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The Fluoride and Sulphate Complexes of Neptunium(IV)

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The complexes formed by neptunium(IV) with sulphate and fluoride ions have been investigated by means of cation exchange, and, in the case of fluoride, also potentiometric measurements (using the Fe^{3+}/Fe^{2+} electrode). All measurements have been performed in a 4 M perchloric acid medium, and at a temperature of 20°C. For the sulphate system, the stability constants of the first two complexes have been determined; further complexes are not formed within the range of ligand concentrations covered by the cation exchange method. Also for the fluoride system, only the constants of the first two complexes can be determined by this method, but an extension of the range is achieved by the emf measurements. These yield reliable values for the constants of the second and third complexes, and an approximate constant for the fourth complex as well. The constants are presented in Table 4. For the second constant, the two methods employed give concordant results.

As expected for a four-valent ion, both the sulphate and, especially, the fluoride complexes are very strong. A peculiar feature of the fluoride system is that the second complex has an unusually narrow range of existence.

This study of the complexes formed by neptunium(IV) with sulphate and fluoride ions is part of a general investigation of the complex formation between tetravalent cations and ligands of various donating properties. Of the systems treated here, the sulphate complexes have previously been studied by Sullivan and Hindman [1] who used a solvent extraction method, but as yet the fluoride complexes do not seem to have been investigated.

For both systems, the cation exchange method developed by Fronæus [2,3] has been successfully used for the elucidation of the first two steps of the complex formation. In the case of sulphate, higher complexes cannot be studied because the sorption has fallen virtually to zero before even the third complex becomes prominent. As to fluoride, the distribution function becomes anomalous with increasing ligand concentration, presumably because the precipitation of the very slightly soluble NpF_4 is promoted by the contact of the solution with the ion exchanger.

The fluoride system has also been investigated by emf measurements according to a modified version of the "ferric" method of Brosset and Orring.[4]

The principle of this method is that the acceptor of actual interest, in the present case Np^{4+}, is allowed to compete with Fe^{3+} for the fluoride ions. If further Fe^{2+} is added to the solutions, the result of this competition can be found from the Fe^{3+}/Fe^{2+} redox potential, which in fact provides a direct measurement of the free ligand concentration.

Because the first fluoride complex of Np^{4+} turns out to be much stronger than that of Fe^{3+}, its formation will not affect the Fe^{3+}/Fe^{2+} potential, and hence cannot be followed by this method. However, at the formation of NpF_2^{2+}, the competition from FeF^{2+} is already sufficient to allow a reliable measurement, and also the next step, leading to NpF_3^{+}, can be easily followed. The emf measurements thus provide not only a check of at least a part of the results found by the cation exchange method, but also an extension of the range accessible to measurement. The upper limit to the measurements is set by the point where NpF_4 precipitates, which occurs when the ligand number, $\bar{n}_M$, of the neptunium(IV) fluoride system has reached a value of $\simeq 2.5$.

In order to reduce the number of equilibria to be taken into account, all measurements have been performed in 4 M perchloric acid, where the hydrolysis of neptunium(IV) is virtually suppressed.*[1,5] Also the hydrolysis of Fe^{3+} is negligible under these conditions. The high acidity furthermore stabilizes the tetravalent state considerably relative to the pentavalent one (existing in this medium as NpO_2^{+}), thus minimizing the complications due to the unwanted oxidation of neptunium(IV) during the measurements (*cf.* p. 334).

The temperature has been maintained throughout at 20 $\pm$ 0.2°C and 20 $\pm$ 1°C for the ion exchange and emf measurements respectively.

DERIVATION OF STABILITY AND DISTRIBUTION CONSTANTS FROM THE CATION EXCHANGE MEASUREMENTS

For investigations of the complex formation of tetravalent cations, the ion exchange method was first used by Grenthe and Norén,[6] in a study of the weak complexes formed in nitrate and chloride solutions of plutonium(IV). For strong complexes, the method becomes rather more complicated to apply, on account of the necessity to calculate the free ligand concentration by some separate procedure. An investigation involving strong complexes of a four-valent cation has been performed before, however, *viz.* for the zirconium fluoride system by Ahrland *et al.*[7]

In the papers mentioned,[6,7] the derivation of the stability and distribution constants has been fully described. In the following, the method will therefore only be outlined as far as is necessary for the introduction of some modifications and amendments which have proved desirable in the case of the systems now treated. Unless otherwise stated, the notation will be the same as before.

* It should be noted that the derivative $-\mathrm{d}\log E'/\mathrm{d}\log[H^+]$ of Ref. 1 is *not* $= \bar{n}$, as stated there (eqn. 7), but rather the number of H^+ set free on formation of the TTA-complex ($= 4-i$). For $\bar{n}$, the average number of OH^- bound per neptunium(IV), the correct expression is $\bar{n}=4 + \mathrm{d}\log E'/\mathrm{d}\log[H^+]$. (The conclusions drawn in Ref. 1 are in accordance with this formula).

The complex formation is presumed to proceed according to the general formula

$$M^{4+} + n\,HA^{1-z} \rightleftharpoons MA_n^{4-nz} + n\,H^+ \qquad (1)$$

where M = Np; HA = HSO_4^- or HF, and z = the number of negative charges on the anion A (2 for SO_4^{2-}, 1 for F^-). The cation exchange will then proceed according to

$$MA_n^{4-nz} + (4-nz)\,H^+(R) \rightleftharpoons MA_n^{4-nz}(R) + (4-nz)\,H^+ \qquad (2)$$

where R denotes the resin phase. If it is further assumed that only cations are sorbed which must be very nearly true under the present conditions, then $0 \leq n < 4/z$.

By application of the law of mass action on these equilibria, the following expression can be deduced for the distribution φ of M between the resin and the solution:

$$\varphi = \frac{C_{MR}}{C_M} = \frac{l_0 + \sum_{n=1}^{3} l_n \beta_n^* h^{-n} [HA]^n}{1 + \sum_{n=1}^{N} \beta_n^* h^{-n} [HA]^n} \qquad (3)$$

It should be noted that the upper limit of 3 for the summation in the numerator of eqn. (3) applies to the fluoride system ($z = 1$); in the case of sulphate ($z = 2$, implying the formation of only one cationic complex), only the first term of this sum can have a value $\neq 0$. Provided the ion exchanger works monofunctionally, and that the activity constants do not change, the distribution coefficients l_0 and l_n for the central ion M^{4+} and the complexes MA_n^{4-nz}, respectively, are constants if h and h_R are both kept constant. The latter conditions have been fulfilled in these measurements where h = 4 M and h_R = the total sorption capacity of the resin, as the load C_{MR} has always been kept very low in comparison with the total capacity. It turns out, however, that the ion exchanger does not behave quite monofunctionally when sorbing neptunium(IV) species. In order that l_0 and l_n be constants in spite of this, C_{MR} must not only be low, but have a constant value for all values of φ introduced in (3). This is achieved by an interpolation procedure, *cf.* Fronæus.[2,3,8] The Dowex resin used in later investigations, including this one, is however much more monofunctional than the Amberlite originally used by Fronæus.[3] The variation of φ with the load C_{MR} is in fact so slight for Dowex that the interpolation becomes quite safe and easy.

For the sake of simplicity, special symbols are introduced for the products of constants present in eqn. (3), thus

$$l_0^{-1} l_n \beta_n^* h^{-n} = l_n^* \qquad (4) \qquad\qquad \beta_n^* h^{-n} = \beta_{nH} \qquad (5)$$

Eqn. (3) can then be written as

$$\varphi = \frac{l_0 (1 + \sum_{n=1}^{3} l_n^* [HA]^n)}{1 + \sum_{n=1}^{N} \beta_{nH} [HA]^n} \qquad (6)$$

where l_0 (= lim φ when [HA] → 0) can be found either by direct measurement in ligand free solutions or by extrapolation, as $\varphi(0)$.

For the evaluation of the constants, a function φ_1 is formed from φ:

$$\varphi_1 = \left(\frac{l_0}{\varphi} - 1\right)\frac{1}{[\mathrm{HA}]} = \frac{\beta_{1\mathrm{H}} - l_1^* - l_2^*[\mathrm{HA}] - l_3^*[\mathrm{HA}]^2 + \beta_{2\mathrm{H}}[\mathrm{HA}] + \sum_{n=3}^{N} \beta_{n\mathrm{H}}[\mathrm{HA}]^{n-1}}{1 + l_1^*[\mathrm{HA}] + l_2^*[\mathrm{HA}]^2 + l_3^*[\mathrm{HA}]^3} \quad (7)$$

As [HA] descreases, φ_1(HA) approaches a straight line, with an intercept

$$\lim_{[\mathrm{HA}]\to 0} \varphi_1 = \varphi_1{}^0 = \beta_{1\mathrm{H}} - l_1^* \quad (8)$$

and a slope

$$\lim_{[\mathrm{HA}]\to 0}\left(\frac{\mathrm{d}\varphi_1}{\mathrm{d}[\mathrm{HA}]}\right) = (\varphi_1')^0 = \beta_{2\mathrm{H}} - l_2^* - l_1^*(\beta_{1\mathrm{H}} - l_1^*) \quad (9)$$

For most systems with anionic ligands investigated so far, the distribution coefficient of even the first complex, l_1, is small in comparison with that of the free central ion, l_0, and the magnitude of l_n moreover falls rapidly with n, *i.e.* with decreasing charge. For a given system, in connexion with a given ion exchanger, this pattern must admittedly become less marked with increasing h, as (*cf.* Ref. 7, p. 413):

$$l_n = k_n (h_\mathrm{R}/h)^{4-nz} \quad (10)$$

Experience shows, however,[6,7] that even at the fairly high acidity used in the present measurements (4 M), l_0 still seems, for most systems, to be large relative to l_1, etc. Consequently, l_1^*, l_2^* and l_3^* will be small in comparison with $\beta_{1\mathrm{H}}$, $\beta_{2\mathrm{H}}$ and $\beta_{3\mathrm{H}}$, respectively, (*cf.* eqns. (4) and (5)) and the course of φ_1 will not deviate fundamentally from that of a polynomial $X_{1\mathrm{H}} = \beta_{1\mathrm{H}} + \sum_{n=2}^{N} \beta_{n\mathrm{H}}[\mathrm{HA}]^{n-1}$, *i.e.* the type of function used for the evaluation of potentiometric measurements. Under such conditions, the intercept and slope of φ_1 as [HA] → 0 are easily determined graphically. It is more difficult to separate the constants constituting the differences thus obtained (eqns. (8) and (9)).

In the past, this has most often been done *via* the functions f and g, allowing the computation of $\beta_{1\mathrm{H}}$ and $\beta_{2\mathrm{H}}$, respectively. These functions are, however, fairly complicated which makes it difficult to get a clear view of the significance of the results. A need has therefore been felt for a more straightforward procedure to evaluate the constants involved.

To meet this need, Fronæus [9] has recently developed a method which makes use of the difference between the function φ_1 and the straight line which φ_1 approaches as [HA] → 0. A very simple expression can be derived for this difference, provided that eqn. (7) is sensibly approximated. This is done by utilizing the experience mentioned above that l_n decreases very rapidly with n. Already l_2^*, and even more l_3^*, of eqn. (7) are therefore presumably negligible.

As a consequence, φ will rapidly fall to a very low value, impossible to determine with the necessary precision, once the complex formation has proceeded appreciably beyond the first complex. This means that at most the first three complexes are likely to exist within that range of ligand concentrations where reliable values of φ can be determined. It should therefore be possible to describe $\varphi_1([HA])$ only by the four parameters β_{1H}, β_{2H}, β_{3H} and l_1^*. Accordingly, eqn. (7) can be written:

$$\varphi_1 = \beta_{1H} - l_1^* + [\beta_{2H} - l_1^*(\beta_{1H} - l_1^*)][HA] + \frac{K[HA]^2}{1 + l_1^*[HA]} \qquad (11)$$

where $K = \beta_{3H} - l_1^*[\beta_{2H} - l_1^*(\beta_{1H} - l_1^*)]$ (12)

The difference Δ between φ_1 and the straight line having the intercept φ_1^0 and slope $(\varphi_1')^0$ is obtained by combining eqns. (8), (9) and (11):

$$\Delta = \frac{K[HA]^2}{1 + l_1^*[HA]} \qquad (13)$$

When $[HA]^2/\Delta$ is plotted against [HA], a straight line should be obtained, with an intercept $= 1/K$ and a slope $= l_1^*/K$. Hence l_1^* is obtained, and then β_{1H}, β_{2H}, and β_{3H} from eqns. (8), (9) (with $l_2^* = 0$) and (12), respectively.

Like the corresponding systems [7] of zirconium(IV), however, neither the sulphate nor the fluoride complexes of neptunium(IV) follow the sorption pattern outlined above. For both central ions, φ_1 is found to be a straight line with positive slope in the case of sulphate, and a decreasing function, concave upwards, in the case of fluoride. In no case does the course of φ_1 thus approach that of a polynomial X_{1H} for a system of three complexes. The method of calculation just outlined will obviously fail completely for the sulphate systems where $\Delta = 0$. Also for the fluoride systems difficulties arise, owing to the strong curvature of φ_1 in the vicinity of the axis which renders the determination of expecially $(\varphi_1')^0$ fairly uncertain. In the following, the possibilities to evaluate constants from functions φ_1 of these unusual shapes will be discussed separately for each type.

φ_1 is a straight line of positive slope (sulphate systems of four-valent ions). This means that $\Delta = 0$; *i.e.* $K = 0$. As is evident from eqn. (12), this will occur if

$$\beta_{3H}/l_1^* = \beta_{2H} - l_1^*(\beta_{1H} - l_1^*) \qquad (14)$$

i.e. if the ratio β_{3H}/l_1^* has a value which is $= (\varphi_1')^0$, within reasonable experimental errors. As all sets β_{3H}, l_1^* satisfying eqn. (14) fit equally well with the experimentally determined function $\varphi([HA])$, no fixed value of l_1^* can be found. In principle, it is thus impossible to find β_{1H} and β_{2H} from eqns. (8) and (9).

Leaning upon the chemical experience, however, we may argue, that most probably $l_1^* << \beta_{1H}$ for such systems where the co-ordination of the first ligand means a decrease of the cationic charge by two units. This implies that $\varphi_1^0 \simeq \beta_{1H}$ (eqn. (8)) and, if l_1^* is sufficiently small, we might even put the slope $(\varphi_1')^0 = \beta_{2H}$, as is evident from eqn. (9). In so doing we have in fact adopted the alternative $\beta_{3H} = l_1^* = 0$ for eqn. (14), as has already been done in the case of the analogous Zr(IV) system.[7]

φ_1 decreases in the beginning (fluoride systems of four-valent ions). As has been pointed out before, such a course generally means that the constants l_n^* are large in comparison with the constants $\beta_{n\mathrm{H}}$. More especially, φ_1 starts as a decreasing function if

$$l_1^*(\beta_{1\mathrm{H}}-l_1^*)>\beta_{2\mathrm{H}}-l_2^* \tag{15}$$

or, approximately,

$$l_1^* > \beta_{2\mathrm{H}}/\beta_{1\mathrm{H}} \tag{16}$$

or, if the consecutive constants K_n^* are introduced

$$l_1/l_0 > K_2^*/K_1^* \tag{17}$$

An initial decrease of φ_1 thus occurs when the distribution coefficients l_n decrease at a slower rate than do the consecutive formation constants K_n^*. This is likely to happen just in the case of fluoride system of four-valent ions, as has already been discussed (Ref. 7, p. 419).

With increasing values of [HA], the quadratic term of eqn. (11) will gain importance, and as K is necessarily > 0 for an initially decreasing function (as is evident by imposing the condition (15) on eqn. (12)), the decrease of φ_1 should rapidly become less steep, as is in fact observed. As [HA] is further increased, φ_1 should even pass through a minimum, though this point has not been reached within the workable range of [HA].

The rapid flattening out of the φ_1 curve makes it difficult to determine the slope $(\varphi_1')^0$, as has already been observed. Consequently, the difference Δ of eqn. (13) will not be very accurately known as a function of [HA], and the constants l_1^* and $\beta_{2\mathrm{H}}$, found from eqns. (13) and (9), will be of limited accuracy. As the intercept φ_1 is easier to determine, $\beta_{1\mathrm{H}}$ will be found with fair accuracy, provided l_1^* is not too large. For the present system, no value of $\beta_{3\mathrm{H}} \neq 0$ can be calculated from the difference formulated in eqn. (12).

One might then assume that the formation of the third complex is negligible within the used range of [HA]. If so, the function φ_1 can be further simplified so as to contain only the three parameters $\beta_{1\mathrm{H}}$, $\beta_{2\mathrm{H}}$ and l_1^*. Eqn. (7) may then be written:

$$\left(\frac{l_0}{\varphi}-1\right)\frac{1}{[\mathrm{HA}]} = \frac{\beta_{1\mathrm{H}}-l_1^*+\beta_{2\mathrm{H}}[\mathrm{HA}]}{1+l_1^*[\mathrm{HA}]} \tag{18}$$

Recalling that $l_1^*\, l_0 = l_1\beta_{1\mathrm{H}}$ (eqns. (4) and (5)), we may rearrange this expression as follows:

$$\varphi_2 = \frac{l_0-\varphi}{[\mathrm{HA}]} - \beta_{1\mathrm{H}}\varphi = -l_1\beta_{1\mathrm{H}} + \beta_{2\mathrm{H}}\varphi[\mathrm{HA}] \tag{19}$$

If, as a first approximation, we put $\beta_{1\mathrm{H}} \simeq \varphi_1{}^0$, φ_2 can be computed from experimental data. A plot of this quantity against $\varphi[\mathrm{HA}]$ should then yield a straight line with a slope $= \beta_{2\mathrm{H}}$ and an intercept $= -l_1\beta_{1\mathrm{H}}$. The provisional value of l_1^* thus found makes a better approximation of $\beta_{1\mathrm{H}}$ possible, which in turn will yield better values of l_1 (l_1^*) and $\beta_{2\mathrm{H}}$ when introduced in eqn. (19).

In the previous deductions it has been tacitly assumed that the free ligand concentration [HA] is known for all solutions whose values of φ are experimentally determined. The values of [HA] are most easily deduced if C_{M} can be chosen so low in comparison with the total concentration of ligand, C_{HA},

that [HA] $\simeq C_{HA}$. As distribution measurements are still possible at very low values of C_M, this can as a rule be arranged, as *e.g.* for the plutonium(IV) systems investigated by Grenthe and Norén[6] and the neptunium(IV) sulphate investigated here. When very strong complexes are formed, however, as is the case for the fluoride system, the initial values of C_{HA} have to be chosen so low, in order to cover also the very beginning of the complex formation, that a considerable part of C_{HA} will be consumed even for the lowest values of C_M which can possibly be used. In a previous investigation of such a strong system,[7] the function φ([HA]) has been found by extrapolating a family of curves $\varphi(C_{HA})$ to $C_M = 0$. This procedure presupposes, however, that the ion exchanger behaves monofunctionally in relation to the sorbed ions. As has already been stated (p. 330), this condition is not fulfilled as far as species of neptunium(IV) are concerned, and another method, involving only calculations at a fixed load C_{MR}, must therefore be used in order to find φ([HA]). To this end a curve $\varphi(C_{HA})$ for a suitably chosen load C_{MR} is first constructed (*cf.* p. 335). From this curve, provisional constants β_{nH} are calculated *via* the function φ_1, as described above, by use of the approximation [HA] $\simeq C_{HA}$. From the constants thus found, the part of C_{HA} bound in complexes can be calculated and hence a better value of [HA]. The function φ([HA]) thus obtained will give better values of the constants β_{nH} *etc.*, and by reiterating the procedure, we will finally arrive at the true values of the constants.

ION EXCHANGE MEASUREMENTS, EXPERIMENTAL

Chemicals. The nuclide ^{237}Np (α; $t_{½} = 2.2 \times 10^6$ years) was obtained from A.E.R.E., Harwell. A stock solution of neptunium(IV) in 4 M perchloric acid was prepared as follows. Perchloric acid was added to the original solution which was evaporated to dryness. The residue, containing the neptunium as five- and/or six-valent, was dissolved in 4 M perchloric acid and then reduced using hydrogen, with platinum black as a catalyst.[10] The reduction went at least partly to neptunium(III) which was, however, rapidly reoxidized to the IV state by standing in air. Further oxidation under these conditions is slow; we have found that stock solutions of neptunium(IV) in 4 M perchloric acid, of a $C_M \leq 20$ mM, are oxidized by < 0.5 % per week when kept in air. In the actual measurements, no solutions were used which contained < 99.5 % neptunium(IV).

The total concentration of neptunium was determined by α-measurement in known geometry, as described below. To find the fraction present as neptunium(IV), the aqueous solution was made to contain 0.5 M acid and then extracted by a 0.5 M solution of thenoyltrifluoroacetone (TTA) in benzene. Under these conditions, the benzene phase will contain virtually all neptunium(IV), while the V (and III) states are not extracted at all.[11,12] By measuring the activity of the aqueous phase after the extraction, a good estimate of the distribution between various redox states will thus be obtained.

The cation exchanger was Dowex 50W−X8, 50−100 mesh, completely converted into the hydrogen form by repeated shaking with 6 M hydrochloric acid. After thorough washing, it was dried in air. The final product was stored in such a way that its water content was kept constant.

The other chemicals were of analytical grade and used without further purification.

Procedure. The distribution φ has been determined by measuring the α-activity of the solution before and after equilibration with the resin, *cf.* Refs. 6, 7. Equilibrium was brought about, with ample margin, by shaking for 15 h. In order to cover the widest possible range of φ, the ratio v/m was varied between 88.3 and 5.3 ml/g resin, the low ratios being used at high ligand concentrations where φ is very low and consequently much resin has to be added if a measurable decrease of the activity should occur. Only for the lowest values of v/m used did the swelling factor δ deviate noticeably from unity,

being 0.98 at 5.3 and 0.99 at 10.6 ml/g. For the α-counting, dry and very thin samples were prepared and measured in a ZnS scintillation counter combining a very favourable geometry (31 %) with a low background (3 cpm). The instrument (constructed by AB Atomenergi) thus allows the convenient registration of even fairly low activities.

In such experiments where most of the neptunium(IV) is sorbed on the resin, even quite a small contamination of neptunium(V) has to be corrected for, as this redox state is not sorbed at all from solutions of the high acidity used here. For most solutions, this correction is known with sufficient accuracy from the neptunium(V) content of the stock solution, but if the distribution is very much in favour of the resin, the actual equilibrium solution has to be analyzed for the various redox states. With the precautions taken here in order to limit the amount of neptunium(V), the correction of φ never exceeded 15 %; in most cases it was < 5 %.

ION EXCHANGE MEASUREMENTS, RESULTS

The sulphate system. The distribution function φ([HA]) has been determined for various concentrations of neptunium(IV), Fig. 1. A slight variation of φ

Table 1. Neptunium(IV) sulphate system. Functions for the calculation of the constants β_{1H} and β_{2H} from ion exchange measurements. $C_{MR} = 4.8 \times 10^{-6}$ mole g^{-1}, $h = 4$ M.

$C_{HA} = [HA]$ mM	$\varphi \times 10^3$ l g^{-1}	φ_1 M^{-1}	$C_{HA} = [HA]$ mM	$\varphi \times 10^3$ l g^{-1}	φ_1 M^{-1}
0	810	*126*	29.4	142	160
0.98	752		49.0	82	181
1.96	648	127	73.5	48.7	212
2.94	577	137	98.0	34.5	229
4.90	495	130	147	18.4	292
6.86	421	135	196	12.1	336
9.80	346	127	294	5.8	473
14.70	252	151	490	2.5	660
19.6	213	143	980	0.5	

with C_M is found for low values of [HA], indicating that the ion exchanger does not behave quite monofunctionally. By interpolation, φ([HA]) is obtained for the constant load $C_{MR} = 4.8 \times 10^{-6}$ moles/g, Table 1, and more especially the value of $\varphi(0) = l_0 = 0.81 \pm 0.03$ l/g. Hence the function φ_1 has been calculated which turns out to be a straight line over the entire range of [HA] investigated, Fig. 2. It is therefore not possible to separate all the constants of eqn. (11). The only way out is to assume that l_1^* is negligible which seems fairly reasonable, on the other hand. From the intercept and slope of the line $\beta_{1H} = 126 \pm 7$ M^{-1} and $\beta_{2H} = (1.13 \pm 0.06) \times 10^3$ M^{-2} are then read, with estimated maximum errors indicated. From the values of l_0, β_{1H}, and β_{2H} thus found, a function φ has been calculated which fits very well to the experimental points, Fig. 1.

By means of the high-speed computer SMIL, values of the constants mentioned have also been calculated directly from the function φ on the same assumption that $l_1^* = 0$, *i.e.* that eqn. (6) can be written

$$\varphi = l_0/(1 + \beta_{1H}[HA] + \beta_{2H}[HA]^2) \qquad (20)$$

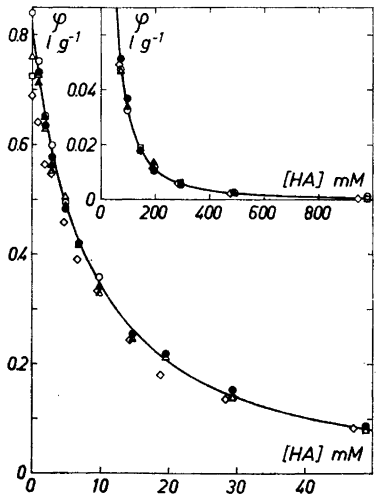

Fig. 1. The distribution function φ([HA]) between ion exchanger and solution for the sulphate system. The signs refer to the following initial concentrations (in M) of neptunium(IV): 6.3×10^{-5} ○ and ●; 10.9×10^{-5}, △ and ▲; 16.7×10^{-5}, □ and ■; 20.0×10^{-5}, ◇. The curve has been calculated from the found constants.

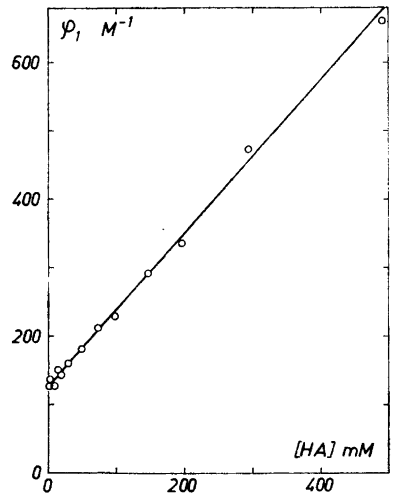

Fig. 2. φ_1 is a linear function of [HA] for the sulphate system.

The following set of constants has been found: $l_0 = 0.82 \pm 0.02$ l g^{-1}, $\beta_{1H} = 127 \pm 4$ M^{-1} and $\beta_{2H} = (1.17 \pm 0.05) \times 10^3$ M^{-2}. In this case, the limits of error give the standard deviations. Evidently both methods of calculation give identical results within the limits of the experimental errors.

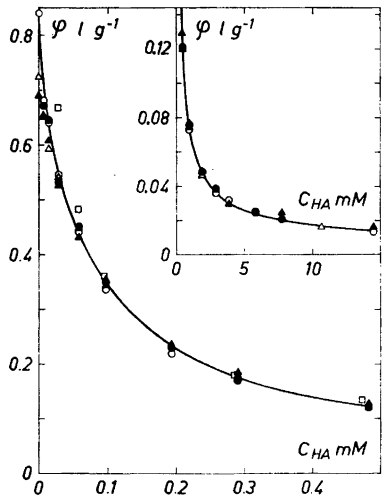

Fig. 3. The distribution function $\varphi(C_{HA})$ between ion exchanger and solution for the fluoride system. The signs refer to the following initial concentrations (in M) of neptunium(IV): 2.21×10^{-5}, □; 6.3×10^{-5}, ○; 9.3×10^{-5}, ●; 16.7×10^{-5}, △; 18.1×10^{-5}, ▲. The curve gives the function for the constant load $C_{MR} = 4.8 \times 10^{-6}$ moles/g.

The fluoride system. The distribution function has been determined for initial concentrations of neptunium(IV) ranging from 2.21×10^{-5} to 18.1×10^{-5} M, Fig. 3. The spread of the curves depends here both on the polyfunctional sorption and on the formation of extremely strong complexes, though the two factors act in opposite directions and also exert their strongest influence in different parts of the curves. The first factor is most important for the very highest values of φ, while the second one makes itself felt mainly at a somewhat later stage (*cf.* Ref. 7). By interpolation, a function $\varphi(C_{HA})$ is obtained for the same load as before, $C_{MR} = 4.8 \times 10^{-6}$ moles/g. This function

Table 2. Neptunium(IV) fluoride system. Functions for the calculation of the constants β_{1H}, β_{2H}, and l_1^* from ion exchange measurements. $C_{MR} = 4.8 \times 10^{-6}$ mole g^{-1}; $h = 4$ M.

	1st approximation				2nd approximation			
$\varphi \times 10^3$ l g^{-1}	$C_{HA} \times 10^5$ M	$\varphi_1 \times 10^{-3}$ M^{-1}	φ_2 l g^{-1} M^{-1}	$C_{HA}\varphi \times 10^6$ M l g^{-1}	[HA] $\times 10^5$ M	$\varphi_1 \times 10^{-3}$ M^{-1}	φ_2 l g^{-1} M^{-1}	[HA]$\varphi \times 10^6$ M l g^{-1}
810	0	*14.4*	*−450*		0	*15.6*	*−540*	
682	0.73				0.67			
652	1.45	16.7			1.33	18.2		
548	2.90	16.4			2.65	18.0		
449	5.80	13.9			5.30	15.1		
350	9.67	13.6			8.90	14.8		
228	19.3	13.2			17.7	14.4		
177	29.0	12.4			26.6	13.5		
123	48.3	11.6			44.7	12.5		
75.2	96.7	10.1	−330	73	90.2	10.8	−404	68
47.8	193	8.3	−299	92	182	8.8	−357	87
37.5	290	7.1	−278	109	275	7.5	−327	103
30.6	387	6.6	−243	118	367	6.9	−284	112
24.8	580	5.5	−227	144	554	5.7	−260	137
20.5	773	5.0	−196	159	740	5.2	−225	152
16.2	1063	4.61	−160	172	1020	4.80	−182	165
14.5	1450	3.78	−155	210	1400	3.92	−178	203

is introduced in Fig. 3 as a fulldrawn curve, and is also found in Table 2. With [HA] $\simeq C_{HA}$, a provisional function φ_1 is then computed, related to the same load, Table 2 (1st approximation) and Fig. 4 (dashed curve). Its extrapolation to $C_{HA} = 0$ yields the provisional value $\beta_{1H} - l_1^* = 14.4 \times 10^3$ M^{-1}.

The tangent at the point of interception is evidently hard to draw on account of the strong curvature. We have, however, tried with the course shown in Fig. 4, the slope of which gives $\beta_{2H} - l_1^*(\beta_{1H} - l_1^*) = -6.9 \times 10^6$ M^{-2}. On formation of the difference Δ, a straight line is further obtained when C_{HA}^2/Δ is plotted *versus* C_{HA} (dashed curve of Fig. 5), as demanded by eqn. (13). Combining the value of the slope $l_1^*/K = 1.45 \times 10^{-7}$ M^2 with that of the intercept $1/K = 0.23 \times 10^{-9}$ M^3, we obtain $l_1^* = (0.63 \pm 0.07) \times 10^3$ M^{-1}, and hence $\beta_{1H} = (15.0 \pm 0.5) \times 10^3$ M^{-1}, $\beta_{2H} = (2.2 \pm 1.0) \times 10^6$ M^{-2} and, from eqn. (12), $\beta_{3H} = 0$.

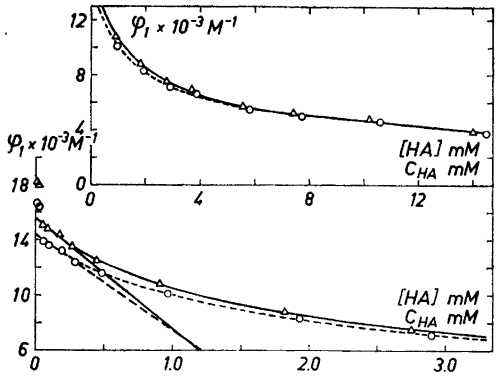

Fig. 4. φ_1 is a decreasing function of C_{HA} (dashed curve) or [HA] (fulldrawn curve) for the fluoride system. The tangents in the points of interception have been drawn.

Considering the very uncertain course of the tangent, we have also formed the function φ_2 (eqn. (19)), especially as the seemingly low value of β_{3H} should warrant its successful application. As before, we first put [HA] $\simeq C_{HA}$ and further, in order not to rely upon any result from the formation of Δ, $\beta_{1H} \simeq \beta_{1H} - l_1^* = \varphi_1^0 = 14.4 \times 10^3\ M^{-1}$. The result, tabulated as φ_2 of the 1st approximation, Table 2, is a straight line, shown dashed in Fig. 6. Its intercept yields $-l_1\beta_{1H} = -450\ l\ g^{-1}\ M^{-1}$, *i.e.* $l_1^* = (0.56 \pm 0.05) \times 10^3\ M^{-1}$ and hence a better value of $\beta_{1H} = (15.0 \pm 0.5) \times 10^3\ M^{-1}$. From the slope, $\beta_{2H} = (1.7 \pm 0.3) \times 10^6\ M^{-2}$ is obtained.

It is thus obvious that the two graphical methods employed for the calculation of l_1^* and β_{2H} give very much the same result. For the subsequent calcula-

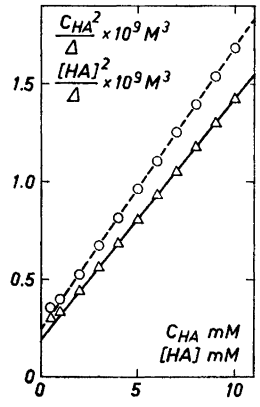

Fig. 5. C_{HA}^2/Δ as a function of C_{HA} (circles and dashed line) and $[HA]^2/\Delta$ as a function of [HA] (triangles and fulldrawn line) for the fluoride system, yielding the constants l_1^* and K of eqn. (13).

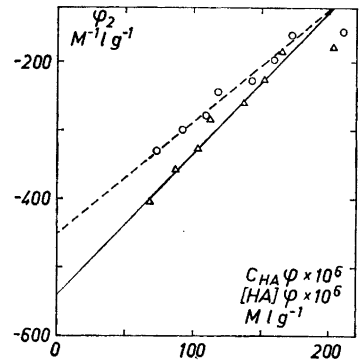

Fig. 6. φ_2 as a function of C_{HA} (1st approximation; circles and dashed line) and φ_2 as a function of [HA] (2nd approximation; triangles and fulldrawn line) for the fluoride system (*cf.* Table 2).

tion of φ_1([HA]), and hence the final constants, the latter set of provisional constants has been preferred. It is applied for the calculation of ligand numbers $\bar{n}$, which are then used for the calculation of [HA] according to

$$[\mathrm{HA}] = C_{\mathrm{HA}} - \bar{n}C_{\mathrm{M}} \qquad (21)$$

The resulting function φ_1 is tabulated as the 2nd approximation in Table 2, and also plotted as the fulldrawn curve of Fig. 4. Its extrapolation yields $\beta_{1\mathrm{H}} - l_1^* = 15.6 \times 10^3\ \mathrm{M}^{-1}$ or, inserting the former value of l_1^*, $\beta_{1\mathrm{H}} = 16.2 \times 10^3\ \mathrm{M}^{-1}$. With the better values of $\beta_{1\mathrm{H}}$ and [HA] thus obtained, the function φ_2 is formed anew, Table 2 and Fig. 6 (fulldrawn curve). The intercept now yields $l_1\beta_{1\mathrm{H}} = 540\ \mathrm{l\ g^{-1}\ M^{-1}}$, *i.e.* $l_1^* = (0.67 \pm 0.05) \times 10^{-3}\ \mathrm{M}^{-1}$, and the slope $\beta_{2\mathrm{H}} = (2.1 \pm 0.3) \times 10^6\ \mathrm{M}^{-2}$. A final value of $\beta_{1\mathrm{H}} = (16.3 \pm 0.5) \times 10^3\ \mathrm{M}^{-1}$ is thus obtained; further reiteration of the procedure does not change the values found.

The straight line course of φ_2 would imply that $\beta_{3\mathrm{H}}$ is indeed negligible, as postulated. If not, φ_2 would turn upwards with increasing [HA], as is easily deduced from eqn. (7). In fact the uppermost point of Fig. 6 is below the line, and this tendency becomes even more pronounced when still higher values of [HA] are employed (not entered in Table 2). This must be due to some reaction not accounted for in the formulas above. Most probably, a precipitation of the slightly soluble NpF_4 occurs, perhaps promoted by the presence of ion-exchanger particles as crystallization nuclei.

Very much the same result is also obtained from the course of the new tangent at the point of interception, Fig. 4, with a slope $(\varphi_1')^0 = -8.1 \times 10^6\ \mathrm{M}^{-2}$. The function $[\mathrm{HA}]^2/\Delta$ *vs* [HA] is a straight line, fulldrawn in Fig. 5, which yields $l_1^*/K = 1.24 \times 10^{-7}\ \mathrm{M}^{-2}$; $1/K = 0.18 \times 10^{-9}\ \mathrm{M}^3$ and hence $l_1^* = (0.69 \pm 0.07) \times 10^3\ \mathrm{M}^{-1}$. Combining with the values φ_1^0 and $(\varphi_1')^0$ we then obtain $\beta_{1\mathrm{H}} = (16.3 \pm 0.5) \times 10^3\ \mathrm{M}^{-1}$, $\beta_{2\mathrm{H}} = (2.7 \pm 1.0) \times 10^6\ \mathrm{M}^{-2}$ and, as for the first computation, $\beta_{3\mathrm{H}} = 0$.

Also for the fluoride system, we have tried to calculate the constants directly from the function φ, by means of SMIL. When all the four constants of importance within the range covered, *i.e.* l_0, l_1^*, $\beta_{1\mathrm{H}}$, and $\beta_{2\mathrm{H}}$, were regarded as unknowns, no useful results were obtained. The reason is certainly that various constants carry very different weight depending upon the range of [HA], and a proper weighting is not easy to introduce. If the experimentally determined value of l_0 is inserted, however, more sensible figures appear for the remaining constants. A still better result is found, however, by restricting the calculations to the higher values of [HA] (> 0.09 mM) where $\beta_{2\mathrm{H}}$ and l_1^* are known to be important, and inserting for $\beta_{1\mathrm{H}}$ a few fixed values, suitably chosen with the aid of the previous graphical treatment. The best fit with the experimental function is then found with the following set of constants (with the standard deviations indicated): $\beta_{1\mathrm{H}} = 16.5 \times 10^3\ \mathrm{M}^{-1}$, $\beta_{2\mathrm{H}} = (2.3 \pm 0.2) \times 10^6\ \mathrm{M}^{-2}$ and $l_1^* = (0.71 \pm 0.03) \times 10^3\ \mathrm{M}^{-1}$, *i.e.* very much, the same values as have been found graphically.

As a final estimate of the constants determined by the ion exchange measurements for the fluoride system, the following values are preferred: $\beta_{1\mathrm{H}} = (16.4 \pm 0.5) \times 10^3\ \mathrm{M}^{-1}$, $\beta_{2\mathrm{H}} = (2.3 \pm 0.4) \times 10^6\ \mathrm{M}^{-2}$ and $l_1^* = (0.69 \pm 0.05) \times 10^3\ \mathrm{M}^{-1}$, while $\beta_{3\mathrm{H}}$ is too small to be determined in this way ($< 0.5 \times 10^9\ \mathrm{M}^{-3}$).

From l_1*, a value of $l_1 = 0.034$ l/g is calculated for the first complex NpF^{3+}, to be compared with $l_0 = 0.81$ l/g for Np^{4+}. The coordination of even a single fluoride ion thus means that the affinity to the ion exchanger falls very sharply. It must be concluded that other factors are more important for the sorption than is the overall charge. Though l_1 is comparatively small, the condition that $l_1/l_0 > K_2^*/K_1^*$ is nevertheless fulfilled, as demanded by eqn. (17). The initial decrease of φ_1 is therefore due to low stability of the second complex relative to the first one, rather than to any strong sorption of the latter complex on the ion exchanger.

DERIVATION OF STABILITY CONSTANTS FROM THE EMF MEASUREMENTS

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

−Ag, AgCl	0.1 M HCl 3.9 M $HClO_4$	4 M $HClO_4$	C_{III} mM Fe(III) C_{II} mM Fe(II) C_M mM Np(IV) C_{HA} mM HF $h = 4$ M; $I \simeq 4$ M	Pt +

The concentrations of iron and neptunium have been kept so low, that the ionic strength of the right halfcell is virtually determined by the 4 M perchloric acid present, the dissociation of HF being negligible. The emf of this cell can be written:

$$E = E^0 + RTF^{-1} \ln [Fe^{3+}] [Fe^{2+}]^{-1} \quad (22)$$

where E^0 denotes the sum of all constant potentials within the cell. As Fe^{2+} does not form fluoride complexes in appreciable amounts under the present conditions,[4] we can put $[Fe^{2+}] = C_{II}$. For Fe(III), the total concentration can be written

$$C_{III} = [Fe^{3+}](1 + \sum_{n=1}^{N'} \beta_{nH}'[HA]^n) \quad (23)$$

where

$$\beta_{nH}' = [FeA_n^{3-n}][Fe^{3+}]^{-1}[HA]^{-n} \quad (24)$$

Hence

$$E = E^0 + RTF^{-1} \ln C_{III}C_{II}^{-1}(1 + \sum_{n=1}^{N'} \beta_{nH}'[HA]^n)^{-1} \quad (25)$$

or, for the initial solution, before any fluoride has been added:

$$E' = E^0 + RTF^{-1} \ln C_{III}C_{II}^{-1} \quad (26)$$

Forming the difference $E' - E = E_A$ we obtain:

$$E_A = RTF^{-1} \ln(1 + \sum_{n=1}^{N'} \beta_{nH}'[HA]^n) \quad (27)$$

i.e. E_A is a function exclusively of [HA], and does not depend upon the concentrations of the iron species. It has then been presumed that the ratio $C_{III}\ C_{II}^{-1}$ does not change during the experiment which implies that no redox reaction must take place between the iron species and neptunium(IV). To judge from the redox potentials of the couples involved, no such reactions are to be feared which is also confirmed by the stability and reproducibility of the emf's actually measured. It can therefore be safely assumed that a certain value of E_A always indicates one and the same value of [HA].

The value of [HA] corresponding to a measured value of E_A is determined experimentally by measuring the emf of cells containing no neptunium, *i.e.* with $C_M = 0$. In principle, E_A should then be measured as a function of C_{HA} for some values of C_{III}, and the resulting family of curves extrapolated to $C_{III} = 0$, thereby yielding $E_A([HA])$. As Fe(II) does not form any fluoride complexes, the value chosen for C_{II} is fairly unimportant.[4] Due to the extremely good function of the Fe^{3+}/Fe^{2+} electrode, however, it is possible in practice to vary C_{III} within such low limits that $[HA] = C_{HA}$ for all series measured. Thus no extrapolation is in fact necessary. The variation of C_{III} only serves to confirm this and to check that the electrodes really work properly at those low concentrations of the redox system which are employed here. For convenience, the ratio C_{III}/C_{II} has been kept at the same value in all series, *viz.* 3/7.

Once the connexion $E_A([HA])$ has been established, it is possible to find, by measuring the emf of cells containing neptunium(IV), the ligand number $\bar{n}$ of the neptunium system according to

$$\bar{n} = (C_{HA} - [HA])/C_M \qquad (28)$$

It is then presumed that the concentration of the iron system is still kept so low that it does not affect the ligand concentration. The concentration of neptunium, C_M, has on the other hand to be fairly high if the complex formation should result in a well measurable difference $C_{HA} - [HA]$, and hence in a reliable value of $\bar{n}$. In measurements employing competing central ions, it is thus advantageous to keep the concentration of the indicator ions as low as is compatible with a good electrode function, but to keep the concentration of the other ion on a high level, in order to make sure that its influence is felt.

In practice, $E_A(C_{HA})$ is determined for various values of C_M and the resulting family of curves plotted together with the $E_A([HA])$ curve determined before. The curves are cut at suitable values of E_A, each corresponding to a

Table 3. Neptunium(IV) fluoride system. Corresponding values of $\bar{n}$ and [HA] found from the emf measurements and the functions X_H/X_{H0}, X_I, X_{II}, and X_{III} hence calculated.

E_A mV	[HA] mM	$\bar{n}$	a*	X_H/X_{H0}	$X_I \times 10^{-3}$ M^{-1}	$X_{II} \times 10^{-5}$ M^{-2}	$X_{III} \times 10^{-6}$ M^{-3}
	0				*0.75*	*1.06*	*5.0*
1	1.1	1.03	0	1.00	0.87	—	—
2	2.2	1.21	0.817	2.26	1.01	1.18	—
3	3.2	1.37	1.306	3.69	1.14	1.22	5.0
4	4.5	1.47	1.797	6.03	1.33	1.29	5.1
5	5.8	1.57	2.186	8.90	1.53	1.34	4.8
6	7.0	1.69	2.493	12.1	1.72	1.39	4.7
7	8.3	1.79	2.791	16.3	1.96	1.46	4.8
8	9.6	1.87	3.059	21.3	2.22	1.53	4.9
9	10.9	1.96	3.303	27.2	2.49	1.60	5.0
10	12.2	2.02	3.528	34.1	2.79	1.67	5.0
11	13.5	2.13	3.739	42.1	3.11	1.75	5.1
12	14.9	2.36	3.960	52.5	3.52	1.86	5.4
14	17.8	2.58	4.401	81.5	4.58	2.15	6.1
16	20.8	2.78	4.821	124.1	5.97	2.51	7.0

$$* \; a = \int_{[HA]_0}^{[HA]_j} \frac{\bar{n}}{[HA]} \, d[HA]$$

certain value of [HA] which is read on the lowest curve. The values of C_{HA} are read for each C_M, and hence $\bar{n}$ is obtained by eqn. (28). For the present system, the values of $\bar{n}$ found for a certain [HA] turn out to be independent of C_M, which means that only mononuclear complexes are formed.

On account of the extremely high stability of the complex NpF^{3+}, no measurable difference E_A is found before the formation of this complex is practically complete, as has already been mentioned (p. 329). As a consequence, the complex formation function $\bar{n}$([HA]) determined as described above starts at a value of $\bar{n} > 1$ (Table 3). Under such circumstances, there is no basis for a determination of the first stability constant; from the point of view of calculation it is found impossible to determine lim $\bar{n}$/[HA] when [HA] $\rightarrow$ 0, which would otherwise yield β_{1H}. However, the constants of the following steps can be found as follows.

The function $\bar{n}$/[HA] can be written (*cf.* Refs. 13, 14):

$$\bar{n}/[HA] = \frac{dX_H}{d[HA]} X_H^{-1} \tag{29}$$

where

$$X_H = 1 + \sum_{n=1}^{N} \beta_{nH}[HA]^n \tag{30}$$

On integration, eqn. (29) yields:

$$\ln \frac{X_H}{X_{H0}} = \int_{[HA]_0}^{[HA]_j} \frac{\bar{n}}{[HA]} d[HA] \tag{31}$$

The evaluation of this integral will give $X_H X_{H0}^{-1}$ as a function of [HA]. Here X_{H0} is a constant, *viz.* the value of X_H for [HA] = $[HA]_0$, the lower limit of integration. This limit is chosen at the lower end of that range of [HA] where measurable values of E_A are found. The integral is preferably evaluated graphically. From eqn. (30):

$$X_H X_{H0}^{-1} = (1 + \sum_{n=1}^{N} \beta_{nH}[HA]^n) X_{H0}^{-1} \tag{32}$$

Thus, if the experimentally determinable function $X_H X_{H0}^{-1}$ could be extrapolated to [HA] = 0, X_{H0}^{-1} would be found as the intercept. It would then be possible to find X_H, and hence the stability constants according to established methods. Because of the extreme strength of NpF^{3+}, however, only a very rough value of $X_{H0}^{-1} = 0.05 \pm 0.05$ can be obtained in this way, yielding no useful value of X_H.

On the other hand, the almost complete absence of Np^{4+} warrants us to treat the term of eqn. (32) originating from this species either as a negligible quantity, or, at least, as a small correction. The value of $X_{H0}^{-1} = 0.05$ quoted above would make the correction just perceptible for the very lowest values of [HA] measured. As this value is moreover substantiated by the results of the ion exchange measurements which yield $X_{H0}^{-1} = 0.046$, it has been considered worthwhile to apply it. We thus compute:

$$X_1 = (X_H X_{H0}^{-1} - X_{H0}^{-1})[HA]^{-1} = (\beta_{1H} + \sum_{n=2}^{N} \beta_{nH}[HA]^{n-1}) X_{H0}^{-1} \tag{33}$$

Note that the value of the predominating term $X_H X_{H0}^{-1}$ is of course that directly determined by the emf measurements.

On extrapolation to [HA] = 0, eqn. (33) gives an easily determined intercept = $\beta_{1H}X_{H0}^{-1}$. It is then possible to compute:

$$X_{II} = (X_I - \beta_{1H}X_{H0}^{-1})[HA]^{-1} = (\beta_{2H} + \sum_{n=3}^{N} \beta_{nH}[HA]^{n-2})X_{H0}^{-1} \quad (34)$$

which on extrapolation gives $\beta_{2H}X_{H0}^{-1}$. Further functions can be formed in the same manner, producing $\beta_{3H}X_{H0}^{-1}$ *etc.* From the composite constants thus obtained, the consecutive constants $K_{nH} = \beta_{nH}/\beta_{(n-1)H}$ can immediately be computed, and hence the constants K_n^*, by the identity (*cf.* eqns. (4) and (9) of Ref. 7):

$$K_n^* = hK_{nH} \quad (35)$$

Within that range of [HA] where Np^{4+} virtually does not exist, $\bar{n}$ can be calculated from the constants K_{nH} according to

$$\bar{n} = \frac{1 + 2K_{2H}[HA] + 3K_{2H}K_{3H}[HA]^2}{1 + K_{2H}[HA] + K_{2H}K_{3H}[HA]^2} \quad (36)$$

and the resulting complex formation function compared with the experimentally found $\bar{n}$ ([HA]). For the lowest [HA] used here, however, the presence of Np^{4+} has to be corrected for, in order that a good fit should be achieved. This is done by using the complete formula for $\bar{n}$ given as eqn. (25) of Ref. 7, with the value of β_{1H} taken from the ion exchange measurements.

EMF MEASUREMENTS, EXPERIMENTAL

Chemicals. A solution of iron(II) was prepared by dissolving iron *pro analysi* in a known volume of 4 M perchloric acid. Part of this solution was then oxidized to iron(III) by hydrogen peroxide. By mixing these solutions, a final stock solution of the two oxidation states in 4 M acid was obtained. Its concentration of iron(II) was determined by direct cerimetric titration. The concentration of iron(III) was found as the difference between iron(II) and total iron, as determined cerimetrically after complete reduction of the solution by cadmium. The other chemicals were the same as before.

Procedure. The solutions of the right half-cell written above were prepared by adding small volumes (0.05—0.5 ml) of an acid fluoride solution T to a certain volume (1.95—5 ml) of a solution S placed in the electrode vessel and containing all the other constituents. The solution T was delivered from micro-pipettes with an accuracy better than 0.2 %. In the measurements with neptunium-free solutions, performed in order to obtain the function E_A([HA]), various values of C_{III}', the initial concentration of iron(III), were chosen for the solution S, as indicated in Fig. 7. The main series, with neptunium present, were performed in a glove-box. In these, C_{III}' was always 0.75 mM, while the initial concentration of Np(IV), C_M', was varied between different series (from $\simeq$ 3 to $\simeq$ 15 mM; *cf.* Fig. 7). On addition of T, these concentrations decreased. As to the iron system, this did not matter, as the deduction of eqn. (27) is valid only the ratio C_{III}/C_{II} is not altered during the series. On the other hand, the actual concentration of neptunium has to be known for each E_A used for the calculation of a value of $\bar{n}$. This concentration is easily found from the value of C_{HA} read on the curve, according to $C_M = C_M'(C_{HA}' - C_{HA})/C_{HA}'$ where C_{HA}' is the initial concentration of HA in the solution T.

EMF MEASUREMENTS, RESULTS

In Fig. 7, the lowest curve is drawn through the points obtained from solutions containing no neptunium. Evidently there is no systematic deviations between points of different C_{III}. The curve thus represents the wanted function E_A([HA]). The upper curves give $E_A(C_{HA})$ for the stated values of

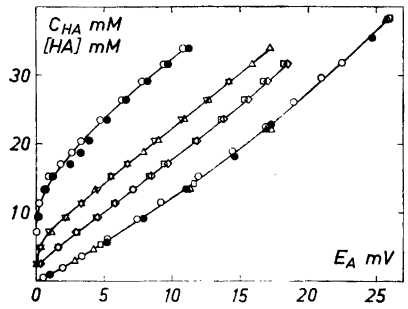

Fig. 7. The connexion between E_A and C_{HA}, or, for the lowest curve, referring to neptunium-free solutions, [HA]. For this curve, the signs refer to the following initial concentrations (in mM) of iron(III): 0.19, ▲; 0.38, △; 0.75, ○ and ●; 1.50, □. The upper curves have been obtained with the following initial concentrations (in mM) of neptunium(IV): 3.04, □ and ◇; 6.07, △ and ▽; 15.4, ○ and ●; with the initial concentration of iron(III) being 0.75 mM in all cases.

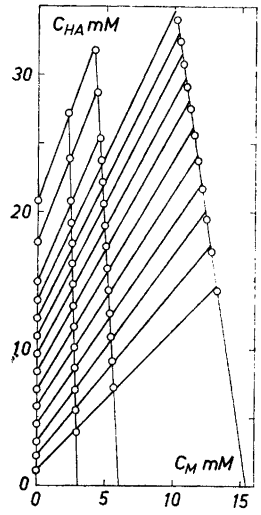

Fig. 8. Graphical determination of [HA] and $\bar{n}$ from the emf measurements of the fluoride system.

C_M'. For values of C_{HA} higher than those plotted in Fig. 7, precipitation occurs, presumably of NpF_4.

The family of curves has been cut at a number of values of E_A and the corresponding values of [HA] and $\bar{n}$ determined, Fig. 8 and Table 3. Even for the lowest value $E_A = 1$ mV, $\bar{n}$ is > 1, the formation of NpF^{3+} being virtually complete. The corresponding value of [HA] = 1.1 mM is chosen as the lower limit of integration $[HA]_0$ when the function X_H/X_{H0} is evaluated. By extrapolation of the function X_I, X_{II} and X_{III}, the constants $K_{2H} = 141 \pm 30$ M^{-1} and $K_{3H} = 47 \pm 15$ M^{-1} are finally obtained. When inserted in eqn. (36), these constants give quite an acceptable fit with the experimental $\bar{n}$([HA]) for $\bar{n} > 1.3$. For $\bar{n} < 1.3$, where Np^{4+} gradually becomes important, eqn. (25) of Ref. 7 has to be used. With the value of $\beta_{1H} = K_{1H} = 1.64 \times 10^4$ M^{-1} from the ion exchange measurements, together with the values of K_{2H} and K_{3H} just quoted, a good fit is obtained also in this range.

A further refinement of the constants can be achieved by systematically varying K_{2H} and K_{3H} until the best possible fit has been found with the experimental data. Such calculations, effected by SMIL, have yielded $K_{2H} = 123$ M^{-1} and $K_{3H} = 55$ M^{-1} as the best values. Both are evidently within the maximum errors indicated for the values found graphically. Out of the fourteen experi-

mental points, eleven will deviate < 5 % from the curve computed with the SMIL values. The deviating points are moreover not distributed at random, but rather the three highest ones. A slightly better fit can be achieved by introducing a further term in eqn. (36), with a value of $K_{4H} = 5$ (ten points then deviate < 2 %), but the improvement is not very spectacular, and the stated value of K_{4H} must certainly not be considered as very reliable. As to the three highest points, they cannot be made to fit acceptably by any value of K_{4H}. Their erratic behaviour presumably depends upon a beginning precipitation of NpF_4, still too slight to be noticeable in other ways.

DISCUSSION

In Table 4, the preferred constants K_n^* and the quotients K_n^*/K_{n+1}^* have been entered for both systems. The only constant which has been determined by both the methods employed is K_2^* of the fluoride system; in this case, at least, concordant results have been found.

The high ratio of K_1^*/K_2^* means that NpF^{3+} is very stable relative to the next complex NpF_2^{2+}. The low value of K_2^*/K_3^* means on the other hand that NpF_2^{2+} is rather unstable relative to NpF_3^+, a condition which is quite unusual within a series of fluoride complexes.[15] Also for the sulphate system, K_1^*/K_2^* has a fairly high value which is, however, of the same order of magnitude as for the analogous zirconium(IV) system.[7]

The peculiarities of the systems stand out very clearly in the complex formation and distribution curves presented in Fig. 9. As to the second constant of the fluoride system, the value from the emf measurements has been used for the construction of the curves.

In Table 4, the values found by Sullivan and Hindman [1] for the sulphate system has also been included for comparison. These values apply to a 2 M perchloric acid medium. They are considerably lower than ours which is also to be expected from considerations of the variations with the ionic strength of the various activity coefficients involved. As to K_1^*, the ratio between the

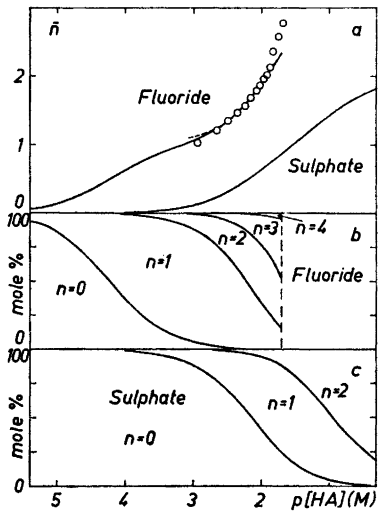

Fig. 9 a). Complex formation curves of the investigated systems. Fulldrawn curves calculated from the preferred constants for all complexes found, as stated in Table 4. Dashed curve for the fluoride system calculated from those constants only which can be found by emf measurements, *i.e.* K_2^* to K_4^* (coincides with the fulldrawn curve for $\bar{n} > 1.3$). Circles represent corresponding values of $\bar{n}$ and [HA] found from Fig. 8. b) and c). The distribution of neptunium(IV) between different complexes NpA_n in the sulphate and fluoride systems, respectively.

Table 4. The stability constants K_n^* for the fluoride and sulphate systems of neptunium(IV) in 4 M perchloric acid at 20°C (the results of Sullivan and Hindman [1] included for comparison apply to 2 M perchloric acid and 25°C).

Ref.	Method	log K_n^*				$\frac{K_1^*}{K_2^*}$	$\frac{K_2^*}{K_3^*}$
	$n \longrightarrow$	1	2	3	4		
			Fluoride				
This work	ion exch.	4.82 ±0.02	2.75 ±0.08			120	
	emf		2.69 ±0.10	2.34 ±0.15	≃ 1.3	130	2
			Sulphate				
This work	ion exch.	2.70 ±0.02	1.56 ±0.05			14	
S. & H.[1]	extr., TTA	2.43 ±0.04	1.04 ±0.08			25	

values found for the two media is about the same as for the zirconium(IV) system.[7] For K_2^*, on the other hand, this ratio seems to be much higher for the neptunium(IV) system. Consequently, the ratio K_1^*/K_2^* comes out even higher in 2 M perchloric acid than in the 4 M acid used presently.

Further discussion of the results will be postponed until investigations of other acceptors of the types M^{4+} and MO_2^{2+}, at present in progress in this Department have been completed.

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