L /mM, E_F /mV, $-E_H$ /mV:

9.975, 0.998, 233.9, 120.8; 9.950, 1.990, 214.3, 123.5; 9.926, 2.978, 201.8, 126.2; 9.901, 3.960, 191.7, 129.5; 9.877, 4.938, 183.3, 132.7; 9.852, 5.911, 175.8, 136.1; 9.828, 6.880, 169.1, 139.7; 9.804, 7.843, 162.7, 143.6; 9.780, 8.802, 157.0, 147.3; 9.756, 9.756, 151.6, 151.1; 9.709, 11.65, 142.2, 158.4; 9.662, 13.53, 134.4, 165.0; 9.615, 15.39, 128.0, 170.7; 9.570, 17.23, 122.6, 175.6; 9.524, 19.05, 117.9, 180.0; 9.412, 23.53, 103.9, 188.9; 9.303, 27.91, 102.3, 195.8; 9.196, 32.18, 97.0, 201.4; 9.091, 36.36, 92.8, 206.2; 8.889, 44.44, 86.1, 213.9; 8.696, 52.17, 81.0, 219.9; 8.511, 59.57, 76.8, 225.2; 8.333, 66.67, 73.4, 229.6; 8.000, 80.00, 67.9, 236.9; 7.692, 92.31, 64.0, 242.8; 7.407, 103.7, 60.7, 247.8; 7.143, 114.3, 57.8, 252.3; 6.897, 124.1, 55.4, 256.1; 6.667, 133.3, 53.5, 259.5; 6.250, 150.0, 50.2, 265.3; 5.882, 164.7, 47.6, 270.4; 5.556, 177.8, 45.5, 274.5; 5.263, 189.5, 43.7, 278.1; 5.000, 200.0, 42.3, 281.4; 4.545, 218.2, 40.0, 286.8;

The quoted errors here and in the following are equal to three standard deviations. For the same temperature and the same medium Farrer and Rossotti⁸ have found $\delta_1 = (890 \pm 20) M^{-1}$ and $\delta_2 = (3400 \pm 600) M^{-2}$ by quinhydrone measurements. The agreement is complete within the experimental errors. The results obtained with the FME method are much more precise, however.

The uranium(VI) fluoride system. Titrations were performed with three different values of C_M . The results are given in Table 3, and the complex formation functions are plotted in Fig. 3. Evidently the same curve is obtained for all the values of C_M used, which proves that no polynuclear fluoride

Table 3. Experimental potentiometric data for the uranyl(VI) fluoride titrations.
The symbols refer to Fig. 3.

a) ○ S: $C_M = 30.75$ mM, $C_H = 20.32$ mM,
 $C_{NaF} = 2.07$ mM, $C_{NaClO_4} = 886$ mM.
T: $C_{NaF} = 400$ mM, $C_{NaClO_4} = 600$ mM.

C_M /mM, C_H /mM, C_L /mM, E_F /mV, $-E_H$ /mV:

30.45, 20.12, 6.01, 306.1, 100.5; 30.15, 19.92, 9.87, 290.1, 100.9; 29.85, 19.73, 13.66, 277.9, 101.5; 29.57, 19.54, 17.37, 267.6, 102.0; 29.29, 19.35, 21.01, 258.3, 102.5; 29.01, 19.17, 24.59, 249.6, 103.2; 28.74, 18.99, 28.10, 241.4, 103.9; 28.47, 18.81, 31.55, 233.8, 104.8; 28.21, 18.64, 34.93, 226.4, 106.0; 27.95, 18.47, 38.25, 219.3, 107.3; 27.66, 18.14, 44.71, 206.4, 110.2; 26.97, 17.82, 50.94, 194.6, 113.9; 26.51, 17.52, 56.96, 183.5, 118.3; 26.06, 17.22, 62.77, 173.0, 123.7; 25.62, 16.93, 68.39, 162.9, 129.9; 25.10, 16.59, 75.16, 150.6, 138.5; 24.60, 16.26, 81.66, 139.0, 148.0; 24.12, 15.94, 87.90, 128.1, 157.8; 23.65, 15.63, 93.90, 118.4, 167.2; 23.21, 15.34, 99.68, 110.2, 175.6; 22.78, 15.05, 105.2, 103.1, 183.0; 22.36, 14.78, 110.6, 97.2, 189.4; 21.96, 14.51, 115.8, 92.3, 195.1; 21.21, 14.01, 125.6, 84.3, 204.5; 20.50, 13.55, 134.7, 78.3, 212.1; 19.84, 13.11, 143.3, 73.5, 218.8; 19.22, 12.70, 151.3, 69.6, 223.6; 18.09, 11.95, 165.9, 63.6, 232.4; 17.08, 11.29, 178.9, 59.1, 239.3; 15.37, 10.16, 201.0, 52.6, 250.0; 13.98, 9.24, 219.1, 48.3, 258.0; 12.81, 8.47, 234.2, 45.2, 264.5; 11.39, 7.53, 252.6, 41.8, 272.3; 10.25, 6.77, 267.4, 39.3, 278.2;

b) □ S: $C_M = 20.50$ mM, $C_H = 20.24$ mM,
 $C_{NaF} = 1.38$ mM, $C_{NaClO_4} = 917$ mM.
T: $C_{NaF} = 400$ mM, $C_{NaClO_4} = 600$ mM.

C_M /mM, C_H /mM, C_L /mM, E_F /mV, $-E_H$ /mV:

20.30, 20.04, 5.33, 297.3, 100.7; 20.10, 19.84, 9.20, 278.1, 101.3; 19.90, 19.65, 12.99, 263.2, 102.0; 19.71, 19.46, 16.71, 250.5, 102.7; 19.52, 19.28, 20.36, 238.7, 103.8; 19.34, 19.09, 23.94, 228.2, 105.0; 19.16, 18.92, 27.46, 218.2, 106.6; 18.98, 18.74, 30.91, 209.3, 108.5; 18.81, 18.57, 34.29, 201.1, 110.7; 18.64, 18.40, 37.62, 193.4, 113.2; 18.47, 18.23, 40.88, 186.1, 116.1; 18.30, 18.07, 44.09, 179.1, 119.3; 18.14, 17.91, 47.24, 172.3, 122.9; 17.98, 17.75, 50.33, 165.7, 126.8; 17.83, 17.60, 53.37, 159.4, 131.1; 17.67, 17.45, 56.36, 153.1, 135.5; 17.52, 17.30, 59.30, 147.0, 140.3; 17.37, 17.15, 62.19, 141.1, 145.1; 17.23, 17.01, 65.03, 135.4, 150.0; 17.08, 16.87, 67.82, 130.0, 154.8; 16.73, 16.52, 74.60, 118.0, 166.4; 16.40, 16.19, 81.10, 108.3, 176.1; 16.08, 15.87, 87.36, 100.5, 184.3; 15.77, 15.57, 93.37, 94.4, 191.1; 15.19, 14.99, 104.7, 85.0, 202.1; 14.64, 14.46, 115.3, 78.1, 210.5; 13.67, 13.49, 134.3, 68.7, 223.0; 12.81, 12.65, 150.9, 62.4, 232.2; 12.06, 11.91, 165.5, 57.8, 239.4; 11.39, 11.24, 178.5, 54.2, 245.3; 10.25, 10.12, 200.7, 49.0, 254.6; 9.32, 9.20, 218.8, 45.4, 261.8; 8.54, 8.43, 233.9, 42.7, 267.8;

c) △ S: $C_M = 10.25$ mM, $C_H = 10.06$ mM,
 $C_{NaF} = 0.69$ mM, $C_{NaClO_4} = 959$ mM.
T: $C_{NaF} = 400$ mM, $C_{NaClO_4} = 600$ mM.

C_M /mM, C_H /mM, C_L /mM, E_F /mV, $-E_H$ /mV:

10.20, 10.01, 2.677, 296.9, 118.6; 10.15, 9.96, 4.644, 277.8, 118.9; 10.10, 9.91, 6.591, 263.2, 119.4; 10.05, 9.86, 8.52, 250.3, 120.0; 10.00, 9.81, 10.43, 238.6, 120.9; 9.95, 9.77, 12.32, 228.1, 122.0; 9.90, 9.72, 14.19, 218.3, 123.5; 9.86, 9.67, 16.05, 209.7, 125.2; 9.76, 9.58, 19.70, 194.2, 129.6; 9.67, 9.49, 23.29, 180.3, 135.1; 9.58, 9.40, 26.81, 167.8, 141.6; 9.49, 9.31, 30.27, 156.2, 149.0; 9.40, 9.23, 33.66, 145.7, 157.0; 9.32, 9.15, 36.99, 136.3, 164.6; 9.23, 9.06, 40.26, 128.1, 172.4; 9.15, 8.98, 43.47, 121.0, 178.7; 9.07, 8.90, 46.63, 115.0, 184.7; 8.99, 8.82, 49.73, 109.9, 189.8; 8.91, 8.75, 52.77, 105.5, 194.4; 8.72, 8.56, 60.16, 96.6, 203.9; 8.54, 8.38, 67.24, 90.2, 211.3; 8.37, 8.21, 74.03, 84.9, 217.5; 8.20, 8.05, 80.55, 80.6, 222.5; 7.88, 7.74, 92.84, 74.0, 231.1; 7.593, 7.45, 104.2, 69.0, 237.7; 7.321, 7.19, 114.8, 65.0, 243.4; 6.833, 6.71, 133.8, 59.1, 252.3; 6.406, 6.29, 150.4, 54.8, 259.4; 6.029, 5.92, 165.1, 51.5, 265.0; 5.694, 5.59, 178.2, 48.9, 270.1; 5.125, 5.03, 200.3, 44.9, 277.8; 4.659, 4.573, 218.5, 42.1, 284.2; 4.271, 4.192, 233.6, 40.0, 289.2;

complexes are formed⁷ within the investigated concentration range. The formation function bends towards $\bar{n} = 4$, which means that the fourth mononuclear complex is the highest one, at least if $[L] < 200$ mM. The constants were calculated *via* integration⁷ of the function $n/[L]$. They were also determined numerically by the least-squares program used before for the calculation of δ_1 and δ_2 . Both methods gave the same result.

$$\begin{aligned}\beta_1 &= (3.43 \pm 0.04) \times 10^4 \text{ M}^{-1} \\ \beta_2 &= (9.5 \pm 0.2) \times 10^7 \text{ M}^{-2} \\ \beta_3 &= (2.60 \pm 0.07) \times 10^{10} \text{ M}^{-3} \\ \beta_4 &= (7.8 \pm 0.5) \times 10^{11} \text{ M}^{-4}\end{aligned}$$

With these values of $\beta_1 - \beta_4$, $\bar{n}([L])$ has been calculated according to eqn. (5) and is introduced in Fig. 3 as a fulldrawn curve. The composition, calculated from eqn. (21), is presented graphically in Fig. 4.

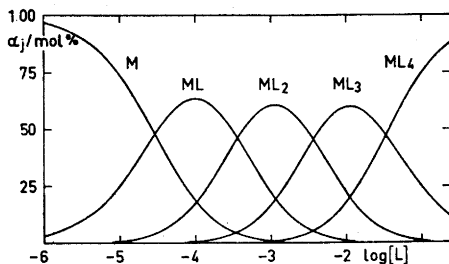


Fig. 4. The distribution of uranyl(VI) between the different complexes, ML_j , at varying fluoride ion concentration, $[L]$ (in M).

The method used in Ref. 3 in determining the stability constants of the uranyl(VI) fluoride complexes utilises the fact that protons act as competitors to the uranyl ions for the fluoride ions. Since the uranyl(VI) complexes are much stronger than those formed by the hydrogen ion, the change in h will be small during the first additions of fluoride solution. It is therefore difficult to get a good value of the first constant, β_1 , by this method. Considering this, the values obtained here agree surprisingly well with those found before,³ see Table 5. It should be remembered, however, that these do not refer to 25°C, but to 20°C. For the ratios K_j/K_{j+1} , the present constants give 13, 10, and 10 for $j = 1, 2$, and 3, as against 16, 6, and 17 found before. The extra stability of the first and third complexes indicated by the previous investigation is therefore probably not real. On the contrary, no complex seems to be much preferred, a result which is in line with the general experience of systems of fluoride complexes.

A perchlorate medium of $I = 1$ M has also been used by Day and Powers¹⁴ who have found $\beta_1 = 2.4 \times 10^4 \text{ M}^{-1}$ at 25°C, using TTA-extraction. Grenthe and Varfeldt¹⁵ have used a perchlorate medium of $I = 4$ M, with $h = 0.60$ M. By measuring the variation of the redox potential for the U(VI)/U(IV) couple with the fluoride concentration, they have found $\beta_1 = 2.7 \times 10^4 \text{ M}^{-1}$ at 25°C. These results are both compatible with the value of β_1 found in the present investigation.

Table 4. Experimental potentiometric data for the vanadyl(IV) fluoride titrations.
The symbols refer to Fig. 3.

- a) ○ S: $C_M = 30.00$ mM, $C_H = 30.00$ mM, $C_{NaClO_4} = 880$ mM.
T: $C_{NaF} = 400$ mM, $C_{NaClO_4} = 600$ mM.

C_M /mM, C_H /mM, C_L /mM, E_F /mV, $-E_H$ /mV:

29.70, 29.70, 3.960, 257.3, 91.2; 29.41, 29.41, 7.843, 238.3, 92.6; 29.13, 29.13, 11.65, 226.1, 94.0; 28.85, 28.85, 15.38, 216.8, 95.5; 28.57, 28.57, 19.05, 209.2, 97.1; 28.30, 28.30, 22.64, 202.5, 98.9; 28.04, 28.04, 26.17, 196.4, 100.9; 27.78, 27.78, 29.63, 190.8, 102.9; 27.52, 27.52, 33.03, 185.4, 105.2; 27.27, 27.27, 36.36, 180.4, 107.5; 27.03, 27.03, 39.64, 175.3, 110.1; 26.79, 26.79, 42.86, 170.7, 112.8; 26.32, 26.32, 49.12, 161.3, 118.8; 25.86, 25.86, 55.17, 152.5, 125.2; 25.42, 25.42, 61.02, 144.0, 132.0; 25.00, 25.00, 66.67, 135.8, 139.0; 24.59, 24.59, 72.13, 128.1, 146.1; 24.19, 24.19, 77.42, 121.1, 152.8; 23.81, 23.81, 82.54, 114.9, 159.1; 23.44, 23.44, 87.50, 109.2, 164.9; 23.03, 23.03, 92.31, 104.2, 170.4; 22.64, 22.64, 98.11, 98.6, 176.4; 22.22, 22.22, 103.7, 93.9, 181.8; 21.82, 21.82, 109.1, 89.7; 186.7; 21.43, 21.43, 114.3, 86.0, 191.1; 20.69, 20.69, 124.1, 80.0, 198.7; 20.00, 20.00, 133.3, 75.1, 205.1; 19.35, 19.35, 141.9, 71.0, 210.6; 18.75, 18.75, 150.0, 67.7, 215.3; 18.18, 18.18, 157.6, 64.8, 219.3;

- b) □ S: $C_M = 20.00$ mM, $C_H = 25.00$ mM, $C_{NaClO_4} = 915$ mM.
T: $C_{NaF} = 400$ mM, $C_{NaClO_4} = 600$ mM.

C_M /mM, C_H /mM, C_L /mM, E_F /mV, $-E_H$ /mV:

19.80, 24.75, 3.960, 248.3, 96.4; 19.61, 24.51, 7.843, 228.8, 98.2; 19.42, 24.27, 11.65, 215.8, 100.3; 19.23, 24.04, 15.38, 205.7, 102.6; 19.05, 23.81, 19.05, 197.1, 105.0; 18.87, 23.58, 22.64, 189.6, 107.7; 18.69, 23.36, 26.17, 182.5, 110.7; 18.52, 23.15, 29.63, 175.9, 114.0; 18.35, 22.94, 33.03, 169.5, 117.6; 18.18, 22.73, 36.36, 163.3, 121.5; 18.02, 22.52, 39.64, 157.1, 125.7; 17.86, 22.32, 42.86, 151.3, 130.1; 17.70, 22.12, 46.02, 145.7, 134.6; 17.54, 21.93, 49.12, 140.3, 139.1; 17.39, 21.74, 52.17, 135.2, 143.5; 17.24, 21.55, 55.17, 130.1, 148.0; 16.95, 21.19, 61.02, 121.2, 156.4; 16.67, 20.83, 66.67, 113.4, 164.2; 16.39, 20.49, 72.13, 106.7, 171.2; 16.13, 20.16, 77.42, 101.0, 177.2; 15.87, 19.84, 82.54, 96.1, 182.5; 15.62, 19.53, 87.50, 91.9, 187.4; 15.38, 19.23, 92.31, 88.3, 191.6; 15.09, 18.87, 98.11, —, 196.4; 14.81, 18.52, 103.7, 81.0, 200.6; 14.29, 17.86, 114.3, 75.3, 207.8; 13.79, 17.24, 124.1, 70.8, 213.9; 13.33, 16.67, 133.3, 67.2, 219.1; 12.90, 16.13, 141.9, 64.2, 223.6;

- c) △ S: $C_M = 10.00$ mM, $C_H = 20.00$ mM, $C_{NaClO_4} = 950$ mM.
T: $C_{NaF} = 400$ mM, $C_{NaClO_4} = 600$ mM.

C_M /mM, C_H /mM, C_L /mM, E_F /mV, $-E_H$ /mV:

9.95, 19.90, 1.990, 253.4, 101.6; 9.90, 19.80, 3.960, 234.4, 103.0; 9.85, 19.70, 5.911, 222.2, 104.5; 9.80, 19.61, 7.84, 213.0, 106.1; 9.76, 19.51, 9.76, 205.4, 107.7; 9.71, 19.42, 11.65, 198.5, 109.6; 9.66, 19.32, 13.53, 192.4, 111.7; 9.62, 19.23, 15.38, 186.9, 113.8; 9.57, 19.14, 17.22, 181.5, 116.0; 9.52, 19.05, 19.05, 176.3, 118.5; 9.48, 18.96, 20.85, 171.4, 121.1; 9.44, 18.87, 22.64, 166.6, 123.9; 9.39, 18.78, 24.41, 162.0, 126.8; 9.35, 18.69, 26.17, 157.5, 129.9; 9.30, 18.60, 27.91, 153.2, 133.0; 9.26, 18.52, 29.63, 148.9, 136.2; 9.17, 18.35, 33.03, 140.8, 142.7; 9.09, 18.18, 36.36, 133.3, 149.2; 9.01, 18.02, 39.64, 126.5, 155.2; 8.93, 17.86, 42.86, 120.6, 160.9; 8.85, 17.70, 46.02, 115.3, 166.3; 8.77, 17.54, 49.12, 110.7, 170.9; 8.70, 17.39, 52.17, 106.6, 175.2; 8.60, 17.20, 55.91, 102.1, 179.9; 8.51, 17.02, 59.57, 98.1, 184.2; 8.33, 16.67, 66.67, 91.7, 191.5; 8.16, 16.33, 73.47, 86.5, 197.6; 8.00, 16.00, 80.00, 82.3, 202.8; 7.69, 15.39, 92.31, 75.5, 211.3; 7.41, 14.81, 103.7, 70.4, 218.1; 7.14, 14.29, 114.3, 66.3, 223.8; 6.90, 13.79, 124.1, 63.1, 228.6; 6.67, 13.33, 133.3, 60.3, 232.9;

The vanadium(IV) fluoride system. Also for this system titration series have been performed with three values of C_M . The results are given in Table 4. The ligand number was determined by two methods described on p. 3460. The one utilizing data obtained from measurements by both the fluoride membrane electrode and the quinhydrone electrode gave the ligand numbers

denoted \bar{n} and the other method using only the h determination gave the ligand numbers denoted \bar{n}' in Fig. 3. The formation functions \bar{n} and \bar{n}' coincide completely within the experimental errors. For a given value of $[L]$ the difference is usually within 0.04 units in \bar{n} at least for values of $\bar{n} < 2.8$. Both the methods used thus function properly for this system, but the FME yields much more precise values of \bar{n} , at least for the low values which are utilized primarily for the determination of the first constants. The formation function is independent of C_M , which proves that no polynuclear complexes are formed.

When $[L]$ reaches a value of ≈ 90 mM a precipitate is formed, of the composition Na_3VOF_5 .⁴ The titrations must then be interrupted, though the complex formation curve is still steeply rising. Therefore the present measurements cannot give any reliable information about the maximum coordination number of the vanadyl(IV)-ion. From the two functions \bar{n} and \bar{n}' two sets of β_i -values were calculated in the way described above (*vide* p. 3460). The graphical integration of the function $\bar{n}/[L]$ gave the following stability constants

$$\begin{aligned}\beta_1 &= (2.35 \pm 0.03) \times 10^3 \text{ M}^{-1} \\ \beta_2 &= (5.5 \pm 0.1) \times 10^5 \text{ M}^{-2} \\ \beta_3 &= (1.97 \pm 0.07) \times 10^7 \text{ M}^{-3} \\ \beta_4 &= (1.2 \pm 0.1) \times 10^8 \text{ M}^{-4}\end{aligned}$$

and the constants obtained from \bar{n}' were

$$\begin{aligned}\beta_1 &= (2.43 \pm 0.06) \times 10^3 \text{ M}^{-1} \\ \beta_2 &= (5.8 \pm 0.2) \times 10^5 \text{ M}^{-2} \\ \beta_3 &= (2.1 \pm 0.1) \times 10^7 \text{ M}^{-3} \\ \beta_4 &= (1.0 \pm 0.1) \times 10^8 \text{ M}^{-4}\end{aligned}$$

The calculations were verified by the above mentioned least-squares program which gave the same results.

From the constants found, the complex formation curves for each set of β_i -values were calculated using eqn. (5) and introduced in Fig. 3. The composition, calculated from eqn. (21), is presented graphically in Fig. 5.

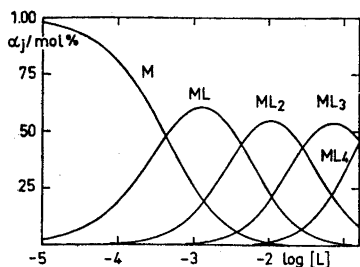


Fig. 5. The distribution of vanadyl(IV) between the different complexes, ML_j , at varying fluoride ion concentration, $[L]$ (in M). For the calculations, the constants found from the function \bar{n} have been used.

In the investigation of the vanadyl(IV) fluoride performed by Ahrlund and Norén⁴ the total metal concentration was varied between 25 and 50 mM and the total hydrogen ion concentration between 25 and 100 mM. According to Rydberg,¹⁶ who has applied a least squares program using an IBM 704 computer on these data, the stability constants depend somewhat on C_M

as well as on C_H . They assume lower values at higher C_M and/or C_H . The stepwise stability constants calculated from the titration series with the lowest C_M (25 mM) and C_H (25 mM) used are shown in Table 5 where also the constants determined by taking all the titration series into consideration are given. The consistency between the results obtained from the titration series with the lowest C_M and C_H used in Ref. 4 and those now found is very good.

Table 5. Stepwise stability constants, K_j/M^{-1} , of the uranyl(VI), vanadyl(IV), and hydrogen fluoride systems.

Metal ion	Temp °C	Medium, I/M and inert salt	$K_1 \times 10^{-3}$	$K_2 \times 10^{-2}$	$K_3 \times 10^{-1}$	K_4	Ref.
U(VI)	25	1 NaClO ₄	34.3	27	28	29	This work
U(VI)	20	1 NaClO ₄	35	22	37	22	3
U(VI)	25	4 (Na,H)ClO ₄	27				15
U(VI)	25	1 NaClO ₄	24				14
V(IV)	25	1 NaClO ₄	2.35	2.3	3.6	6.1	This work ^a
V(IV)	25	1 NaClO ₄	2.43	2.4	3.6	4.8	This work ^b
V(IV)	20	1 NaClO ₄	2.0	1.5	5.0	2	4
V(IV)	20	1 NaClO ₄	2.29	2.1	3.6	5	4, 16 ^c
H	25	1 NaClO ₄	0.899	0.030			This work
H	25	1 NaClO ₄	0.890	0.038			8
H	20	1 NaClO ₄	0.850	0.031			3

^a Calculated from the β_j -values obtained from the n function.

^b Calculated from the β_j -values obtained from the n' function.

^c Calculated from the titration series with $C_M = C_H = 25$ mM.

DISCUSSION

The fluoride complexes of the uranyl ion, UO_2^{2+} , and the vanadyl ion, VO^{2+} , are much stronger than those of divalent central ions of similar sizes possessing spherical symmetry.¹⁷ This depends upon that the effective charges on these metal atoms are higher than +2, due to the high electronegativity of the attached oxygen atoms. From the intensity of the infrared asymmetric stretching vibration of the UO_2^{2+} -ion, Larsson¹⁸ has inferred that the effective charge on the uranium atom would be $\approx +4$. A similar study¹⁹ of the vibration of the VO^{2+} -ion has suggested an effective charge on the vanadium atom of $\approx +2.4$.

A more detailed discussion will be postponed until the experimental results from the enthalpy measurements have been presented.

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REFERENCES

1. Ahrland, S. *Struct. Bonding (Berlin)* 5 (1968) 118.
2. Ahrland, S. and Kullberg, L. *Acta Chem. Scand.* 25 (1971) 3471.
3. Ahrland, S., Larsson, R. and Rosengren, K. *Acta Chem. Scand.* 10 (1956) 705.
4. Ahrland, S. and Norén, B. *Acta Chem. Scand.* 12 (1958) 1595.
5. Durst, R. A. and Butler, J. N. *Ion-selective Electrodes, Natl. Bur. Std. U.S., Spec. Publ.* 314 (1969) 143.
6. Norén, B. *Acta Chem. Scand.* 23 (1969) 931.
7. Fronæus, S. In Jonassen, H. B. and Weissberger, A. *Techniques of Inorg. Chem.* Interscience, New York, London 1963, Vol. 1, Chapt. 1.
8. Farrer, H. N. and Rossotti, F. J. C. *J. Inorg. Nucl. Chem.* 26 (1964) 1959.
9. Ingri, N. and Sillén, L. G. *Arkiv Kemi* 23 (1965) 97.
10. Ahrland, S. *Acta Chem. Scand.* 3 (1949) 374.
11. Rossotti, F. J. C. and Rossotti, H. S. *Acta Chem. Scand.* 9 (1955) 1177.
12. Furman, N. H. *J. Am. Chem. Soc.* 50 (1928) 1675.
13. Brown, A. S. *J. Am. Chem. Soc.* 56 (1934) 646.
14. Day, Jr., R. A. and Powers, R. M. *J. Am. Chem. Soc.* 76 (1954) 3895.
15. Grenthe, I. and Varfeldt, J. *Acta Chem. Scand.* 23 (1969) 988.
16. Rydberg, J. *Acta Chem. Scand.* 15 (1961) 1723.
17. Sillén, L. G. and Martell, A. E., Eds., *Stability Constants of Metal-Ion Complexes, Spec. Publ. Nos. 17 and 25*, The Chemical Society, London 1964 and 1971.
18. Larsson, R. *Acta Chem. Scand.* 22 (1968) 983.
19. Larsson, R. and Nunziata, G. *Acta Chem. Scand.* 24 (1970) 1.

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