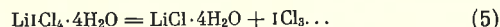


This mechanism of the decomposition of the monohydrate is confirmed when the loss in mass is compared with that expected from theory (TGA curve in Fig. 1e) (Eqns. 3 and 4). According to Eqns. (3) and (4), the volatile products lost in the first and second stages correspond to 23.0 wt. % and 75.7 wt. % respectively, whereas the corresponding figures from the TGA curve (Fig. 1e) are 30.0 wt. % and 75.4 wt. % respectively.

When heated, lithium tetrachloroiodate decomposes according to the equation:



followed by dehydration of the lithium chloride hydrate. Loss of iodine trichloride begins at 27°C and is complete at 105°C; it corresponds to a loss in mass of 64.9 wt. % on the TGA curve (Fig. 1f)—theoretical according to Eqn. (5) is 67.0 wt. %. The decomposition of $\text{LiICl}_4 \cdot 4\text{H}_2\text{O}$, unlike that of the other tetrachloroiodates, does not pass through a stage involving the formation of the dichloroiodate, since the latter is unstable in the solid state. The two stages in the thermal decomposition of $\text{LiICl}_4 \cdot 4\text{H}_2\text{O}$ are fairly distinctly separated, as is indicated by the fact that the DTGA curve (Fig. 1f) returns to its initial position. Determination of the water with the Karl Fischer reagent in the intermediate and final products of the decomposition of lithium tetrachloroiodate confirmed results from the derivatographic method.

SUMMARY

The mechanism of the thermal decomposition of lithium, potassium, ammonium, rubidium, and caesium tetrachloroiodates has been studied by derivatographic, X-ray diffraction, and chemical analyses. Ammonium, rubidium, and caesium tetrachloroiodates decompose when heated with the formation of an intermediate product—the anhydrous dichloroiodate. When heated, potassium tetrachloroiodate monohydrate forms $\text{KICl}_2 \cdot \text{H}_2\text{O}$, which then decomposes to KCl , ICl , and H_2O . When heated, lithium tetrachloroiodate decomposes to iodine trichloride and hydrated lithium chloride.

13. R.P. Lastovskii and Yu.I. Vainshtein, "Tekhnicheskii Analiz v Proizvodstve Promezhutochnykh Produktov i Krasitelei" (Technical Analysis in the Production of Dyes and Intermediates), Goskhimizdat, Moscow, 1958, p.17.
14. H.L. Wells, H.L. Wheeler, and S.L. Penfield, Amer. J. Sci., [3], 44, 42 (1892).
15. M.G. de Celis and E. Moles, Anales Real Soc. Espan. Fis. Quim. (Madrid), 30, 540 (1932); Chem. Abs., 26, 5508 (1932).
16. M.G. de Celis, Anales Real Soc. Espan. Fis. Quim. (Madrid), 33, 203 (1935); Chem. Abs., 29, 6521 (1935).
17. E. Filhol, J. Pharm. Chim., 25, 431 (1839); J. prakt. Chem., 18, 457 (1839).
18. A.A. Fakeev, B.D. Stepin, and V.N. Kulyukin, Zhur. Neorg. Khim., 11, 1469 (1966) [Russ. J. Inorg. Chem., 785 (1966)].
19. B.D. Stepin, V.I. Safonova, A.A. Fakeev, and V.N. Kulyukin, USSR P. 176 272 (1965); Byull. Izobret., No. 22, 24 (1965).
20. F. Paulik, J. Paulik, and L. Erdey, Acta Chim. Acad. Sci. Hung., 10, 61 (1956).
21. F. Paulik, J. Paulik, and L. Erdey, Z. analyt. Chem., 160, 241 (1958).
22. L. Erdey, F. Paulik, and J. Paulik, Nature, 174, 885 (1954).
23. L.I. Mirkin, "Spravochnik po Rentgenostrukturnomu Analizu Polikristallov" (Reference Book on the X-Ray Diffraction Study of Polycrystalline Materials), Fizmatgiz, Moscow, 1961.
24. P.J. Elema, J.L. de Boer, and A. Vos, Acta Cryst., 16, 243 (1963).

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INTERACTION OF HYDRATED NIOBIUM PENTOXIDE WITH HYDROFLUORIC ACID

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and V.V. Lukachina

Relatively little work has been done on the fluoro-complexes of niobium in solutions. The studies on the solubility and hydrolysis in the system hydrofluoric acid-niobium pentafluoride-water established¹ that in the presence of a considerable excess of fluoride the complex H_2NbOF_5 is formed. It has been shown² by investigating the solubility in the system $\text{K}_2\text{NbF}_7\text{-HF-H}_2\text{O}$ that in the presence of the solid phase the compounds K_2NbOF_5 , K_2NbF_7 , or KNbF_6 are formed, depending on the concentration of hydrofluoric acid. The existence of the last compound in acetonitrile solution was established by infrared spectroscopy³. In the above experiments a considerable excess of fluoride relative to niobium was present and there were moderately acid solutions in which the pH was determined by the free hydrofluoric acid. Presumably, however, when freshly precipitated niobium hydroxide and hydrofluoric acid react, a number of compounds consisting of products in which the OH groups of the hydroxide are replaced by fluoride ions, will be formed, depending on the excess of the hydrofluoric acid and the acidity.

1. B.D. Stepin, V.E. Plyushchev, and A.A. Fakeev, Uspekhi Khim., 34, 1881 (1965) [Russ. Chem. Rev., 811 (1965)].
2. W.N. Rae, J. Chem. Soc., 107, 1286 (1915).
3. W.N. Rae, J. Chem. Soc., 113, 880 (1918).
4. R.C.L. Mooney, Z. Krist., 98, 377 (1937).
5. V. Cagliotti and G. Centola, Gazzetta, 63, 907 (1933).
6. H. Erdmann, Arch. Pharm., 232, 30 (1894).
7. Ya. A. Fialkov, "Mezhhalogidnye Soedineniya" (Interhalogen Compounds), Kiev, 1958, p. 284.
8. D. Smith and M.E. Cutler, J. Amer. Chem. Soc., 80, 4462 (1958).
9. B.D. Stepin and A.A. Fakeev, in Collected Papers, "Sovremennye Khimicheskie i Spekttral'nye Metody Analiza" (Modern Chemical and Spectroscopic Methods of Analysis), Metallurgizdat, Moscow, 1966.
10. W. Geilmann and W. Gebauhr, Z. analyt. Chem., 139, 161 (1953).
11. J. Mitchell and D.M. Smith, "Aquametry, the Application of the Karl Fischer Reagent to Quantitative Analyses Involving Water" (Translated into Russian), Inostr. Lit., Moscow-Leningrad, 1952.
12. "Khimicheskie Reaktivy i Preparaty" (Chemical Reagents and Materials), No. 2, Moscow, 1960, p. 44.

Here we have attempted to investigate the first stages of the interaction between $\text{Nb}(\text{OH})_5$ † and hydrofluoric acid at low fluoride concentrations over a wide range of acidities. To do this, we had to develop a sensitive method for the determination of low fluoride concentrations in the presence of niobium. The technique was based on the decolorisation of the ternary complex niobium-catechol-ethylenediaminetetra-acetic acid by fluoride. With a number of details omitted, the technique was as follows.

The concentration of niobium in the test solution was determined photometrically from its reaction with Xylenol Orange⁴ after the removal of fluoride by evaporation with sulphuric acid. Then an amount of the test solution, such that after dilution to 25 ml the concentration of niobium in it was 1×10^{-4} M, was treated with the calculated amount of standard potassium niobate solution, and with 5 ml of 1×10^{-2} M solution of disodium ethylenediaminetetra-acetate. To this phenolphthalein was added, and then 1 M potassium hydroxide solution, dropwise, until the appearance of a pink colour. The mixture was boiled for 20–30 s. It was cooled, treated dropwise with 1 M sulphuric acid solution until the disappearance of the colour of the indicator, and then with 2.5 ml of 1 M catechol solution and 2.5 ml of a buffer solution at pH approx. 2.5 (9.45 g of monochloroacetic acid and 2.80 g of potassium hydroxide dissolved in 100 ml of water); it was finally diluted with water to 25 ml. After 30 min, the optical density of the solution was measured with an FEKN-57 photoelectric colorimeter provided with a No. 3 filter ($\lambda_{\text{max}} = 453$ nm), a cuvette with an optical pathlength of 20 mm being used. Water served as the reference solution. The concentration of fluoride in the test solution was found from the calibration curve shown in Fig. 1.

We investigated the effect of the pH on the solubility of freshly precipitated niobium hydroxide in the presence of various amounts of hydrofluoric acid in excess.

Alkaline 0.1 M solution of potassium niobate was placed in a series of flasks (5 ml in each) and 1 N nitric acid was added until the pH was approx. 5 (according to indicator paper); niobium hydroxide was then precipitated. The

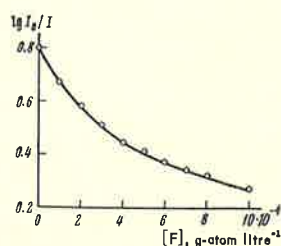


Fig. 1. Calibration curve for the determination of the concentration of fluoride: $c_{\text{Nb}} = 1 \times 10^{-4}$ M; $[\text{EDTA}] = 2 \times 10^{-3}$ M; $[\text{catechol}] = 0.1$ M; pH 2.5; $l = 2$ cm; $\lambda_{\text{eff}} = 453$ nm.

† By this formula we emphasise the presence in niobium hydroxide of OH^- groups; however, it is possible that the formula $\text{NbO}(\text{OH})_3$ is more correct, but this is unimportant in further discussion.

precipitate was treated with nitric acid, to ensure a definite acidity of the solution, and various amounts of hydrofluoric acid. Potassium nitrate was added to solutions with $[\text{H}^+] < 0.5$ N to set up an ionic strength of 0.5. The volume was adjusted to 100 ml with water and the solutions were allowed to stand for 2–3 weeks, with periodic shaking, to attain equilibrium. The acidity of the equilibrium solutions was checked potentiometrically with the quinhydrone electrode ($\text{pH} > 0$) and by titration with alkali (for $\text{pH} \leq 0$). After the attainment of equilibrium, the precipitates were separated by centrifugation at $10\,000 \text{ rev min}^{-1}$ for 1 h, after which the solutions did not show the Tyndall effect. The concentration of niobium in the equilibrium solutions was determined photometrically by reaction with Xylenol Orange⁴ after the removal of hydrofluoric acid by evaporation with sulphuric acid. The total concentration of fluoride was determined as described above. The results (Fig. 2) reveal a complex dependence of the solubility on the pH. We postulated that this dependence is due to the fact that at $\text{pH} < 0$ and $\text{pH} > 0$ deposits of different composition dissolve. To confirm this hypothesis, we further investigated the effect of fluoride concentration on the composition of the solid phases at different pH values.

Composition of the Deposits and Their Solubility

The experiments were similar to those described above. The results (Table 1) show that the interaction of $\text{Nb}(\text{OH})_5$ with fluoride results in partial precipitation of the former; in 3 N nitric acid the composition of the deposit corresponds to the ratio $\text{F}:\text{Nb} = 2:1$, while in the range $[\text{H}^+] = 1.0\text{--}0.1$ N it corresponds to the ratio $\text{F}:\text{Nb} = 1:1$. At $\text{pH} > 2$ (these results are not included in the Table) the $\text{F}:\text{Nb}$ ratio in the precipitate increases with the amount of fluoride added; probably under these conditions niobium penta-, hexa-, and hepta-fluorides, which have been described², are formed. The results confirm our hypothesis concerning the reason for the complex variation of the solubility with the pH (Fig. 2).

A precipitate of $\text{Nb}(\text{OH})_3\text{F}_2$ is formed in 3 N nitric acid and also probably in more acid solutions, in the range of

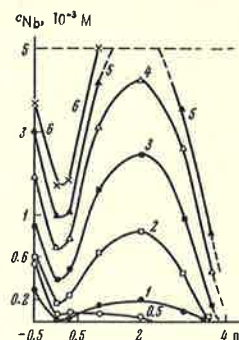


Fig. 2. Variation of the solubility of freshly precipitated $\text{Nb}(\text{OH})_5$ with the pH and the amount of fluoride added; the numerals against the curves denote the ratio of the total amount of added fluoride (in moles) to the total amount of niobium (in moles).

TABLE 1. Determination of the composition of the solid phases in the dissolution of hydrated niobium pentoxide in hydrofluoric acid [total concentration of niobium (solution together with precipitate) = 5×10^{-3} g-atom litre $^{-1}$; temperature 18°C].

$[\text{HF}]_{\text{add}} \times 10^3, \text{M}$	$\frac{\text{HF}_{\text{add}}}{\text{Nb}_{\text{add}}}$	3 N HNO ₃			1 N HNO ₃			0.5 N HNO ₃			pH 1.0			pH 2.0		
		$[\text{Nb}] \times 10^4$ soln.	$[\text{HF}] \times 10^3$ soln.	F:Nb ppt.	$[\text{Nb}] \times 10^4$ soln.	$[\text{HF}] \times 10^3$ soln.	F:Nb ppt.	$[\text{Nb}] \times 10^4$ soln.	$[\text{HF}] \times 10^3$ soln.	F:Nb ppt.	$[\text{Nb}] \times 10^4$ soln.	$[\text{HF}] \times 10^3$ soln.	F:Nb ppt.	$[\text{Nb}] \times 10^4$ soln.	$[\text{HF}] \times 10^3$ soln.	F:Nb ppt.
0	—	0.23	—	—	0.14	—	—	0.14	—	—	0.14	—	—	0.14	—	—
1.00	0.20	6.47	0.96	0	1.26	1.10	0	0.28	0.41	0.12	0.16	—	—	—	—	—
1.60	0.32	6.20	1.70	0	1.70	1.70	0	0.31	0.64	0.19	0.19	—	—	—	—	—
2.50	0.50	5.45	2.56	0	0.92	1.56	0.19	0.77	0.72	0.36	0.22	0.24	0.45	0.14	—	—
4.00	0.80	4.20	2.30	0.37	0.17	0.40	0.72	0.16	0.60	0.68	0.71	0.75	0.65	1.02	1.12	0.59
6.00	1.20	2.84	1.56	0.95	0.24	0.70	1.06	0.58	0.67	1.08	1.96	1.70	0.90	3.30	2.40	0.77
10.00	2.00	3.52	1.83	1.76	1.94	4.60	1.04	2.50	4.37	1.18	7.55	5.50	1.06	7.72	4.40	1.33
16.00	3.20	10.0	6.50	2.37	4.00	12.1	0.81	5.55	10.5	1.23	18.90	13.00	0.97	28.00	13.00	1.36
25.00	5.00	30.4	21.00	2.00	10.2	21.0	1.00	11.1	20.6	1.13	42.00	24.0	1.25	complete dissolution of precipitate		
40.00	8.00	43.0	38.5	2.14	30.0	38.1	0.95	31.6	38.2	0.98	complete dissolution of precipitate			complete dissolution of precipitate		

pH 0–2 the precipitate is $\text{Nb}(\text{OH})_4\text{F}$ †, and, on further increase of the pH, precipitates with a higher fluorine content are formed (we did not investigate in greater detail this acidity range). The complex variation of the solubility with the pH is due to the dissolution of precipitates of various compositions in media of different acidity and, as will be shown below, the chemistry of their dissolution is also different.

The solubilities of $\text{Nb}(\text{OH})_3\text{F}_2$ and $\text{Nb}(\text{OH})_4\text{F}$ cannot be determined directly, since in the absence of an excess of fluoride they are hydrolysed. Therefore, we determined their solubility by the graphical extrapolation previously used for the oxalato-complexes of tantalum⁵. Using the data of Table 1, we constructed a logarithmic plot of the total concentration of niobium in the solutions in equilibrium with the deposits (c_{Nb}) against the ratio $F_{\text{add}}/\text{Nb}_{\text{add}}$ for $c_{\text{HNO}_3} = 3 \text{ N}$ and pH 1 (F_{add} and Nb_{add} are the total amounts of fluoride and niobium in moles)§.

The relations obtained were extrapolated to $F_{\text{add}}/\text{Nb}_{\text{add}}$ corresponding to the composition of the deposit at the given acidity of the medium. Thus curve 1 in Fig. 3 was extrapolated to $\lg(F_{\text{add}}/\text{Nb}_{\text{add}}) = 0.3$, since in 3 N nitric acid the sparingly soluble compound with F:Nb = 2 is formed. Curve 2 in Fig. 3 was extrapolated to $\lg(F_{\text{add}}/\text{Nb}_{\text{add}}) = 0$, which corresponds to the formation at pH 1 of the sparingly soluble compound with F:Nb = 1.

The results (Fig. 3) show that the solubility of $\text{Nb}(\text{OH})_4\text{F}$ is about 0.6×10^{-5} mole litre $^{-1}$ (pH 1.0) and that of $\text{Nb}(\text{OH})_3\text{F}_2$ is about 1.5×10^{-5} mole litre $^{-1}$ (3 N HNO₃). Under the same conditions in the absence of fluoride the solubility of $\text{Nb}(\text{OH})_5$ is somewhat higher, amounting to 1.4×10^{-5} mole litre $^{-1}$ (pH 1.0) and 2.3×10^{-5} mole litre $^{-1}$ (3 N HNO₃).⁶ Although the solubilities of $\text{Nb}(\text{OH})_4\text{F}$ and

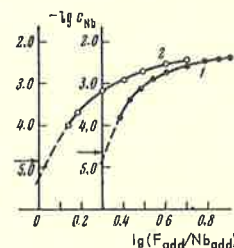


Fig. 3. Graphical determination of the solubilities of $\text{Nb}(\text{OH})_3\text{F}_2$ and $\text{Nb}(\text{OH})_4\text{F}$: 1) 3 N HNO₃; 2) pH 1.0; the arrows indicate the solubility of $\text{Nb}(\text{OH})_5$ in the absence of fluoride.

$\text{Nb}(\text{OH})_3\text{F}_2$ obtained are only approximate due to the possible error in the extrapolation, they nevertheless show that in our system there is a conversion of the more soluble $\text{Nb}(\text{OH})_5$ solid phase into less soluble deposits containing fluoride ions.

The Composition and Chemistry of the Formation of Soluble Fluoride Complexes

Fig. 4 shows the dependence of the concentration of niobium in the solutions in equilibrium with the deposits on the $F_{\text{add}}/\text{Nb}_{\text{add}}$ ratio for various acidities of the medium. The solubility curves have maxima at $F_{\text{add}}/\text{Nb}_{\text{add}} < 1$. Under these conditions (Table 1) the solid is niobium hydroxide. The maxima on the solubility curves are probably due to the fact that in the absence of an excess of fluoride the polymeric niobium species containing fluoride ions are dissolved. With increase in the total amount of fluoride, the solid hydroxide is converted into sparingly soluble fluoride compounds; this causes first a breakdown of the polymers and a decrease of the solubility and then an increase due to the formation of soluble fluoride complexes.

To determine the composition of the soluble complexes, we subjected the ascending branches of the curve in Fig. 4 to a mathematical treatment based on the principle of the equilibrium displacement method. The dissolution of

† Addition experiments established that at pH 1.8 the interaction between $\text{Nb}(\text{OH})_5$ and hydrofluoric acid (in the presence of nitric acid and potassium nitrate) takes place without change in the acidity of the medium. This suggests the reaction $\text{Nb}(\text{OH})_5 + \text{HF} = \text{Nb}(\text{OH})_4\text{F} + \text{H}_2\text{O}$; a compound of the type $\text{Nb}(\text{OH})_5 \cdot \text{KF}$ does not form, since this would result in a lowering of the pH, which does not in fact happen.

§ Using results in Table 1 we initially plotted the function $c_{\text{Nb}} = f(F_{\text{add}}/\text{Nb}_{\text{add}})$, which is shown in Fig. 4. In the graphical determination of the solubilities of $\text{Nb}(\text{OH})_4\text{F}$ and $\text{Nb}(\text{OH})_3\text{F}_2$ we used only those sections of the curves in Fig. 4 along which c_{Nb} increases continuously with $F_{\text{add}}/\text{Nb}_{\text{add}}$.

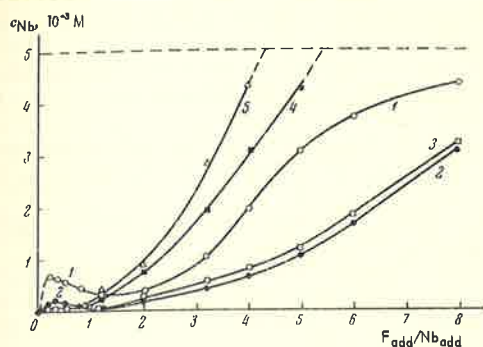
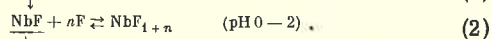
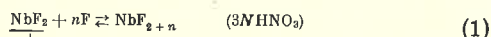


Fig. 4. Effect of an excess of fluoride on the solubility of the fluoride compounds of niobium for different acidities of the medium:
1) 3 N HNO₃; 2) 1 N HNO₃; 3) 0.5 N HNO₃; 4) pH 1.0; 5) pH 2.0; overall concentration of niobium (solution together with precipitate) 5×10^{-3} M.

Nb(OH)₃F₂ and Nb(OH)₄F after the concentration of fluoride has been increased can be represented by the mechanism†



When the concentration of niobium (c_{Nb}) appreciably exceeds the intrinsic solubilities of Nb(OH)₃F₂ and Nb(OH)₄F, the equilibrium constants for reactions (1) and (2) can be represented by a formula of the form

$$K_{\text{eq}} = \frac{c_{\text{Nb}}}{[\text{F}]^n} \quad (3)$$

where $[\text{F}]$ is the concentration of non-complexed fluoride.

Table 2 presents the values of c_{Nb} and of the overall concentrations c_{HF} in solutions in equilibrium with the deposits for various $F_{\text{add}}/\text{Nb}_{\text{add}}$ ratios and various acidities of the solutions. It is evident that c_{Nb} is comparable with the overall concentration of hydrofluoric acid in the solution: therefore, to determine n in Eqn. (3), one cannot use the usual logarithmic method, assuming that $[\text{F}] \approx c_{\text{HF}}$. We calculated K_{eq} for various values of n taking into account the fractions of fluoride bound to niobium; it was found that K_{eq} remains constant only for $n = 1$ when c_{Nb} and c_{HF} are varied. The data required for the calculation are presented in Table 2. Using these data, $\lg c_{\text{Nb}}$ was plotted against $\lg [\text{HF}]$; the slopes of the lines in Fig. 5 are unity.

Thus in this range of acidities and fluoride concentrations the deposits are dissolved by the addition of one fluoride ion, and complexes with the compositions Nb:F = 1:3 (3 N HNO₃) and Nb:F = 1:2 (pH 0-2) are formed in solution.

To elucidate the chemistry of the formation of soluble fluoride complexes, we determined their charges by electroanalysis and ion-exchange chromatography. The solutions in equilibrium with the precipitates were used in the electroanalysis experiments the solutions in which

† In the presence of an excess of fluoride polymeric forms of niobium do not form⁷.

TABLE 2. Calculation of the equilibrium constants.

3N HNO ₃ ; [Nb(OH) ₃ F ₂] = 1.5×10^{-5} M					0.5N HNO ₃ ; [Nb(OH) ₃ F ₂] = 0.6×10^{-5} M					pH 1; [Nb(OH) ₃ F ₂] = 0.6×10^{-5} M				
Initial F: Nb	$c_{\text{Nb}} \cdot 10^3$	$c_{\text{HF}} \cdot 10^3$	$[\text{HF}] \cdot 10^3$	$K_{\text{eq}} \cdot 10^5$	$c_{\text{Nb}} \cdot 10^3$	$c_{\text{HF}} \cdot 10^3$	$[\text{HF}] \cdot 10^3$	$K_{\text{eq}} \cdot 10^5$		$c_{\text{Nb}} \cdot 10^3$	$c_{\text{HF}} \cdot 10^3$	$[\text{HF}] \cdot 10^3$	$K_{\text{eq}} \cdot 10^5$	
2.0	—	—	—	—	0.25	4.40	3.90	1.87		0.65	5.70	4.20	3.88	
2.5	0.55	2.80	1.15	(1.34)	0.38	7.00	6.24	1.97		1.05	8.50	7.40	4.22	
3.0	0.87	5.00	2.39	4.12	0.51	9.40	8.38	1.97		1.60	11.5	8.30	3.12	
3.5	1.30	9.00	5.10	5.90	0.65	11.9	10.6	1.96		2.35	15.0	10.3	2.63	
4.0	1.90	12.7	7.00	5.53	0.79	14.5	12.9	1.96		3.07	18.0	11.9	2.33	
4.5	2.40	17.5	10.3	6.45	0.94	17.0	15.1	1.93		3.70	22.0	14.6	2.37	
5.0	3.00	21.0	12.0	6.00	1.11	20.6	18.4	1.98		4.20	23.5	15.1	2.16	
6.0	3.65	29.0	18.0	7.40	1.80	30.6	27.0	1.80		—	—	—	—	
7.0	4.10	34.5	22.2	8.10	2.50	33.0	28.0	1.80		—	—	—	—	
8.0	4.30	38.5	25.6	(8.93)	3.16	38.2	31.9	1.21		—	—	—	—	

$$\text{mean } K_{\text{eq}1} = (6.2 \pm 1.6) \cdot 10^{-5}$$

$$\text{mean } K_{\text{eq}2} = (2.3 \pm 0.6) \cdot 10^{-4}$$

$$* [\text{HF}] = c_{\text{HF}} - 3c_{\text{Nb}}$$

$$** [\text{HF}] = c_{\text{HF}} - 2c_{\text{Nb}}$$

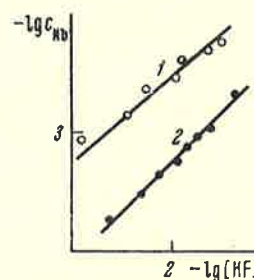


Fig. 5. The effect of the concentration of hydrofluoric acid on the dissolution of Nb(OH)₃F₂ (line 1) and Nb(OH)₄F (line 2):
1) 3 N HNO₃; 2) 0.5 N HNO₃.

the concentrations of nitric and hydrofluoric acids were equal to those in the test solution were placed in the side chambers of the apparatus. The results (Table 3) show that an electrically neutral complex forms in 3 N HNO₃ and an anionic complex in the pH range 0-2. In accordance with the composition of the complexes, their formation can be represented by the reactions

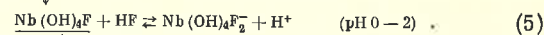
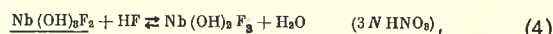


Table 2 presents the results of the calculation of the equilibrium constants for reactions (4) and (5). In the calculation account was taken of the fact that $[\text{Nb(OH)}_3\text{F}_2] = \text{const.} \approx 1.5 \times 10^{-5}$ M and $[\text{Nb(OH)}_4\text{F}] = \text{const.} \approx 0.6 \times 10^{-5}$ M, and the concentration of the soluble fluoride complex is almost equal to the concentration of niobium (c_{Nb}) in the solutions in equilibrium with the deposit. The following values were obtained:

$$K_{\text{eq}1} = \frac{[\text{Nb(OH)}_3\text{F}_3] \cdot [\text{HF}]}{[\text{Nb(OH)}_3\text{F}_2]} = (6.2 \pm 1.6) \times 10^{-5} \quad (\mu = 3.0)$$

$$K_{\text{eq}2} = \frac{[\text{Nb(OH)}_4\text{F}_2^-] \cdot [\text{H}^+]}{[\text{Nb(OH)}_4\text{F}]} = (2.3 \pm 0.6) \times 10^{-4} \quad (\mu = 0.5)$$

Using the equilibrium constants $K_{\text{eq}2}$ and the dissociation constants of hydrofluoric acid (6.8×10^{-4}), we calculated

TABLE 3. Electrodialysis and absorption of niobium by an anion exchanger* in fluoride solutions (0.1 g of Dowex 1×2, 10 ml of solution).

Medium	C_{Nb} 10^{-3} M	C_{HF} 10^{-2} M	Electrodialysis, $I = 160$ mA					Percentage absorption by anion ex- changer
			E , V	duration, min	Nb found, 10^{-4} mole			
					catho- lyte	anolyte	control expt. (no current)	
3 N HNO ₃	2.0	1.3	9.0	300	8.9 9.5 9.0	9.1 9.2 9.1	8.8 9.4 9.0	not absorbed
1 N HNO ₃	0.7	1.6	10	300	8.9 9.1 8.7	11.1 10.5 10.9	8.7 9.1 8.6	12.0 10.3 12.1
0.5 N HNO ₃	0.8	1.5	13	240	7.3 7.0 7.1	13.0 11.8 12.2	7.2 7.1 7.5	22.5 23.0 21.0
0.1 N HNO ₃ pH 1	3.0	1.8	—	—	—	—	—	24.0 21.0
pH 2	2.8	1.6	—	—	—	—	—	22.5 25.0

* KU-2 cation-exchange resin does not absorb niobium from fluoride solutions.

the second stepwise instability constant of the fluoride complex of niobium:

$$K_2 = \frac{[\text{Nb}(\text{OH})_4\text{F}^+][\text{F}^-]}{[\text{Nb}(\text{OH})_4\text{F}_2^-]} = (1.6 \pm 0.6) \times 10^{-7} \quad (\mu = 0.5).$$

The value obtained shows that the stability of the fluoride complexes of niobium is close to the stability of the fluoride complexes of zirconium ($K_2 = 0.48 \times 10^{-7}$).⁸

The experimental results show that the system $\text{Nb}(\text{OH})_5$ -HF is very complex; because of the formation of sparingly soluble fluoride compounds of niobium of different compositions, it is impossible to apply the solubility method for a more complete investigation of the compositions and stabilities of the soluble fluoride complexes. However, confirmation has been obtained for the initial hypothesis that a number of fluoride complexes of niobium, which are products of the addition of fluoride ions to the hydroxo-cations of niobium of different compositions, may be formed.

SUMMARY

The first stages of the interaction between freshly precipitated niobium hydroxide and hydrofluoric acid have been investigated in the range of acidities of the medium between 3 N HNO₃ and pH 2 by solubility, electrodialysis, and ion-exchange chromatographic methods. The formation of the sparingly soluble compounds $\text{Nb}(\text{OH})_3\text{F}_2$ and $\text{Nb}(\text{OH})_4\text{F}$ (their solubilities are 1.5×10^{-5} and 0.6×10^{-5} mole litre⁻¹) has been established. In the presence of a slight excess of fluoride, the soluble complexes $\text{Nb}(\text{OH})_2\text{F}_3$ and $\text{Nb}(\text{OH})_4\text{F}_2^-$ are formed; the corresponding equilibrium constants have been determined. The instability constant $K_2 = [\text{Nb}(\text{OH})_4\text{F}][\text{F}^-]/[\text{Nb}(\text{OH})_4\text{F}_2^-] = (1.6 \pm 0.6) \times 10^{-7}$.

1. N. S. Nikolaev and Yu. A. Buslaev, Zhur. Neorg. Khim., **4**, 205, 543 (1959) [Russ. J. Inorg. Chem., **84**, 246 (1959)].
2. G. S. Savchenko and I. V. Tananaev, Zhur. Prikl. Khim., **19**, 1093 (1946).
3. K. J. Packer and E. L. Mvetteties, J. Amer. Chem. Soc., **85**, 3035 (1963).

4. E. K. Babko and M. I. Shtokalo, Zhur. Anal. Khim., **7**, 1068 (1962).
5. A. K. Babko, V. V. Lukachina, and B. I. Nabivanets, Zhur. Neorg. Khim., **10**, 865 (1965) [Russ. J. Inorg. Chem., **467** (1965)].
6. A. K. Babko, V. V. Lukachina, and B. I. Nabivanets, Zhur. Neorg. Khim., **8**, 1839 (1963) [Russ. J. Inorg. Chem., **957** (1963)].
7. G. I. Gridchina, Zhur. Neorg. Khim., **8**, 634 (1963) [Russ. J. Inorg. Chem., **322** (1963)].
8. K. B. Yatsimirskii and V. P. Vasil'ev, "Konstanty Nestoikosti Kompleksnykh Soedinenii" (Instability Constants of Complex Compounds), Izd. Akad. Nauk SSSR, Moscow, 1959, p. 118.

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MIXED INDIUM(III) HEXACYANOFERRATES(II)

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Published data on indium hexacyanoferrates(II) are contradictory¹⁻⁵. The present paper gives the results of a study of reaction in In^{3+} - $\text{M}_4[\text{Fe}(\text{CN})_6]\text{-H}_2\text{O}$ systems, where $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{or Cs}$.

Investigation of the compositions of mixed copper hexacyanoferrates(II)⁶ and uranyl hexacyanoferrates(II)^{7,8} showed that the potentiometric method is convenient for finding the composition of mixed hexacyanoferrates(II), particularly as many hexacyanoferrates(II) are very readily peptised and this creates considerable difficulties when other methods are used.

The redox potentials were determined on an LP-5 potentiometer with a platinum indicator electrode and a saturated calomel electrode. We used 0.1 M and 0.01 M working solutions of indium(III) nitrate and alkali metal hexacyanoferrates(II) and hexacyanoferrates(III). Lithium hexacyanoferrate(II) solution was prepared from potassium hexacyanoferrate(II) with the intermediate formation of lead hexacyanoferrate(II)⁹. Lithium hexacyanoferrate(III) was prepared by oxidising lithium hexacyanoferrate(II) with chlorine water. Hexacyanoferrate(II) in the solutions was determined by titrating with potassium permanganate in 1 N sulphuric acid. Indium nitrate in the solutions was determined by precipitating with ammonia; the precipitate was filtered off, calcined, and weighed⁹.

To observe how the composition of the precipitate depended on the alkali metal present in the solution, we carried out the potentiometric titration of the original indium nitrate solution with lithium, sodium, and potassium hexacyanoferrate(II) solutions, to which, in separate experiments, equivalent quantities of the following reagents were added: NaCl, KCl, RbCl, or CsCl; KCl, RbCl, or CsCl; and RbCl or CsCl. Thus twelve titrants were used. The titration was made with vigorous stirring for definite time intervals. The experiments were carried out with the addition of the corresponding hexacyanoferrates(III) to the hexacyanoferrate(II) solutions, and also with the addition of the hexacyanoferrates(III) to the indium nitrate solution. It was found that in the potentiometric titration of indium