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A potentiometric study of the system Nb(V) - OH^- - F^- in 3 M K(Cl) medium

By GEORG NEUMANN

ABSTRACT

The formation of mixed complexes between Nb(V), OH^- and F^- in 3 M K(Cl) at 25°C with total niobium concentrations (B) 0.01 and 0.02 M has been studied by emf methods.

The hydrogen ion concentration was determined with the quinhydrone electrode, whereas the free fluoride ion concentration was measured with a specific fluoride ion electrode. The performance of the latter was tested by studies of $H^+ - F^-$ equilibria.

The data can be explained adequately assuming the presence of only two Nb-containing species, namely $Nb(OH)_2F_4^-$ and $Nb(OH)_2F_5^{2-}$. The following equilibrium constants are suggested (deviations 3 σ; σ is the standard deviation)

$Nb(OH)_2F_4^- + F^- \rightleftarrows Nb(OH)_2F_5^{2-}$; $\log K = 2.51 \pm 0.03$

$H^+ + F^- \rightleftarrows HF$; $\log K_{11} = 3.31_6 \pm 0.003$

$H^+ + 2F^- \rightleftarrows HF_2^-$; $\log K_{12} = 4.04 \pm 0.01$

Introduction

A well-known feature in the chemistry of pentavalent niobium is the high solubility of hydrous niobium(V) oxide ($Nb_2O_5 \cdot aq$, "niobic acid") in aqueous solutions of hydrofluoric acid in acidified alkali metal fluoride solutions. This is ascribed to the formation of very strong fluoroniobate(V) complexes.

Since little information is available concerning fluoroniobate(V) ions in aqueous solution it seemed appropriate to study the equilibria involved. The most promising method of investigation seemed to be emf-measurements of the concentration of free hydrogen ions and free fluoride ions in solutions of known stoichiometric composition.

The present experimental work deals only with fluoroniobate(V) ions, but some previous investigations on similar Ta(V) compounds will also be mentioned, since the many similarities between the chemistry of Nb(V) and Ta(V) make comparisons natural.

Previous work

Investigations on solid phases. A number of crystalline alkali metal fluoroniobates(V) and -tantalates(V) have been described by Marignac in 1866 [1, 2] and by Balke and Smith in 1908 [3]. The overall formulas of some of these salts are: $K_2NbOF_5(H_2O)$, $CsNbF_6$, K_3NbOF_6, K_3HNbOF_7, $K_4Nb_3O_3F_{13}(H_2O)_2$, $K_5Nb_3O_3F_{14}(H_2O)$ and K_3TaF_8. Some of these compounds have also been prepared with other alkali metal cations (or

with ammonium), and the Ta analogues of some of these Nb compounds could also be prepared.

J. L. Hoard and his co-workers examined a few of these substances by X-ray crystallography and found the following isolated complexes:
NbF_7^{2-} in K_2NbF_7 [4], $NbOF_6^{3-}$ in K_3NbOF_6 [5], $NbOF_5^{2-}$ in K_3HNbOF_7 [6], and TaF_8^{3-} in K_3TaF_8 [7]. The existence of NbF_6^- in the solid state does not seem to have been proved by X-ray methods.

Species in solution. The only potentiometric studies of these complexes reported hitherto seem to be those of Nikolaev and Buslaev [8]. Using the quinhydrone electrode they followed the pH changes obtained when dilute KOH is added to a solution containing NbF_5 and HF. The Nb(V) concentration of the solutions was $\approx 5 \cdot 10^{-4}$ M, and no attempt was made to keep the activity factors constant. The results were explained qualitatively by assuming the reaction

$$H_2NbOF_5 + 2OH^- \rightleftharpoons NbOF_5^{2-} + 2H_2O$$

From Raman spectra of solutions of K_2NbF_7 in aqueous HF of various concentrations, Keller [9] inferred that $NbOF_5^{2-}$ dominates in 0–11 M HF, whereas NbF_6^- prevails at higher HF contents. A similar Raman study by Keller and Chetham-Strode [10] of solutions of Ta(V) and F^- seemed to show that TaF_6^- dominates at high HF concentrations (22 M HF, 2 M NH_4F), whereas in neutral solutions (2 M NH_4F) TaF_7^{2-} was found.

Symbols often used in the text

$B = [Nb(V)]_{tot}$ = total concentration of niobium, added as "7/6" ($= K_7HNb_6O_{19}$)

$C = [F^-]_{tot}$ = total concentration of fluoride

$c = [F^-]$ = concentration of fluoride ions

$H = [HCl]_{added} - 6.167B$ = analytical hydrogen-ion concentration in excess of Nb^{5+}, F^- and H_2O. The salt "7/6" can be formulated as $K_7Nb_6(OH)_{37}$. Thus it contains $37/6 = 6.167$ OH^- per Nb^{5+}.

$h = [H^+]$ = concentration of free hydrogen ions

p,q,r = positive integers in the general formula $Nb_q(OH)_pF_r^{(5q-p-r)}$, for niobium-containing species in solution.

Method of investigation

In the present work the formation of mixed complexes of Nb(V) with OH^- and F^- was studied by emf-measurements of the concentration of H^+ and (in a few cases) F^- in a number of solutions prepared from stock solutions of $K_7HNb_6O_{19}$ (potassium hexaniobate(V)), KF, HCl and KCl.

Solutions with two different concentrations of Nb(V), namely $B = 0.01$ M and 0.02 M were studied (see Fig. 1 and Table 1). For each of these values of B five different values for $C = [F^-]_{tot}$ were used so that the ratio C/B (viz. total fluoride to total Nb) equalled 6, 8, 10, 13 or 20. The acidity of the solutions was varied by adding HCl. KCl was added in such quantities as to keep $[K^+] = 3$ M in all solutions in order to ensure reasonable constancy of the activity factors of the reacting species.

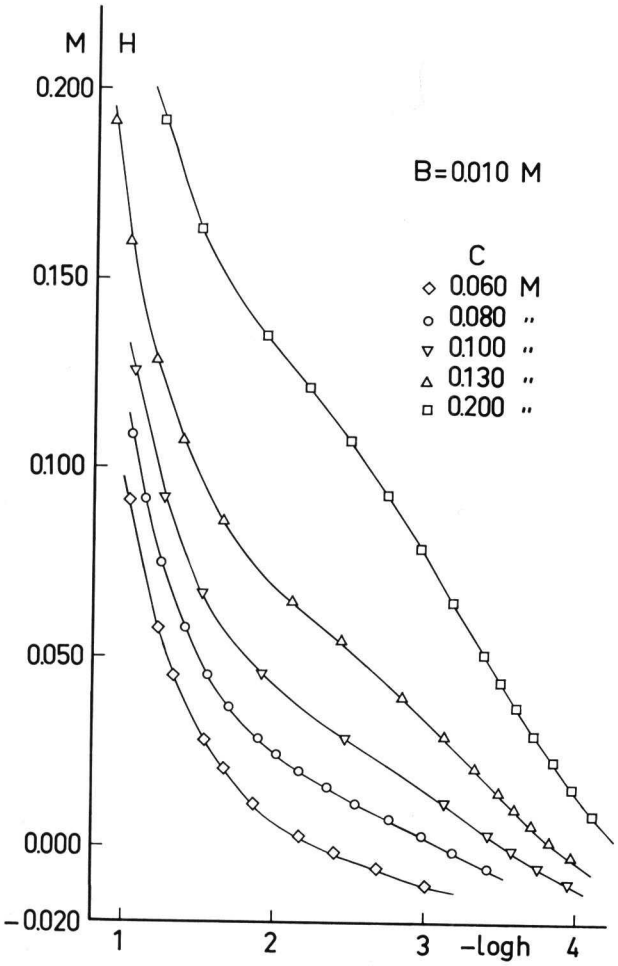

Fig. 1. Proton concentration H in excess of Nb^{5+} and F^- as a function of $\log h$ at constant total Nb and F concentrations, B and C. In all curves $B = 0.010$ M. The curves are calculated with the equilibrium constants in set II of Table 6. The difference from the ones with set I and III (Table 6) is barely visible in the present scale. The agreement is equally as good for $B = 0.020$ M (see Table 6).

The concentrations of hydrogen ions and of fluoride ions were determined by measuring the emf of the cells

$$-\text{SE/Test solution, saturated with quinhydrone } (Q_2H_2)/\text{Pt}+ \quad (=\text{cell Q})$$

$$-\text{SE/Test solution/FE}+ \quad (=\text{cell F})$$

where FE denotes a specific fluoride ion electrode (see under "The EMF measurements") and SE is a reference half-cell of the composition

Table 1. Results from potentiometric measurements with the quinhydrone electrode in solutions containing Nb.

The data are given in the form: $-\log h$, H (mM), $10(H_{calc}-H_{exp})$ (mM). In calculating H_{calc} we used $\log K_{11}=3.316$, $\log K_{12}=4.04$ and $\log K=2.51$ (set II, Table 6). For each set of data the systematic error $\delta E_{Q,0}$ is given. The $\log h$ values have been corrected for $\delta E_{Q,0}$.

B = 0.010 M

(1) $C=0.060$ M. $\delta E_{Q,0}=+0.1$ mV. 3.006, −10.0, +4; 2.683, −5.8, +1; 2.402, −1.6, 0; 2.172, 2.6, +1; 1.866, 11.1, +2; 1.669, 20.1, −3; 1.538, 27.9, −2; 1.339, 44.8, +2; 1.235, 57.5, +1; 1.038, 91.2, −1;

(2) $C=0.080$ M. $\delta E_{Q,0}=+0.2$ mV. 3.413, −5.4, 0; 3.192, −1.2, −1; 2.980, 3.0, −1; 2.762, 7.2, −1; 2.544, 11.4, 0; 2.347, 15.7, −1; 2.170, 19.9, −1; 2.020, 24.1, −2; 1.901, 28.3, −4; 1.702, 36.7, −2; 1.561, 45.2, −2; 1.403, 57.8, −2; 1.253, 74.6, −2; 1.139, 91.6, 0; 1.047, 108.4, +5;

(3) $C=0.100$ M. $\delta E_{Q,0}=+0.4$ mV. 3.951, −9.3, +1; 3.754, −5.1, −1; 3.580, −0.9, −2; 3.417, 3.4, −1; 3.126, 11.8, −4; 2.477, 28.7, +1; 1.914, 45.5, −1; 1.521, 66.6, +1; 1.265, 91.9, +4; 1.061, 125.7, −2;

(4) $C=0.130$ M. (fluoride stock II). $\delta E_{Q,0}=+0.6$ mV. 3.976, −2.6, −2; 3.833, 1.6, −1; 3.709, 5.8, −2; 3.594, 10.0, −2; 3.491, 14.2, −4; 3.334, 20.6, −4; 3.131, 29.0, −5; 2.852, 39.5, 0; 2.449, 54.3, −5; 2.124, 64.8, −2; 1.660, 85.9, −4; 1.397, 107.0, −9; 1.218, 128.1, −3; 1.035, 159.7, +7; 0.909, 191.3, +4;

(5) $C=0.200$ M. (fluoride stock II). $\delta E_{Q,0}=+0.5$ mV. 4.110, 8.6, −1; 3.969, 15.6, −4; 3.841, 22.7, −4; 3.717, 29.7, −2; 3.604, 36.7, −1; 3.496, 43.7, −1; 3.389, 50.8, 0; 3.183, 64.8, 0; 2.965, 78.9, +4; 2.747, 92.9, +1; 2.496, 107.0, +2; 2.219, 121.1, +2; 1.932, 135.1, +1; 1.499, 163.2, +1; 1.247, 191.3, 0;

B = 0.020 M

(6) $C=0.120$ M. $\delta E_{Q,0}=+0.2$ mV. 2.888, −20.0, +1; 2.669, −15.8, +2; 2.475, −11.6, +2; 2.150, −3.1, 0; 1.902, 5.3, 0; 1.580, 22.2, −1; 1.338, 43.3, −1; 1.155, 68.6, −5; 1.040, 89.6, +1; 0.934, 114.9, +2;

(7) $C=0.160$ M. $\delta E_{Q,0}=+0.2$ mV. 3.514, −15.1, +1; 3.388, −11.3, +4; 3.268, −7.2, +3; 3.141, −2.4, −2; 3.011, 1.8, 0; 2.882, 6.0, +1; 2.752, 10.2, +1; 2.618, 14.4, +2; 2.361, 22.9, −1; 1.912, 39.7, −2; 1.605, 56.6, +1; 1.407, 73.5, −1; 1.262, 90.3, −1; 1.149, 107.2, +1; 1.060, 124.1, −1;

(8) $C=0.200$ M. $\delta E_{Q,0}=+0.5$ mV. 3.993, −18.6, +1; 3.888, −14.4, −3; 3.781, −10.1, −3; 3.590, −1.7, −4; 3.414, 6.7, −4; 2.614, 44.7, 0; 1.639, 91.1, 0; 1.355, 116.4, +2; 1.227, 133.2, 0; 1.039, 167.0, +2;

(9) $C=0.260$ M. (fluoride stock II). $\delta E_{Q,0}=+0.6$ mV. 4.031, −5.3, +1; 3.921, 1.0, −3; 3.782, 9.5, −4; 3.686, 15.8, −5; 3.561, 24.2, −6; 3.414, 34.8, −8; 3.121, 55.9, −9; 2.900, 70.6, −1; 2.697, 83.3, +6; 2.269, 108.6, +3; 1.887, 129.7, +2; 1.582, 150.7, +1; 1.363, 172.2, +1; 1.209, 192.9, +3; 1.089, 214.0, +5;

(10) $C=0.400$ M. (fluoride stock II). $\delta E_{Q,0}=+0.4$ mV. 4.500, −3.9, +2; 4.397, 3.1, 0; 4.296, 10.2, +4; 4.210, 17.2, +3; 4.108, 25.6, +7; 3.988, 36.9, +7; 3.838, 52.3, +4; 3.648, 73.4, −4; 3.452, 94.5, +7; 3.276, 115.6, −2; 3.031, 143.7, −1; 2.635, 185.9, +10; 1.409, 298.3, +6; 0.955, 382.7, −14;

SE/=Ag, AgCl(s)/3 M KCl (saturated with AgCl)/3 M KCl/

The emf of cell Q at 25°C can be written

$$E_Q = E_{Q,0} + 29.58 \log \frac{[Q]}{[QH_2]} + 59.15 \log h + E_j \qquad (1)$$

Here $E_{Q,0}$ is a constant, [Q] and [QH_2] are the concentrations of quinone and hydroquinone in the solution, h is the free hydrogen ion concentration and E_j represents the liquid junction potential between the test solution and 3 M KCl. Since the ratio [Q]/[QH_2] should equal unity in a solution saturated with quinhydrone we can write eqn (1)

$$E_Q = E_{Q,0} + 59.15 \log h + E_j \qquad (1')$$

The constant $E_{Q,0}$ as well as the liquid junction potential, E_j, were determined by measuring the emf of cell Q using a series of test solutions of the composition

$$h \text{ M } H^+, \text{ 3 M } K^+ \text{ and } (3+h) \text{ M } Cl^-.$$

It was found that E_j equalled $-(10 \pm 1)\ h$ mV in good agreement with Ciavatta [11] who found $E_j = -(11 \pm 1)\ h$ mV.

The emf (E_F) of cell F at 25°C as a function of the free fluoride concentration (c) can be written

$$E_F = E_{F,0} - 59.15 \log c + E_j \qquad (2)$$

In eqn (2) $E_{F,0}$ is a constant and E_j has the same meaning as in eqn (1).

The constant $E_{F,0}$ in eqn (2) was determined by measuring the emf of cell F, when the test solutions had the composition

$$3 \text{ M } K^+, \ C \text{ M } F^- \text{ and } (3-C) \text{ M } Cl^-.$$

Experimental

Reagents and solutions

All alkaline solutions and solutions containing fluoride were handled and stored in polythene vessels.

Potassium niobate(V), $K_7HNb_6O_{19}(H_2O)_n$. $n = 13$–14. A mixture of 155 g Nb_2O_5 (Fansteel Metallurgical Corporation, Research Grade, Nb_2O_5 99.9 %, Ta_2O_5 0.05 %) and 452 g KOH (EKA, p.a.) was mixed carefully and heated in small portions in a silver crucible for 20 min at 800°C. The product was cooled and crushed, and leached with 1800 ml H_2O. After decantation from unreacted Nb_2O_5, the solution was filtered through a G4 glass filter, and from the clear solution the salt $K_8Nb_6O_{19}(H_2O)_{16}$ ("8/6") was precipitated by addition of 1800 ml ethanol.

The precipitate was filtered off, sucked free from mother liquor in a stream of N_2 and dissolved in 1500 ml H_2O. To this solution an equal quantity of 96 % ethanol was added in small portions. A crystalline precipitate of $K_7HNb_6O_{19}(H_2O)_n$ ($n = 13$–14, "7/6") was thus obtained. It was washed on a glass filter with 0.1 M KOH in 50 % ethanol under a stream of N_2, and carefully sucked dry.

According to single crystal and powder X-ray data our substances "8/6" and "7/6" were identical with those described by Halla and co-workers [12] except that a small monoclinic distortion was found in "7/6", for which phase Halla *et al.* reported orthorhombic symmetry (Söderquist and Neumann [13]).

A stock solution of Nb(V) was now prepared by dissolving approximately 100 g of "7/6" in 1000 ml H_2O.

The solution was analysed by Lindqvist's method [14]: Diluted aliquots of the stock solution were passed through columns charged with ammonium-saturated cation exchanger. In this way an ammonium niobate solution was obtained from which hydrous Nb_2O_5 was precipitated by adding dilute H_2SO_4 at approximately 80°C until pH ≈ 4. The precipitate was filtered off and ignited at strong red heat until constant weight, giving Nb_2O_5. The potassium retained in the ion exchange column (together with remaining ammonium) was washed out with dilute HCl. After evaporation of HCl and complete expulsion of NH_4Cl, the remaining KCl was determined by titration with $AgNO_3$ according to Mohr [15].

The K and Nb determinations were reproducible to within ±0.2 %. The composition of our Nb(V)-stock solution was 0.4371 M K^+ and 0.3742 M Nb(V) (average of three determinations).

The ratio K/Nb was 1.168 (calc. for "7/6" 1.1667). In an earlier paper [16] the present author prepared and analysed three other batches of "7/6" with the same method as described above. The ratio K/Nb was then 1.168, 1.167 and 1.171. This gives good confidence in the composition of the Nb(V)-stock.

The stock solution was tested for the presence of CO_3^{2-} by acidifying a sample in a closed system and taking up the CO_2 formed in $Ba(OH)_2$. The quantity of precipitated $BaCO_3$ was compared visually with the amounts of precipitate obtained when known quantities of $KHCO_3$ were treated in the same way. The molar ratio CO_3^{2-}/Nb was estimated to be $<10^{-3}$.

Potassium fluoride. KHF_2 was crystallized by evaporating and cooling a solution containing equal molar quantities of $KF(H_2O)_2$ (Mallinkrodt, analytical reagent) and hydrofluoric acid (Merck). The KHF_2 was once recrystallized from water, dried between filter papers and then heated in a Pt dish under a rapid stream of N_2. The temperature was first kept just above the melting point of KHF_2 and when most HF had been expelled and solid KF was left in the dish, residual HF was removed by heating the product for some time. From this product stock solutions of KF were prepared.

The K-content was determined as K_2SO_4 by evaporating small quantities of the KF stock together with an excess of conc. H_2SO_4 under heating lamp until HF was expelled, and then heating in an electric furnace at 850°C to constant weight. The possible residual acidity, $[H^+]_{tot}$, of the KF stocks was determined by titration with standard KOH using phenolphthalein as an indicator. The total fluoride content was calculated as $[F^-]_{tot} = [H^+]_{tot} + [K^+]$. The $[F^-]_{tot}$ value was checked by passing aliquots of the KF stock through a polythene column charged with cation exchanger (Dowex 50 × 8) in H^+ form. The HF formed was titrated with standard KOH. The result agreed within 0.3 % with $[F^-]_{tot}$ calculated from $[H^+]_{tot} + [K^+]$.

In the two KF stock solutions (I and II) used in this work the ratio $[F^-]_{tot}/[K^+]$ was 1.0179 for I and 1.0000 for II.

The excess acidity in solution I was most probably due to insufficient heating of the KF sample so that some HF was left. In those sets of data in which stock I was used (sets 1, 2, 3, 6, 7 and 8, see Table 1) the necessary correction for the residual acidity of

the KF-stock was made. There was no significant difference between the results with stock I and II.

Dilute hydrochloric acid was prepared from conc. HCl (Merck) and standardized with recrystallized $KHCO_3$. Sometimes the standardization was made independently with NaOH solution which had been standardized with hydrazine sulfate. The results for the concentrations of the hydrochloric acid obtained by the two methods agreed to within 0.2 %.

Quinhydrone (*p.a. Merck*) was recrystallized once from water.

KCl (p.a. Merck) was in most cases used directly as ionic medium without further purification. By heating to 400°C the moisture content was found to be 0.3 % or less. By potentiometric pH-titration and construction of a Gran plot [17] the content of acidic or basic impurities was found to be negligible.

All other chemicals, if not otherwise mentioned, were of p.a. quality.

Preparation of the solutions for emf measurements

Every individual test solution in this work was prepared separately in a bottle and introduced into the emf cell for measurement of $[H^+]$ and, for some solutions, $[F^-]$. This technique was preferred to continuous change of the test solutions by titration, because of the slight intrinsic instability of the emfs of the two cells Q and F (see under "The EMF measurements").

For the preparation of the individual solutions some or all of the following solutions were used, all containing 3 M K^+

(a) 0.1000 M Nb (from the $K_7HNb_6O_{19}$ stock) + 2.8334 M KCl
(b) C M KF + (3.000 − C) M KCl (C = constant)
(c) H M HCl + 3.000 M KCl (H = constant)
(d) 3 M KCl

These solutions were mixed in polythene bottles which could be tightly closed with screw caps. The solutions were added from calibrated Metrohm piston burets in the order named (i.e. first solution (a), then solution (b), etc).

When HCl was added to solutions containing Nb(V) and KF, a white flocculent precipitate (possibly hydrous Nb_2O_5) was first formed, but on further addition of acid it again dissolved so that clear solutions could be obtained at pH less than 3–4.5 (depending on the concentrations of Nb(V) and F^-). The mixed solutions (volume 50 ml) were stored in water thermostats at 25.0°C ±0.1°C and small samples (10–15 ml) were withdrawn from each bottle whenever $[H^+]$ or $[F^-]$ were to be determined.

The EMF measurements

The cells Q and F with the test solution were kept in an oil thermostat at 25°C±0.1°C, which was placed in a room thermostated at 25°C.

The emf of cell Q was measured with a Vernier compensator, which could be read with an accuracy of ±0.01 mV using a Multiflex galvanometer. The emf of cell F was measured with a Radiometer PHM4 valve potentiometer.

The reference half cell, SE, was of the "Wilhelm" type [18], in which the glass tube, coming into contact with the test solution, was replaced by a polythene tube.

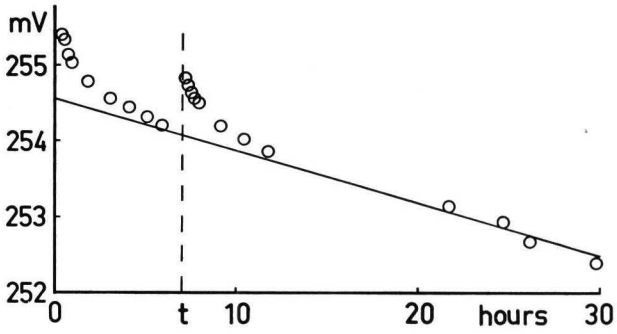

Fig. 2. Drift of the emf with time for ignited Pt electrodes which were immersed into the same solution at time 0 and, after renewed ignition, again at time t. Solution: 0.020 M Nb, 0.400 M F, 3 M K(Cl), log $h = -4.1$. The circles give the average E for two simultaneously immersed electrodes. The difference between their E values was usually less than 0.1 mV.

Some observations on the quinhydrone electrode

In preliminary measurements it was found that the hydrogen electrode did not assume well-defined emfs in acidic Nb(V) solutions containing fluoride. The cause of this is not yet known. For this reason the quinhydrone electrode was used instead of the hydrogen electrode. The container for cell Q was a ca. 35 ml polythene beaker tightly closed with a rubber stopper, through which the reference electrode, two bright Pt-electrodes and a mechanical stirrer (polythene rod) were introduced into the cell solutions. Stirring by a stream of N_2 was rejected in order to prevent loss of volatile quinone.

The bright Pt electrodes were treated with hot HNO_3, washed in distilled water and ignited in an ethanol flame before immersion into the solution. It has been found by many workers that igniting platinum electrodes in an ethanol flame is a routine that seems to remove impurities from the electrode surface and make the emfs more reproducible in many systems. The procedure was used in the present case because of this apparently well-established observation.

However, after the present quinhydrone measurements had been completed it was found that slightly more accurate emf-data (see below) could be obtained if the electrodes were not ignited immediately before use, but instead left after ignition for at least 12 hours in a 0.01 M HCl solution saturated with quinhydrone before immersion in the test solution. Since the data agreed well with a very simple main reaction (see under "Discussion"), it was not considered worthwhile to repeat the measurements for a very small possible gain in accuracy.

"Creeping" of the quinhydrone electrode. A description of the behavior of both the non-ignited and the ignited Pt electrode is of interest, although only the latter was used in the actual measurements.

In the determinations of log h 10–15 ml of the test solution was introduced into the cell and ca 200 mg of quinhydrone was added, the two Pt electrodes were immersed and the mechanical stirrer was started. The emf of both Pt electrodes against SE was then measured at intervals. Pt electrodes that had been pretreated in the same way, usually agreed within better than 0.1 mV when read simultaneously, but constant emfs could not be obtained although much effort was put into purification

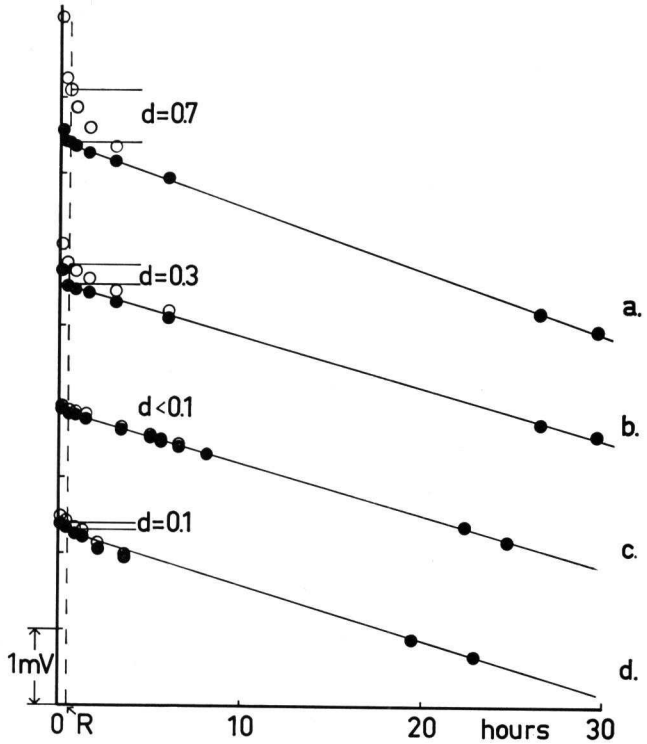

Fig. 3. The drift of an ignited (symbol ○) and of a non-ignited electrode (symbol ●) which were both introduced into the same solution at time 0. In the main series of experiments the emfs of the ignited electrodes were determined at time 0.5 *h* (dashed vertical line at *R*). The difference from the value extrapolated to 0 is indicated by *d*. Solutions: curve *a–c*: 0.010 M Nb, 0.200 M F, $\log h = -3.7$ (*a*), -2.2 (*b*) and -1.5 (*c*), curve *d*: 0.02 M HCl, $\log h = -1.7$. All solutions contain 3 M K(Cl).

of the solutions and the quinhydrone. For a number of solutions, which had been arbitrarily selected among those studied in the final $[H^+]$-measurements, the drift of the emf was followed for longer periods.

Some typical curves showing the change of the emf with time are shown in Fig. 2–3.

After introduction of the quinhydrone and the Pt electrodes the emf first had an initial period of more rapid change, and then changed at a limiting rate of 0.05–0.10 mV/h, irrespective of the composition of the solution. The same rate was also observed in acidified fluoride solutions without Nb and in solutions of HCl + KCl. A drift of the same magnitude for the quinhydrone electrode in chloride medium was reported by Granger and Nelson [19] and recently by Mesmer and Baes [20]. The former workers observed a drift of 0.07 mV/h in 0.1 M HCl, whereas the later found 0.06 mV/h in 1 M NaCl at pH = 3–6.

In Fig. 2 are shown the results obtained when the quinhydrone and two freshly ignited Pt electrodes were introduced at the time 0 (hours). At a later time *t* (dashed vertical line *t*, Fig. 2), when the limiting rate had been reached, freshly ignited Pt-electrodes were again introduced into the solution. The same asymptote as before

was reached after an initial period of more rapid change. This seems to show that the creep of potential of the quinhydrone electrode was due to two different effects:

(1) Adjustment of the ignited Pt electrodes to the solution.

(2) A slow creep of constant rate due to changes in the solution itself. Harned and Wright [21] suggested that there might proceed a slow formation of chlorohydroquinone in the acidified chloride medium, causing a gradual decrease of the ratio $[Q]/[QH_2]$ (the ratio between the concentrations of quinone and hydroquinone, see eqn (1)). According to eqn (1) this would result in the decrease of E_Q, which was indeed observed in the present measurements.

It is thus reasonable to assume that the correct emf would be obtained by extrapolating the linear part of the creep curves to the moment of introducing the quinhydrone into the test solution. At this moment the ratio $[Q]/[QH_2]$ should be strictly equal to unity and eqn (1′) would be valid.

Fig. 3 compares some results with Pt electrodes that had been ignited immediately before immersion ("ignited", open symbols) and electrodes that had been left in contact with an acidic quinhydrone solution 12 hours after ignition ("non-ignited", black symbols). Obviously the latter approach much more rapidly to the limiting line, so that the latter procedure would have been preferable.

Procedure with cell Q

In all main series of experiments the emf of the cell Q was measured 30 minutes (vertical dashed line R in Fig. 3) after time 0 when the quinhydrone was added and the freshly ignited Pt electrodes introduced into the test solution. The emf was later corrected by subtracting a small quantity d which would correspond to vertical distance to the asymptote; see Fig. 3. The value of d was estimated by studying the drift of the emf in the case of a few typical solutions, of which some are shown in Fig. 3. The value of d seemed to decrease with increasing $\log h$ of the solution and was less than 0.3 mV for $\log h > -3$. For solutions with $\log h < -3$, d-values of 0.3–0.8 mV were found, and it was decided to substract an average value $d = 0.5$ mV from all emf-values in the region $\log h < -3$. This corresponds to ≈ 0.01 units in $\log h$.

The small change 0.03–0.05 mV due to the limiting creep during the first 30 minutes after introduction of the quinhydrone was negligible. The d-correction has already been applied to the data in Tables 1 and 3 and in Figs. 1 and 6.

$E_{Q,0}$ (see eqn (1)) was determined before and after the measurements with every set of solutions (generally every day or second day). These $E_{Q,0}$ values generally agreed to within ± 0.2 mV.

The $\log h$ values of the solutions containing Nb(V) were measured for the first time approximately one week after mixing the individual solutions. In order to check that equilibrium had been attained in these solutions, every second one of them (nos. 1, 3, 5 ... etc. in every set; see Table 1) was measured a second time one to three weeks after the first measurement. The emf-values from both these determinations generally agreed to within ± 0.3 mV (changes in $E_{Q,0}$ (eqn (1)) are corrected for), except in a few cases for $\log h < -3.5$, where the measurements deviated by as much as 0.7–0.8 mV. The deviation between the first and the second emf measurement was positive in 37 cases (average 0.1 mV) and negative in 23 cases (average 0.2 mV).

Thus there seems to be little doubt that equilibrium had been attained one week after mixing the Nb(V)-solutions. However, no attempt was made to test whether equilibrium could have been obtained in a much shorter time.

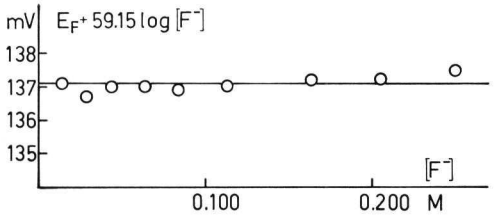

Fig. 4. $E_F + 59.15 \log [F^-] = E_{F,0} - E_j$ as a function of [F⁻], for solutions of KCl and KF only.

Test of the specific fluoride ion electrode

The electrode used was a model 94-09 (white teflon body), Specific Ion Electrode (Orion Research Inc., Cambridge, Mass.) described in reference [22]. According to the manufacturers the potential varies with the fluoride ion activity according to Nernst's equation in the fluoride concentration range 1 M to below 10^{-5} M and even in the presence of 10^3–10^4 times excess of e.g. Cl^- or NO_3^-.

Since we had no previous experience of the specific fluoride electrode its behavior was checked carefully.

When the fluoride electrode was introduced into cell F, the emf generally reached an apparently constant value within 1 or 2 minutes. This emf value remained constant to within better than ± 0.5 mV for at least half-an-hour. All E_F-values (eqn 2) utilized in this work were recorded approx. 5 minutes after immersion of the electrode into the solution. $E_{F,0}$ (eqn 2) was checked before and after each determination of [F⁻] in the test solutions. The checks were made by introducing a solution of known [F⁻] into cell F. If the two $E_{F,0}$ values disagreed by more than 0.3 mV, the measurement of the test solution was repeated.

As a first item it was checked that the fluoride electrode used obeyed eqn (2) above. Test solutions of the composition

$$3 \text{ M } K^+,\ C \text{ M } F^-,\ (3-C) \text{ M } Cl^-$$

were introduced into cell F and the emf between the fluoride electrode and the reference half-cell (SE) was measured for different values of C. The result of a typical series of such measurements is shown in Fig. 4. As seen from the figure the measured values of $E_F + 59.15 \log C$ generally agreed to within ± 0.3 mV with the straight horizontal line expected from eqn (2). E_j is practically zero in the neutral or slightly basic solutions used.

The function of the fluoride electrode was also checked in acidic solutions, where irregular behavior might be feared due to possible dissolution of the rare earth fluorides from the electrode membrane.

The equilibrium constants K_{11} and K_{12} for the reactions

$$F^- + H^+ \rightleftharpoons HF;\ K_{11} = [HF]\, c^{-1} h^{-1} \tag{3}$$

$$2F^- + H^+ \rightleftharpoons HF_2^-;\ K_{12} = [HF_2^-]\, c^{-2} h^{-1} \tag{4}$$

were determined both by measuring the fluoride ion concentration, c, with the specific fluoride electrode employing cell F, and independently by measuring the hydrogen ion concentration, h, with the quinhydrone electrode in cell Q.

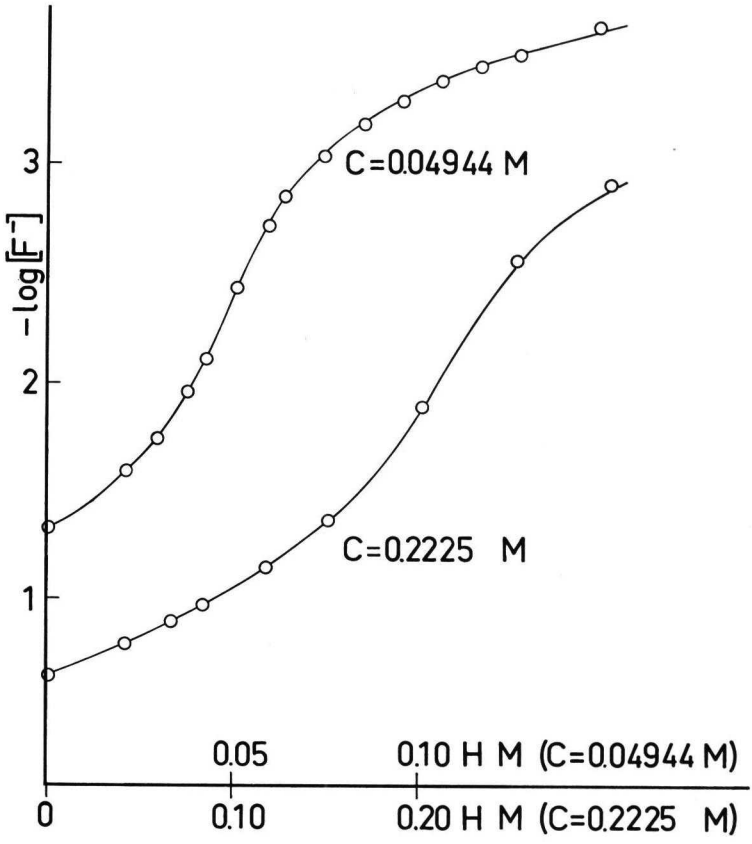

Fig. 5. Log [F^-], determined with the specific fluoride electrode, as a function of H for two constant values of total fluoride (C), viz. $C = 0.04944$ M and $C = 0.2225$ M. No Nb present. Curves calculated for $\log K_{11} = 3.31$ and $\log K_{12} = 4.03$.

Good agreement between the pairs of constants (K_{11} and K_{12}) obtained independently with the two electrodes would indicate that the fluoride electrode functions properly also in acidic solutions.

(a) *Determination of K_{11} and K_{12} with the fluoride electrode.* The general composition of the test solutions in cell F was

$$3 \text{ M } K^+,\ H \text{ M } H^+,\ C \text{ M } F^- \text{ and } (3 + H - C) \text{ M } Cl^-$$

In these measurements two concentrations of total fluoride were studied, namely $C = 0.04944$ M and $C = 0.2225$ M. Table 2 gives –log [F^-] as a function of total H for C = const. The data were treated by means of the generalized least squares program LETAGROPVRID [23]. In the special case considered here the computer calculated those values of K_{11} and K_{12} which minimized the function

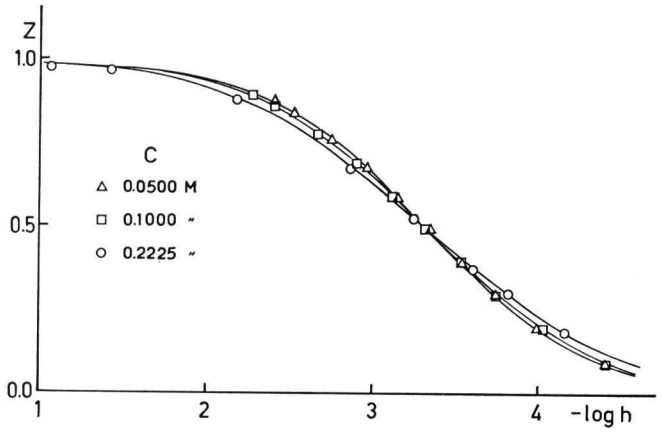

Fig. 6. Z as a function of $\log h$ determined with the quinhydrone electrode. No Nb present. Curves calculated for $\log K_{11} = 3.32$ and $\log K_{12} = 4.07$.

$$U = \Sigma (\zeta_{calc} - \zeta_{exp})^2$$

where ζ is the number of F^- bound per H^+, viz. $\zeta = (C - c)H^{-1}$.

The experimental data were introduced into the program as triplets ($\log c$, H, ζ). The results are given in Table 5. The errors given as usual here represent 3σ where σ is the standard deviation. Fig. 5 shows the experimental points obtained with cell F, together with the curves calculated with the values obtained for K_{11} and K_{12}.

(b) *Determination of K_{11} and K_{12} with the quinhydrone electrode.* In these measurements solutions of the same general composition as named above under (a) were used, but the measurements were now carried out in cell Q. Three sets of data, with the total fluoride concentration C equal to 0.050, 0.100 and 0.2225 M, were measured. The data are given in Table 3 and Fig. 6 as $Z(\log h)$. Here Z is the average number of H^+ bound per fluoride, thus $Z = (H - h)C^{-1}$.

K_{11} and K_{12} were obtained by means of the LETAGROPVRID program, in which this time the error square sum

$$U = \Sigma (Z_{calc} - Z_{exp})^2$$

was minimized in order to get the best fitting values of K_{11} and K_{12}.

As seen in Table 5 the values of $\log K_{11}$ and $\log K_{12}$ obtained by measurements with cell F and cell Q agree well with each other. In Table 5 Ciavatta's [11] values

Table 2. Results from potentiometric measurements with the specific fluoride electrode in the absence of Nb.

Experimental data in the form: H(mM), $-\log[F^-]$.

(1) $C = 0.04944$ M. 21.1, 1.579; 29.6, 1.733; 38.0, 1.954; 42.2, 2.095; 50.6, 2.421; 59.0, 2.713; 63.3, 2.838; 73.8, 3.031; 84.3, 3.185; 94.9, 3.290; 105.4, 3.388; 116.0, 3.447; 126.5, 3.523; 147.6, 3.635;

(2) $C = 0.2225$ M. 42.2, 0.791; 67.5, 0.891; 84.3, 0.974; 118.1, 1.143; 151.8, 1.363; 202.4, 1.890; 253.0, 2.570; 303.6, 2.921;

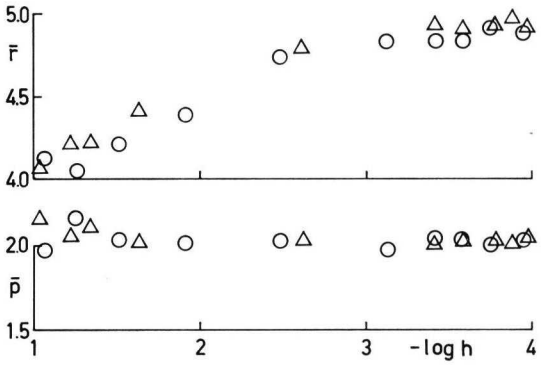

Fig. 7. Average number of fluoride and hydroxide bound per Nb ($\bar{r}$ and $\bar{p}$ respectively). B = 0.010 M (symbol ○) and B = 0.020 M (symbol △). For all points $C/B = 10$.

are also included. The latter agree approximately with our results; note that Ciavatta's data are valid for 3 M K(Cl, F) at 25°C, with C in the range 0.5–2.7 M.

The curves for $\log[F^-]$ as a function of H at constant total fluoride concentration were also calculated using K_{11} and K_{12} from *cell Q*. The curves agreed to within ± 0.01 $\log[F^-]$ units with those obtained with K_{11} and K_{12} from *cell F*. The deviation is barely visible in the small scale of Fig. 5.

These experiments thus indicate that the fluoride electrode gave a Nernst response, eqn (2), with good accuracy also in acidic solutions.

Results for Nb solutions

Determination of the average number of fluoride and hydroxide bound per Nb(V)

Let us write the general overall formula of our Nb(V) complexes in solution as follows

$$Nb_q(OH)_pF_r^{(5q-p-r)}$$

where p, q and r are positive integers.

We shall further try the assumption that our major complexes are mononuclear ($q = 1$).

Our task would now be to find those complexes $Nb(OH)_pF_r^{(5-p-r)}$ which best

Table 3. Results from potentiometric measurements with the quinhydrone electrode in the absence of Nb.

Experimental data in the form: $-\log h$, Z.

(1) $C = 0.050$ M. 4.422, 0.099; 4.010, 0.198; 3.760, 0.296; 3.545, 0.394; 3.359, 0.491; 3.158, 0.586; 2.958, 0.678; 2.747, 0.764; 2.519, 0.839; 2.404, 0.871;

(2) $C = 0.100$ M. 4.415, 0.100; 4.032, 0.199; 3.758, 0.298; 3.535, 0.397; 3.325, 0.495; 3.122, 0.592; 2.894, 0.687; 2.663, 0.778; 2.401, 0.860; 2.257, 0.895;

(3) $C = 0.2225$ M. 4.167, 0.189; 3.827, 0.302; 3.616, 0.378; 3.249, 0.528; 2.857, 0.676; 2.178, 0.880; 1.424, 0.968; 1.061, 0.974;

explain our emf data. For this purpose it is useful to calculate the average values of p and r in our species.

In the mass balance for H and F we must consider, besides the Nb species, also H^+, F^-, HF and HF_2^- whereas $[OH^-]$ is negligible.

We define $\bar{p}$ as the average number of OH^- groups bound per Nb(V) thus

$$\bar{p} = \frac{h + K_{11}hc + K_{12}hc^2 - H}{B} \tag{5}$$

where B is the total niobium concentration and H is the total acidity in excess of F^-, Nb^{5+} and H_2O, and finally h and c denote $[H^+]$ and $[F^-]$.

In the same way $\bar{r}$ is defined as the average number of F^- bound per Nb(V)

$$\bar{r} = \frac{C - c - K_{11}hc - 2K_{12}hc^2}{B} \tag{6}$$

Here C is the total concentration of fluoride added and the other symbols are the same as used in eqn 5.

In Fig. 7 $\bar{p}$ and $\bar{r}$ are plotted as functions of $\log h$ using the values $\log K_{11} = 3.32$ and $\log K_{12} = 4.07$ which were obtained with the quinhydrone electrode. Approximately the same curves $\bar{p}$ ($\log h$) and $\bar{r}$ ($\log h$) are obtained both for $B = 0.01$ M and $B = 0.02$ M. When $\log h$ is varied from -4 to -1, $\bar{r}$ decreases from 5.0 to ca. 4 whereas $\bar{p}$ equals 2 in the whole $\log h$ range. This suggests that Nb(V) is mainly present as the mononuclear species $Nb(OH)_2F_4^-$ and $Nb(OH)_2F_5^{2-}$ in the solutions studied.

In order to check that the fluoride electrode shows no appreciable systematic error in the solutions containing Nb(V) the $\log c$ values obtained by direct measurement were compared with those obtained indirectly by applying an integration procedure suggested by Österberg [24].

This procedure in the present case, gives the relation

$$(\log c)_{\text{calc}} - I = \varphi(\log h) = \int^{\log h} \left(\frac{\delta H}{\delta C}\right)_{B,\log h} d(\log h) \tag{7}$$

where I is an integration constant. If we know the value of the integral in (7) at every $\log h$ measured and also know the $\log c$ value for at least one measured value of $\log h$, we are able to find all other $(\log c)_{\text{calc}}$.

From smoothed curves $H(\log h)_{B,c}$ (see Fig. 1) we constructed curves $H(C)_{B,\log h}$ for intervals of 0.2 in $\log h$. They came out to be straight lines. Their slope gave the derivative $(\delta H/\delta C)_{B,\log h}$ as a function of $\log h$ and the integral was now estimated by graphical integration.

The "best" value for the integration constant I (eqn 7) was calculated as the arithmetic average of the values $(\log c)_{\text{exp}} - \varphi(\log h)$ for the various solutions. From the value of I so obtained, corresponding pairs of $(\log c)_{\text{calc}}$ and $(\log c)_{\text{exp}}$ were calculated. These values are shown in Table 4. The absolute value for $(\log c)_{\text{calc}} - (\log c)_{\text{exp}}$ is on the average 0.012 $\log[F^-]$ units, which corresponds to 0.7 mV. Considering the inavoidable errors introduced in the process of integration the agreement is as good as could be expected, and it seems clear that the fluoride electrode can be used also in the presence of Nb(V).

Table 4. Comparison between $(\log c)_{calc}$ obtained by integration using eqn 7, and $(\log c)_{exp}$ obtained with the specific fluoride electrode.

The two sets of solutions studied with the fluoride electrode are identical with nos. 3 and 8 in Table 1.

$B = 0.010$ M, $C = 0.100$ M			$B = 0.020$ M, $C = 0.200$ M		
$-\log h$	$-(\log c)_{calc}$	$-(\log c)_{exp}$	$-\log h$	$-(\log c)_{calc}$	$-\log c)_{exp}$
3.946	1.417	1.417	3.984	1.145	1.136
3.748	1.478	1.472	3.880	1.175	1.168
3.574	1.542	1.527	3.773	1.210	1.197
3.411	1.611	1.594	3.582	1.280	1.265
3.120	1.757	1.746	3.406	1.355	1.342
2.471	2.195	2.201	2.606	1.824	1.827
1.908	2.673	2.686	1.631	2.639	2.658
1.515	3.034	3.051	1.346	2.904	2.920
1.259	3.280	3.291	1.219	3.023	3.043
1.055	—	3.496	1.031	—	3.217

Determination of the equilibrium constants

The final determination of the equilibrium constants involved in the system studied was made using the data $H(\log h)_{B,C}$ (Table 1), viz. the proton excess H as a function of $\log h$ at constant total niobium and fluoride concentrations.

The values of $\bar{p}$ and $\bar{r}$ (see Fig. 7) indicate that the most probable reaction involving Nb(V)-species is

$$Nb(OH)_2F_4^- + F^- \rightleftharpoons Nb(OH)_2F_5^{2-}$$

with the equilibrium constant

$$K = \frac{[Nb(OH)_2F_5^{2-}]}{[Nb(OH)_2F_4^-]\,[F^-]}$$

Of course, the two equilibria (3) and (4) with the constants K_{11} and K_{12} have also to be taken into account.

If H^+, F^-, HF, HF_2^-, $Nb(OH)_2F_4^-$ and $Nb(OH)_2F_5^{2-}$ are the only species to be considered, the total concentrations of excess protons and of total fluoride can be expressed by

$$H = h + K_{11}hc + K_{12}hc^2 - 2B \tag{8}$$

$$C = c + K_{11}hc + 2K_{12}hc^2 + B(4 + 5Kc)\,(1 + Kc)^{-1} \tag{9}$$

We chose to apply the parameter adjustment to the cell Q data $H(\log h)_{B,C}$, as these data covered a broader range in total fluoride (C), than the data obtained with cell F.

With the computer program LETAGROPVRID [23] we now minimized the function

$$U = \Sigma (H_{calc} - H_{exp})^2 \tag{10}$$

under three different assumptions (I, II and III) which gave different sets of the parameters K_{11}, K_{12} and K in Table 6.

Table 5. Values of $\log K_{11}$ and $\log K_{12}$ obtained from measurements in solutions not containing Nb.

The errors are given as 3σ (σ is the standard deviation).

	$\log K_{11}$	$\log K_{12}$
Data with F^- electrode (cell F)	3.31 ± 0.02	4.03 ± 0.03
Data with quinhydrone electrode (cell Q)	3.32 ± 0.01	4.07 ± 0.06
Ciavatta's data [11]	3.26 ± 0.05	4.00 ± 0.05

I. *No systematic errors assumed.* For a given set of K_{11}, K_{12} and K we know h from E_Q and $E_{Q,0}$, and B and C from the analytical data, and hence could eliminate c from (9) and insert into (8) to get H_{calc}, which was used in calculating U.

We also tested whether, besides $Nb(OH)_2F_4^-$ and $Nb(OH)_2F_5^{2-}$, a few additional complexes of the type $Nb(OH)_pF_r^{(5-p-r)}$ could further decrease the U value (eqn 10). It was assumed that these additional complexes were formed from $Nb(OH)_2F_5^-$ by the reactions

$$Nb(OH)_2F_5^{2-} + (p-2)\,OH^- + (r-5)F^- \rightleftharpoons Nb(OH)_pF_r^{(5-p-r)}$$

with the equilibrium constants β_{pr}. With the help of a "species selector" we tried all reactions with $1 \leqslant p \leqslant 3$ and $3 \leqslant r \leqslant 6$, as well as $p=0$, $r=6$ (NbF_6^-) and $p=0$, $r=7$ (NbF_7^{2-}). The new complexes (all together 12) are now added in turn one after another, and the β_{pr} of the new reactions are varied alone at first to get a better value, and then together with K_{11}, K_{12} and K. The calculation gives the values of β_{pr}, which give a minimum in U, together with their standard deviations $\sigma(\beta_{pr})$. A complex is rejected if the quotient β_{pr}/σ is smaller than a given value "*sigfak*", which was set to 3. It was found that, besides $Nb(OH)_2F_4^-$ and $Nb(OH)_2F_5^{2-}$, none of the other suggested complexes was accepted. Of the rejected complexes, two had β_{pr}/σ values which were only slightly below 3, namely: $Nb(OH)F_6^{2-}$ ($\beta_{pr}/\sigma = 2.9$, $\log \beta_{pr} = -3.4$) and $Nb(OH)_3F_3^-$ ($\beta_{pr}/\sigma = 2.4$, $\log \beta_{pr} = 7.8$). Anyhow, the β_{pr} values for these two complexes were rather undefined compared with our K value ($K/\sigma(K) = 43$). Furthermore the addition of the two complexes did not lead to any significant decrease in U.

II. *Systematic errors in $E_{Q,0}$ assumed.* Systematic errors in $E_{Q,0}$ (eqn 1) were treated as sepa rate parameters, one for each of the ten sets of data given in Table 1, and varied

Table 6. Summary of the LETAGROP calculations for solutions containing Nb.

The errors are given as 3σ (σ is the standard deviation).

set	$\log K_{11}$	$\log K_{12}$	$\log K$	Calculated errors	$\sigma(H)$
I	$3.31_0 \pm 0.005$	4.03 ± 0.02	2.59 ± 0.04	No systematic errors assumed	0.00061
II	$3.31_6 \pm 0.003$	4.04 ± 0.01	2.51 ± 0.03	$\delta E_{Q,0} = 0.1 - 0.6$ mV	0.00034
III	3.34 ± 0.01	4.07 ± 0.02	2.44 ± 0.08	Error in proton concentration of F and Nb stock (see text)	0.00048

in the usual way in a LETAGROP calculation. The errors, $\delta E_{Q,0}$, varied between 0.1 mV and 0.6 mV for the different sets of data (Table 1). This seems to be within what might be expected in our measurements.

III. *Systematic errors in H assumed.* Small systematic errors in H were assumed to originate from an excess (or deficiency) of H^+ in the stock solutions of $K_7HNb_6O_{19}$ and KF, whereas our HCl stock was assumed to have the correct composition. The "best" values for this proton error were found to be about 0.7–1.1 % of C, which seems to be bigger than plausible, considering the good agreement between the two methods of analysis for our KF stock solution, as well as the excellent reproducibility of the K and Nb analyses. Also, the log K_{11} value in set III deviated significantly from log K_{11} obtained with the cells F and Q in the absence of Nb (Table 5). Thus there seems to be good reason to prefer the equilibrium constants in set II, which furthermore also gave the lowest $\sigma(H)$ value. In Table 1 the difference $(H_{calc} - H_{exp})$ has been calculated using the equilibrium constants of set II and the corrections $\delta E_{Q,0}$.

Discussion

As seen from the previous section the present data do not suggest that complexes with more than five fluoride atoms bound to one Nb, such as NbF_6^-, $NbOF_6^{3-}$ or NbF_7^{2-} (see "previous work"), are present to any significant extent in the solutions studied. On the other hand, there is clear evidence for the presence of $NbOF_5^{2-}$ which has previously been found in crystalline K_3HNbOF_7 [6].

When $\log h > -2$ the ion $Nb(OH)_2F_4^-$ dominated in our solutions. This ion does not seem to have been reported earlier, either in the solid state or in solution. It is, however, of some interest that Hoard and Martin [6] suggested that the substance $K_5Nb_3O_3F_{14} \cdot H_2O$ might contain mononuclear groups, and its formula consequently be written $K_5[NbOF_5]_2\,[Nb(OH)_2F_4]$. On the other hand, there is as yet no experimental evidence for that assumption. In this connection one should remember that Raman spectra of solutions of K_2NbOF_5 in 23 M HF [9] are said to indicate the presence of NbF_6^-. However, Raman active lines for those molecular vibrations, in which the OH^-group can be regarded as *one* vibrating unit ("skeletal" vibration, see ref [25]) should be rather similar to corresponding F^- vibrations [9]. Examples of this are the similarity of the Raman spectra of $B(OH)_3$ and BF_3 [25] as well as those of $Te(OH)_6$ [26] and TeF_6 [27]. Thus it can not be excluded that $Nb(OH)_2F_4^-$ could be present in 23 M HF instead of the NbF_6^- suggested in ref [9].

Although the difference in the activity factors might be appreciable when changing from 3 M KCl medium to 23 M HF, it still seems reasonable to assume that in 23 M HF the activity ratio F^-/OH^- is not high enough to cause the formation of NbF_6^-, rather than of $Nb(OH)_2F_4^-$.

The present data are somewhat less accurate than those usually sought for and obtained by precise potentiometry. On the other hand the simple reaction supposed agrees well with all the sets of data and the deviations can be explained with reasonable experimental errors. It seems most unlikely that there is any systematic error in the data that could influence the conclusions as to which major Nb(V)-species are present in the solutions.

The reliability of the methods is supported by the excellent agreement of the equilibrium constants K_{11} and K_{12} (log K_{11} to 0.01 units) when independently measured with the fluoride electrode and the quinhydrone electrode, with the latter both in the presence and absence of Nb(V), see Tables 5 and 6.

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