

A Potentiometric Study of Fluoride Complexes of Uranium(IV) and Uranium(VI) Using the U(VI)/U(IV) Redox Couple

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The stability constants for the formation of fluoride complexes of U(IV) and U(VI) have been determined at a temperature of 25.00°C in solutions containing 0.60 M HClO₄ and 3.40 M NaClO₄ as ionic medium. The measurements have been made using a potentiometric technique where the variation of the redox potential for the U(VI)/U(IV) couple with the ligand concentration was used for the determination of the various stability constants.

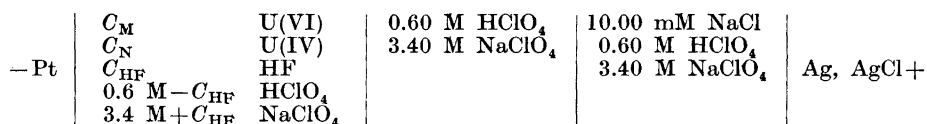
The complex formation between uranium(IV) and the fluoride ion has been studied by different methods. Day, Wilhite and Hamilton¹ determined the stability constants for the first two uranium(IV) fluoride complexes using a solvent extraction method with TTA as the auxiliary ligand. Savage and Browne² measured stability constants for five different fluoride complexes using a solubility method. Vdovenko, Romanov and Shcherbakov³ obtained numerical values for β_1 – β_3 using an NMR-method.

Some remarks can be passed upon the previous investigations. The distribution coefficients determined in the solvent-extraction study have low accuracy because of the unsymmetrical distributions of the metal between the aqueous and the organic phase. The solubility was investigated at a hydrogen ion concentration ($h=0.12$ M) where hydrolysis of uranium(IV) must influence the result, especially at low fluoride concentrations. No experimental details are available from the NMR-investigation. Because of these remarks we have decided to reinvestigate the uranium(IV)-fluoride system in order to get some more information on the complexes formed. A potentiometric method of investigation was preferred as this method in general gives the most accurate data. The ferric method of Brosset and Orring has been used in similar investigations on other four-valent metal ions *e.g.* 4,5 but cannot be used in our case due to the rapid oxidation of uranium(IV) by iron(III) even in solutions containing fluoride. We have instead

measured the variation of the redox potential for the couple U(VI)/U(IV) with the fluoride concentration. From these data we have determined the stability constants for fluoride complexes of both uranium(IV) and uranium(VI). The same method has previously been used by Ahrlund and Larsson⁶ and by Hietanen.⁷ The measurements are complicated by the fact that the equilibrium potentials are attained rather slowly. This problem was solved by Ahrlund and Larsson by the use of a mediator system and by Hietanen by using platinised electrodes. We have used the latter method as this gives a faster and more reproducible attainment of the equilibrium potential. All measurements were made in an approximately constant ionic medium of the composition 3.40 M NaClO₄+0.60 M HClO₄. The hydrolysis of uranium(IV) can be neglected in this medium due to the high acidity.⁷

CALCULATION OF STABILITY CONSTANTS

The emf E of cells of the following type has been measured:



C_M , C_N , and C_{HF} denote the total concentrations of U(VI), U(IV), and hydrofluoric acid in the left half-cell.

$[M]$ and $[N]$ are the concentrations of $[\text{UO}_2^{2+}]$ and $[\text{U}^{4+}]$, respectively. If the hydrogen ion concentration is constant the emf of the element can be written as

$$E = E^\circ - \frac{RT}{2F} \ln \frac{[M]}{[N]} \quad (1)$$

where E° is a constant if the liquid junction potential and the various activity coefficients are constant. This situation is attained by keeping the ionic medium approximately constant. The value of E° is determined in solutions with $C_{HF}=0$ where eqn. (1) takes the form

$$E' = E^\circ - \frac{RT}{2F} \ln \frac{C_M}{C_N} \quad (2)$$

Combination of eqns. (1) and (2) gives

$$E' - E = E_{MN} = \frac{RT}{2F} \ln \frac{[M]}{C_M} \frac{C_N}{[N]} \quad (3)$$

The investigation has been performed in solutions with high acidity *i.e.* $[\text{HF}] \gg [\text{F}^-]$. The concentration of free hydrofluoric acid is small, always less than 10 mM, and $[\text{HF}] \gg [\text{H}_2\text{F}_2]$. The hydrogen ion concentration is kept approximately constant (*cf.* p. 992) and we thus have

$$[\text{F}^-] = k [\text{HF}]$$

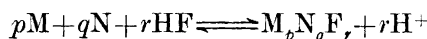
Eqn. (3) can now be expressed as

$$E_{\text{MN}} = \frac{RT}{2F} \ln \frac{\sum_p \sum_q \sum_r q \beta_{pqr} [\text{M}]^p [\text{N}]^{q-1} [\text{HF}]^r}{\sum_p \sum_q \sum_r p \beta_{pqr} [\text{M}]^{p-1} [\text{N}]^q [\text{HF}]^r} \quad (4)$$

if complexes of the general type $\text{M}_p\text{N}_q\text{F}_r$ are formed in solution. The stability constants β_{pqr} are equal to

$$\beta_{pqr} = \frac{[\text{M}_p\text{N}_q\text{F}_r]}{[\text{M}]^p [\text{N}]^q [\text{HF}]^r}$$

and are conditional equilibrium constants. The true stability constants for the reaction



are equal to β_{pqr}^* and are obtained by multiplication of β_{pqr} with $[\text{H}^+]^r$.

E_{MN} is a function of $[\text{HF}]$ only, if no polynuclear or mixed complexes are formed. Eqn. (4) may then be written as

$$E_{\text{MN}} = \frac{RT}{2F} \ln \frac{X_{\text{N}}}{X_{\text{M}}} \quad (5)$$

where

$$X_{\text{M}} = \sum_{r=0}^R \beta_{10r} [\text{HF}]^r \quad \text{and} \quad X_{\text{N}} = \sum_{r=0}^R \beta_{01r} [\text{HF}]^r$$

We have used eqn. (5) to determine the various uranium fluoride stability constants (*cf.* p. 997 for a discussion of the validity of the assumptions above).

The general procedure for determining stability constants from corresponding values of E_{MN} and C_{HF} has been described several times.^{8, p. 127} This procedure has to be modified in this particular case as complexes are formed with both M and N. Our first aim is to determine the concentration of free hydrofluoric acid, $[\text{HF}]$, and the average ligand numbers \bar{n}_{M} and \bar{n}_{N} . This can be accomplished by a modification of the usual procedure if only mononuclear complexes are formed.

The ratio $X_{\text{N}}/X_{\text{M}}$ is determined by E_{MN} only. Because X_{M} , X_{N} , \bar{n}_{M} , and \bar{n}_{N} are functions only of $[\text{HF}]$ these numbers are all independent of the total concentrations of central ions and ligand in solutions with the same value of E_{MN} . The free ligand concentration and the average ligand numbers are then determined from plots of C_{HF} versus C_{M} (or C_{N}) at constant values of E_{MN} .

The total ligand concentration is equal to

$$C_{\text{HF}} = \bar{n}_{\text{M}} \cdot C_{\text{M}} + \bar{n}_{\text{N}} \cdot C_{\text{N}} + [\text{HF}]$$

We shall use this relation for the determination of \bar{n}_{M} , \bar{n}_{N} , and $[\text{HF}]$.

C_{HF} is varied systematically by a titration procedure. The total concentrations of the central ions varied during the titration as the titrator must have $C_{\text{N}}=0$ in order to avoid precipitation of UF_4 (for convenience C_{M} was also equal to zero). The initial concentrations of U(VI), U(IV), and HF are equal

to C_M' , C_N' , and 0, respectively. The total ligand concentration in the titrant is C_{HF}' and

$$C_N = C_N' - \frac{C_N'}{C_{HF}'} \cdot C_{HF}$$

i.e. C_N (or C_M) is a linear function of C_{HF} . This fact is practical to use when the C_{HF} vs. C_N -curves in Fig. 3 are plotted.

The most convenient way of determining the various stability constants is to perform two different sets of titrations. In the first set \bar{n}_M is determined and in the second set \bar{n}_N and $[HF]$. The concentration C_N' is kept constant and the ratio C_M/C_N is varied in the first set of titrations. The total ligand concentration can then be expressed as

$$\frac{C_{HF} \cdot C_{HF}'}{C_{HF}' - C_{HF}} = \bar{n}_M \cdot C_M' + \bar{n}_N \cdot C_N' + [HF] \cdot \frac{1}{1 - C_{HF}/C_{HF}'} \quad (6a)$$

The last term in eqn. (6a) is at the most 15 % of $\bar{n}_N \cdot C_N$ and is furthermore approximately constant in solutions with the same E_{MN} , *i.e.* $C_{HF} \cdot C_{HF}' / (C_{HF}' - C_{HF})$ is a linear function of C_M' and \bar{n}_M is obtained from the slope of this line.

In the second set of titrations the ratio C_M/C_N is kept constant as the total concentration of central ion is varied. The total ligand concentration is equal to

$$C_{HF} = \left(\bar{n}_N + \frac{C_M}{C_N} \bar{n}_M \right) C_N + [HF] \quad (6b)$$

Values of $[\bar{n}_N + \bar{n}_M(C_M/C_N)]$ and $[HF]$ are determined from the slope and intercept of the straight lines (6b) for various values of E_{MN} ; *cf.* Fig. 3.

The values of \bar{n}_M , \bar{n}_N , and $[HF]$ thus determined contain all the information necessary for computation of the various stability constants. The uranium(IV) fluoride complexes are very stable and the free ligand concentration can for this reason only be determined by the extrapolation method at the highest values of E_{MN} . In order to determine the free ligand concentration for all values of E_{MN} the following procedure was used:

a. Only one U(VI) fluoride complex was formed in the ligand concentration range used in this investigation (the U(VI) fluoride complexes are very much weaker than the corresponding U(IV) complexes). The stability constant for this complex was determined from corresponding values of \bar{n}_M and $[HF]$ obtained from eqns. (6a) and (6b).

b. A value of X_M is calculated from the known U(VI) stability constants and a value of $\log X_N$ is then calculated from eqn. (5).

c. A graphical integration of the expression

$$\log \frac{[HF]_0}{[HF]} = \int_{\log X_N([HF])}^{\log X_N([HF]_0)} \frac{1}{\bar{n}_N} d \log X_N([HF]) \quad (7)$$

will then give corresponding values of $\log X_N$ and $[\text{HF}]$ if one set of $\log X_N - [\text{HF}]$ values, say $\log X_N([\text{HF}]_0)$, $[\text{HF}]_0$ can be determined by the extrapolation method.

d. Corresponding values of X_N and $[\text{HF}]$ have now been obtained and the various stability constants are then determined by the usual graphical extrapolation methods of Leden and Fronæus,⁸ p. 108

EXPERIMENTAL

Chemicals used. A uranium(VI) perchlorate solution was prepared and analysed as described by Ahrlund *et al.*⁹ Part of this solution was used for preparation of a uranium(IV) solution by electrolytic reduction. The procedure has been described in detail before.⁹ The total uranium concentration was determined by passing part of the solution through a cadmium reductor followed by a cerimetric titration.

Uranium(IV) was determined by a direct cerimetric titration and the uranium(VI) concentration was finally obtained from the difference between the two titrations. The hydrogen ion concentration in the uranium(IV) stock solution was determined in the following way: Uranium(IV) was oxidised to uranium(VI) with hydrogen peroxide. The hydrogen ion concentration in this solution was then determined by a potentiometric titration with a sodium hydroxide solution. The initial hydrogen ion concentration was calculated from a Gran-plot using the $\log h$ values in the range where hydrolysis of U(VI) can be neglected. Sodium perchlorate was prepared as described before.¹⁰ Perchloric acid and hydrofluoric acid stock solutions were prepared from concentrated acids of analytical grade. Nitrogen and hydrogen were purified from oxygen according to Meyer and Ronge.¹¹

Titration procedure. The titrations were made in the left half-cell of the galvanic element described on p. 989. The titration vessel was of polyethene and all glass equipment was covered with a film of the same material in order to prevent them from being attacked by hydrogen fluoride. 20 ml of a solution of the composition: $C_M' \text{U(VI)}$; $C_N' \text{U(IV)}$; 0.60 M HClO_4 , and 3.40 M $-2C_M' - 4C_N' \text{NaClO}_4$ was mixed directly in the nitrogen-filled titration vessel from the various stock solutions. The titrator was in all cases a solution with the composition: $C_{\text{HF}}' = 0.1879 \text{ (M)}$; 0.60 M $-C_{\text{HF}}' \text{HClO}_4$, and 3.40 M $+C_{\text{HF}}' \text{NaClO}_4$. This solution was added to the titration vessel from calibrated micro pipettes.

Stable and fairly reproducible electrode potentials were attained in 60 to 90 min. We tried several different types of electrodes and found that new platinised platinum electrodes gave the best performance. The electrode potentials were sensitive to light and a dark-painted electrode vessel had therefore to be used.^{12,13} The potential is also sensitive to stirring and stirring was therefore not used during the equilibration. The stability and reproducibility of the potential is dependent on the hydrogen ion concentration and the ligand concentration in solution. A faster and more reproducible attainment of the equilibrium potential is obtained at lower hydrogen ion concentrations and higher ligand concentrations. This fact is probably connected with the kinetic processes at the electrodes as discussed, *e.g.*, by Fronæus.¹⁴ In order to prevent oxidation of U(IV) by air a constant stream of oxygen free nitrogen was passed over the solution in the titration vessel. Three different series of titrations were performed. In the first series the total concentration of U(VI) and U(IV) were varied systematically in the absence of ligand. In this way we could check the validity of Nernst's law for the system. In the first series of ligand titrations C_N' was constant as the ratio C_M'/C_N' was varied and this series was used for the determination of \bar{n}_M . In the second series of ligand titrations the ratio C_M'/C_N' was kept constant as the total concentration of central ion was varied. This series was used for determination of the free ligand concentration and \bar{n}_N . All titrations were repeated several times and the reproducibility of the E_{MN} values was usually within 0.2 mV. The performance of the electrodes was checked by having at least three electrodes in the same titration vessel. The hydrogen ion concentration is decreasing as the concentration of free ligand is increasing in the titrant (because $C_{\text{HF}}' + C_{\text{HClO}_4} = 0.60$). The emf is dependent on the hydrogen ion concentration and the values of E_{MN} must

therefore be corrected for the decrease in hydrogen ion concentration. The correction is calculated from the expression

$$\Delta E_{MN} = \frac{RT}{2F} \ln \left(\frac{h}{0.60} \right)^4$$

where h is the hydrogen ion concentration in the solution, equal to $0.6000 - [\text{HF}]$ where $[\text{HF}]$ is an approximate value of the concentration of free HF calculated on the assumption that $h = 0.600$ M. The correction is always small, at the most 0.6 mV.

RESULTS

Validity of Nernst's law. The performance of the redox electrode was checked by systematic variations of the concentrations of U(VI) and U(IV) in solutions with $C_{\text{HF}} = 0$. The measured E' -values are given in Table 1 and

Table 1. Experimental values of E' as function of C_N and C_M in solutions with $C_{\text{HF}} = 0$.

Series	$C_N \times 10^3$ (M)	$C_M \times 10^3$ (M)	E' (mV)	$-E^\circ$ (mV)
1	30.57	0.72	33.0	15.2
	30.42	1.51	23.0	15.6
	29.97	3.82	10.6	15.9
	27.92	14.44	- 7.0	15.5
	25.58	21.52	-15.7	15.2
2	29.92	1.70	20.9	16.0
	29.63	3.25	12.7	15.7
	28.64	8.45	0.2	15.5
	22.26	41.94	-24.5	16.4
	18.77	60.22	-31.0	16.0
3	13.68	12.98	-15.6	16.3
	7.84	14.50	-23.8	15.9
	4.19	15.48	-32.8	16.0
	2.08	16.03	-42.6	16.4
4	37.96	1.69	23.5	16.4
	35.95	9.92	0.1	16.4
	31.09	30.14	-14.9	15.3
	26.32	49.87	-25.0	16.8
	16.72	89.65	-38.0	16.4
	11.67	110.56	-45.6	16.7

show that the value of E° is constant within 0.5 mV in the various titration series. Larger differences, at the most 1 mV, may exist between the E° -values of different titration series. The measured emf-values are rather well described by the Nernst equation (2) and we have thus proved that it is possible to use the U(VI)/U(IV) redox electrode for concentration determinations.

The uranium(VI) fluoride system. In Fig. 1 E_{MN} has been plotted versus C_{HF} for varying values of the ratio C_M/C_N . Values of \bar{n}_M at 5 mV intervals were determined as described before. The highest value of \bar{n}_M was equal to

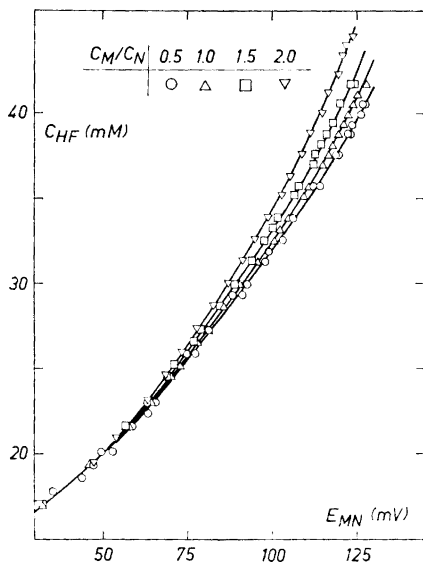


Fig. 1. C_{HF} as a function of E_{MN} for various values of the ratio C_M/C_N .

Table 2. Experimental values of E_{MN} vs. C_{HF} in titrations with C_M/C_N as a parameter and C_N' constant equal to 0.0200 M.

$$C_M/C_N = 0.5$$

$$E_{MN} \text{ (mV)} - C_{HF} \times 10^3 \text{ (M)}.$$

Series a. 6.1, 7.23; 14.2, 12.29; 32.5, 17.08; 58.5, 21.62; 81.3, 27.30; 106.4, 33.88; 119.0, 37.58; 123.7, 39.36.

Series b. 8.7, 8.95; 21.2, 14.72; 47.1, 19.38; 65.4, 23.08; 92.9, 30.00; 103.3, 32.61; 114.3, 35.75; 122.8, 38.77; 127.5, 40.53.

Series c. 2.9, 3.68; 4.6, 5.47; 8.8, 8.95; 22.3, 14.72; 44.0, 18.62; 53.0, 20.13; 63.5, 22.35; 77.5, 25.92; 98.1, 31.32; 119.7, 37.58.

Series d. 2.9, 3.68; 20.4, 14.72; 35.5, 17.86; 63.2, 23.08; 99.2, 31.97; 122.3, 38.77; 127.0, 40.53.

Series e. 6.5, 7.23; 12.3, 11.47; 49.6, 20.13; 74.9, 25.92; 88.3, 29.34; 112.2, 35.75.

Series f. 3.0, 3.68; 6.6, 7.23; 13.1, 11.47; 53.1, 20.13; 91.6, 29.34; 114.5, 35.75; 123.6, 38.77; 126.7, 39.95.

$$C_M/C_N = 1.0$$

$$E_{MN} \text{ (mV)} - C_{HF} \times 10^3 \text{ (M)}.$$

Series a. 4.5, 5.47; 14.5, 12.29; 32.5, 17.08; 58.2, 21.62; 73.2, 25.22; 81.3, 27.30; 105.3, 33.88; 117.2, 37.58; 122.9, 39.95.

Series b. 8.2, 8.95; 20.5, 14.72; 46.3, 19.38; 64.3, 23.08; 91.2, 30.00; 100.7, 32.61; 111.0, 35.75; 119.7, 38.77; 125.5, 41.10.

Series c. 70.1, 24.51; 86.0, 28.66; 102.5, 33.25; 115.1, 36.98; 121.6, 39.36; 128.2, 41.67.

Series d. 70.2, 24.51; 78.1, 26.61; 96.1, 31.32; 109.7, 35.14; 118.1, 38.18; 124.2, 40.53.

$$C_M/C_N = 1.5$$

$$E_{MN} \text{ (mV)} - C_{HF} \times 10^3 \text{ (M)}.$$

Series a. 8.8, 8.95; 21.2, 14.72; 46.4, 19.38; 63.9, 23.08; 89.0, 30.00; 98.2, 32.61; 108.3, 35.75; 116.5, 38.77; 123.8, 41.67.

Series b. 5.9, 7.23; 14.2, 12.29; 32.2, 17.08; 57.0, 21.62; 71.4, 25.22; 79.3, 27.30; 102.1, 33.88; 112.9, 37.58; 120.6, 40.53.

Series c. 69.6, 24.51; 84.8, 28.66; 100.8, 33.25; 112.7, 36.98; 118.7, 39.36; 124.0, 41.67.

Series d. 69.5, 24.51; 77.6, 26.61; 94.6, 31.32; 106.9, 35.14; 114.9, 38.18.

$$C_M/C_N=2.5$$

$$E_{MN} \text{ (mV)} - C_{HF} \times 10^3 \text{ (M)}.$$

Series a. 33.8, 17.08; 47.2, 19.38; 63.7, 23.08; 73.8, 25.92; 82.8, 28.66; 91.2, 31.32; 98.8, 33.88; 105.5, 36.37; 111.3, 38.77; 116.4, 41.10; 120.9, 43.36; 122.0, 43.92.

Series b. 32.1, 17.08; 54.0, 20.88; 68.6, 24.51; 78.1, 27.30; 87.3, 30.00; 95.1, 32.61; 103.0, 35.14; 109.0, 37.58; 115.0, 39.95; 119.8, 42.24; 124.2, 44.47.

0.36 and only one U(VI) fluoride complex is thus formed within the fluoride concentration range used. The concentration of free HF was determined from the titrations where the ratio C_M/C_N was constant. Values of β_{101} and β_{101}^* were determined from corresponding values of \bar{n}_M and [HF]. The following result was obtained:

$$\beta_{101} = 50 \pm 10 \text{ (M}^{-1}\text{)}$$

$$\beta_{101}^* = 30 \pm 6$$

The errors quoted are maximum errors and are fairly large due to the difficulty in obtaining accurate [HF]-values. The value of β_{101}^* is in good agreement with the value of Ahrland *et al.*⁹ ($\beta^* = 40 \pm 4$). This investigation was, however, performed at a different ionic strength (1 M) and a different temperature (20.00°C).

The uranium(IV) fluoride system. Experimental values of E_{MN} and C_{HF} for $C_M/C_N=0.5$ are given in Table 3 and Fig. 2.

Table 3. Experimental values of E_{MN} as a function of C_{HF} in solutions with the ratio C_M/C_N constant equal to 0.500.

$$C_M' = 0.0100 \text{ M}$$

$$E_{MN} \text{ (mV)} - C_{HF} \times 10^3 \text{ (M)}$$

Series a. 1.3, 0.94; 2.5, 1.86; 4.5, 2.78; 6.1, 3.69; 8.8, 4.58; 11.3, 5.47; 14.8, 6.35; 18.8, 7.23; 43.7, 9.80.

Series b. 4.5, 2.78; 19.0, 7.23; 43.2, 9.80; 75.0, 13.92; 109.4, 20.13; 122.6, 23.80; 126.9, 25.22.

Series c. 8.8, 4.58; 24.6, 8.09; 64.1, 12.29; 89.3, 16.30; 101.6, 18.62; 117.9, 22.35; 125.2, 24.51.

Series d. 2.8, 1.86; 4.5, 2.78; 11.6, 5.47; 24.8, 8.09; 43.4, 9.80; 58.0, 11.47; 74.9, 13.92; 84.3, 15.52; 97.4, 17.86; 109.4, 20.13; 117.7, 22.35.

Series e. 24.7, 8.09; 33.4, 8.95; 102.5, 18.62; 109.9, 20.13; 118.9, 22.35; 126.7, 24.51.

Series f. 24.7, 8.09; 58.7, 11.47; 102.5, 18.62; 115.6, 21.62; 122.9, 23.80; 129.7, 25.92.

$$C_N' = 0.0150 \text{ M}$$

$$E_{MN} \text{ (mV)} - C_{HF} \times 10^3 \text{ (M)}$$

Series a. 2.0, 1.86; 7.9, 6.35; 18.7, 10.64; 56.3, 16.30; 83.0, 21.62; 107.8, 27.30; 122.7, 31.97.

Series b. 4.0, 3.68; 13.2, 8.95; 38.6, 13.92; 50.6, 15.52; 72.0, 19.38; 96.1, 24.51; 117.2, 30.00.

Series c. 2.0, 1.86; 4.1, 3.68; 7.6, 6.35; 13.4, 8.95; 18.8, 10.64; 33.1, 13.11; 45.7, 14.72; 68.6, 18.62; 102.4, 25.92; 115.2, 29.34; 125.1, 32.61.

Series d. 2.0, 1.86; 7.6, 6.35; 22.3, 11.47; 56.3, 16.30; 76.1, 20.13; 86.4, 22.35; 93.2, 23.80; 110.5, 27.99; 121.2, 31.32.

$$C_N' = 0.0300 \text{ M}$$

$$E_{MN} \text{ (mV)} - C_{HF} \times 10^3 \text{ (M)}$$

Series a. 5.0, 8.95; 13.0, 17.08; 32.0, 24.51; 55.7, 30.00; 71.5, 34.51.

Series b. 3.1, 5.47; 8.8, 13.11; 22.7, 21.62; 46.7, 27.30; 63.9, 31.97; 80.5, 36.98.

Series c. 3.0, 5.47; 8.0, 13.11; 19.0, 20.13; 40.0, 25.92; 71.9, 34.51; 92.9, 41.10; 111.9, 47.15; 122.5, 51.25.

Series d. 5.0, 8.95; 13.4, 17.08; 29.8, 23.80; 52.3, 28.66; 64.1, 31.97; 83.8, 38.18; 101.9, 43.92; 117.2, 49.23; 125.1, 52.22.

Series e. 8.5, 13.11; 22.5, 21.62; 46.0, 27.30; 63.8, 31.97; 79.8, 36.98; 115.6, 48.20; 121.9, 50.75.

Series f. 5.0, 8.95; 14.6, 17.86; 32.2, 24.51; 56.5, 30.00; 71.3, 34.51; 88.0, 39.36; 105.5, 45.01; 114.5, 48.20; 119.7, 50.24; 125.6, 51.74.

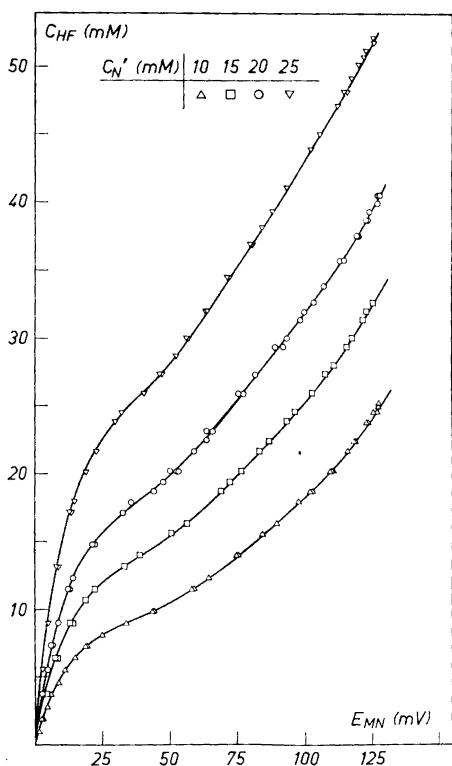


Fig. 2. C_{HF} as a function of E_{MN} for various values of C_N' .

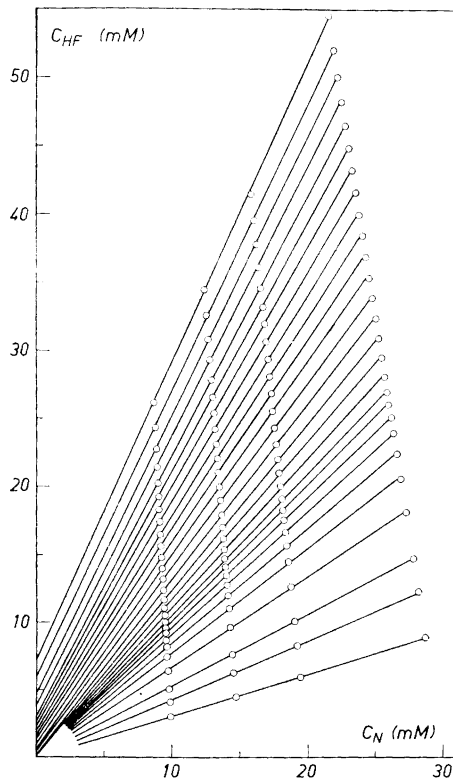


Fig. 3. C_{HF} versus C_N used for the determination of \bar{n}_N .

\bar{n}_N and [HF] were determined by the procedure described on p. 990. A graphical integration gave corresponding values of X_N and [HF] from which the various stability constants were determined by the graphical methods of Leden and Fronæus. The following values were obtained for the constants β_{01r} and β_{01r}^* :

$$\begin{aligned}\beta_{011} &= (3.90 \pm 0.10) \times 10^5 \text{ (M}^{-1}\text{)} & \beta_{011}^* &= (2.34 \pm 0.06) \times 10^5 \\ \beta_{012} &= (5.4 \pm 0.1) \times 10^8 \text{ (M}^{-2}\text{)} & \beta_{012}^* &= (1.94 \pm 0.04) \times 10^8 \\ \beta_{013} &= (1.3 \pm 0.1) \times 10^{10} \text{ (M}^{-3}\text{)} & \beta_{013}^* &= (2.8 \pm 0.2) \times 10^9\end{aligned}$$

The errors quoted are graphically estimated maximum errors. The full-drawn curves in Figs. 1 and 2 have been calculated using the experimentally determined stability constants and it is obvious from these figures that this set describes the experimental $E_{\text{MN}}-C_{\text{HF}}$ curves fairly well.

All calculations have been based on the assumption that no mixed or polynuclear complexes are formed. Fig. 1 shows that E_{MN} is independent of the concentration U(VI) for $E_{\text{MN}} < 60$ mV. No complexes containing U(VI) are thus formed within this concentration range. The variation of E_{MN} with C_{M} found for $E_{\text{MN}} > 60$ mV is best explained by the formation of fluoride complexes containing only U(VI), *i.e.* no mixed complexes of the type $M_pN_qF_r$ are formed.

The fact that the $C_{\text{HF}}-C_{\text{M}}$ curves of Fig. 3 are linear is an indication of mononuclearity. Hence the assumptions on which the calculation procedure is based seem to be reasonable.

The set of stability constants may be systematically in error due to the difficulty in determining an accurate [HF]-value at the upper integration limit in eqn. (7). Several attempts to get [HF]₀ values of higher accuracy have been made. All our efforts were hampered by the fact that UF₄ precipitated and that the redox-electrode did not function well in solutions where the total concentrations of the central ions were less than 10 mM.

When the results of this investigation were available a new study of uranium(IV) fluoride complexes using a fluoride membrane electrode was made in this laboratory.¹⁵ This paper of Norén will include a discussion of the merits of the two methods for studying U(IV) fluoride complexes and will also include a discussion of fluoride complexes of other four-valent metal ions.

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