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Solubility of Niobic Oxide and Niobium Dioxyfluoride in Nitric Acid–Hydrofluoric Acid Solutions at 25° C.

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The solubilities of niobic oxide and niobium dioxyfluoride were determined at 25° C. in hydrofluoric acid solutions that initially were up to 25M in HF and in nitric acid–hydrofluoric acid solutions that initially were up to ~20M in HNO_3 and 5M in HF. In all cases, the niobium concentration in the saturated solution was about one fifth the total fluorine concentration, indicating that niobium was present in these solutions primarily as the $NbOF_5^{-2}$ ion. The solid phases at equilibrium always contained NbO_2F, indicating that the equilibria involved were $2NbO_2F_{(s)} + 8HF_{(aq)} \leftrightarrows 2H_2NbOF_{5(aq)} + 2H_2O$ and $Nb_2O_{5(s)} + 6HF_{(aq)} \leftrightarrows NbO_2F_{(s)} + H_2NbOF_{5(aq)} + 2H_2O$, depending on the initial compound used.

A PRIOR STUDY of the solubility of niobic oxide in hydrofluoric acid solutions was made by Nikolaev and Buslaev (9), who concluded that the oxide reacted with 0 to 25M HF according to the equation $Nb_2O_{5(s)} + 10HF_{(aq)} \leftrightarrows 2H_2NbOF_{5(aq)} + 3H_2O$, and that $Nb_2O_5 \cdot 2H_2O$ was the solid phase at equilibrium. During studies at this laboratory on the dissolution of niobium oxide in nitric acid–hydrofluoric acid solutions (2), it was noted that a solid, identified as NbO_2F by x-ray diffraction analysis, precipitated under certain conditions. This observation prompted the present investigation of the solubility of niobic oxide and the dioxyfluoride in HF-HNO₃ solutions.

EXPERIMENTAL

Materials Used. Hydrous niobic oxide was obtained by dissolving sintered Nb_2O_5 (Kawecki Chemical Co.; total metal impurities, less than 300 p.p.m.) in hydrofluoric acid, then precipitating the hydrous oxide with ammonium hydroxide. The precipitate was washed alternately with water and 0.1M HNO₃ and then air-dried at room temperature before use. The hydrous oxide contained about 50% niobium, 25% water, 0.1% fluorine, and less than 0.5% nitrogen.

Hydrated dioxyfluoride was obtained by allowing high purity niobium metal to react with boiling 16M HNO₃–1M HF (F/Nb atom ratio of less than 5). The hydrated dioxyfluoride flaked off the surface of the metal and settled to the bottom of the Teflon reaction vessel; it was then collected by filtration, washed with acetone, air-dried, and finally dried over Drierite in a desiccator. Analyses: Nb, 61.6%; F, 12.4%; H₂O, 5.12%. Calculated for $NbO_2F \cdot \frac{1}{2}$ H₂O: Nb, 60.8%; F, 12.4%; H₂O, 5.89%. The existence of a hydrate was confirmed by infrared analysis. The water deformation band appeared at 1630 cm.$^{-1}$ and the –OH stretching bands at 3240 and 3360 cm.$^{-1}$. The x-ray powder pattern of $NbO_2F \cdot \frac{1}{2}H_2O$ was the same as that reported for NbO_2F by Frevel and Tinn (3). This is not surprising,

since Frevel and Rinn found no change in lattice parameter with NbO_2F having water contents between 1.9 and 5.7%. The formula NbO_2F is used throughout this paper since, in general, the presence of the dioxyfluoride in equilibrium solid phases was confirmed by x-ray diffraction and not by chemical analysis. The hydrated dioxyfluoride was fairly stable on heating in dry helium at about 3° per minute in a thermobalance. Noticeable weight loss occurred only above about 200° C. On heating to 900° C., complete decomposition of the dioxyfluoride to Nb_2O_5 occurred.

All solutions were prepared from reagent grade acids and distilled water.

Procedure. Series of samples were prepared by adding excess oxide or dioxyfluoride to hydrofluoric acid or HF-HNO₃ solutions. The samples were equilibrated at 25° ± 1° C. Periodic analyses showed that samples originally containing the hydrous oxide attained equilibrium in a few days, but equilibration in samples initially containing the dioxyfluoride required nearly 2 years. After equilibration, samples of the saturated solutions were removed, clarified by centrifugation at 25° C., and analyzed. In some cases, wet residues were removed to allow determination of the equilibrium solid phase by the method of Schreinemakers (10). In all cases, the residual solids were recovered by filtration, washed with water, and subjected to x-ray diffraction and chemical analyses. No detectable hydrolysis of the dioxyfluoride occurred during washing.

Analytical. Niobium was determined both by an x-ray absorption method (1) and by ignition of samples to Nb_2O_5 at 900° C. The results from the two methods generally agreed within 3%. Total fluorine in solution and in wet residues was determined by differential potentiometric titration using standard NaOH as the titrant. This method is similar to the one used by Nikolaev and Buslaev (9). The over-all reaction (with the end point at pH 7 to 8) is: $2H_2NbOF_5 + 10NaOH \rightarrow Nb_2O_5 + 10NaF + 7H_2O$. Pyrohydrolysis (4, 8), after drying of the sample in the presence

of an equimolar mixture of WO_3 and Na_2WO_4, was used for the determination of fluorine in solid compounds and to confirm fluorine values obtained by the titration method. The free fluoride concentration in solution was determined by a spectrophotometric titration method (6, 7) using a thorium-bearing solution as the titrant and SPADNS [the trisodium salt of 4,5-dihydroxy-3-(p-sulfophenylazo)-2,7-naphthalene disulfonic acid] as the indicator. The absorbency of the sample solution is recorded during the titration. A sharp increase in absorbency occurs at the end point. Nitrogen was determined by a modified Kjeldahl method.

X-ray powder patterns were obtained with a Debye-Scherrer 114.59-mm.-diameter camera using filtered $CuK\alpha$ radiation. Infrared spectra were obtained with a Beckman IR7 spectrometer, using both the Nujol mull and KBr pellet methods.

RESULTS

The solubilities of hydrous niobic oxide and the dioxyfluoride in hydrofluoric acid solutions increased linearly with increasing total fluorine concentration. The niobium concentration in the saturated solutions was about one fifth the total fluorine concentration (Tables I and II, Figure 1). The plot of niobium concentration in the saturated solutions vs. total fluorine concentration (Figure 1) was a straight line of slope 0.220, corresponding to a F/Nb atom ratio of 4.54 in solution. This result suggested that the niobium was present in solution primarily as the $NbOF_5^{-2}$ ion. Raman spectra of selected saturated solutions were identical to that of the $NbOF_5^{-2}$ ion reported by Keller (5). Thus, the saturated solutions can be considered as solutions of H_2NbOF_5. The densities of these solutions at 25° C. increased linearly with increasing niobium concentration: ρ(g./ml.) = 1.000 + 0.1355 (Nb concn., M).

An attempt was made to determine the solid phase present at equilibrium by applying Schreinemakers' wet residue method (10) to several of the samples that originally contained hydrous oxide. No single compound was indicated as the equilibrium solid phase (Figure 2). Instead, the solid phases appeared to be mixtures of the oxide and the dioxyfluoride. The results of chemical and x-ray analyses of solids recovered from the wet residues after thorough water-washing were consistent with this hypothesis. Solids that were indicated by Schreinemakers' method to contain mostly niobic oxide gave x-ray patterns similar to that of the original hydrous oxide, but also contained appreciable amounts of fluorine. On the other hand, samples that were indicated to contain mostly the dioxyfluoride yielded the x-ray pattern for this compound; the F/Nb atom ratios in these solids were generally about 0.9, indicating the presence of some niobic oxide.

Residues from the equilibration of $NbO_2F \cdot 1/2H_2O$ with hydrofluoric acid solutions were recovered by filtration and washed with water before x-ray diffraction and chemical

Table I. Solubility of Niobic Oxide in Hydrofluoric Acid Solutions at 25° C.

(Samples equilibrated about 4 months)

		Saturated Solution					Wet Residue, Wt. %	
Sample	Density, g./ml.	Nb concn., M	Nb_2O_5 concn., wt. %	F concn., M	HF concn., wt. %	F/Nb atom ratio	Nb_2O_5	HF
1	1.0079	0.053	...	0.237	...	4.47	...	...
2	1.0334	0.237	...	1.06	...	4.47	...	...
3[a]	1.0773	0.589	7.26	2.63	4.87	4.46	27.8	5.34
4[a]	1.1326	0.956	11.2	4.44	7.83	4.64	35.2	6.85
5	...	1.23	...	6.26	...	5.09	...	...
6[a]	1.2594	1.88	19.9	8.69	13.8	4.62	37.0	11.5
7	1.3143	2.34	...	10.6	...	4.55	...	...
8[a]	1.3805	2.74	26.4	12.4	18.0	4.53	37.1	15.9
9	1.4394	3.23	...	14.3	...	4.41	...	...
10[a]	1.4644	3.40	31.0	15.6	21.2	4.57	41.5	19.4
11	1.5003	3.69	...	17.4	...	4.70	...	...
12[a]	1.5857	4.34	36.4	18.9	23.8	4.35	43.8	22.0
13	...	5.29	...	25.2	...	4.76	...	...

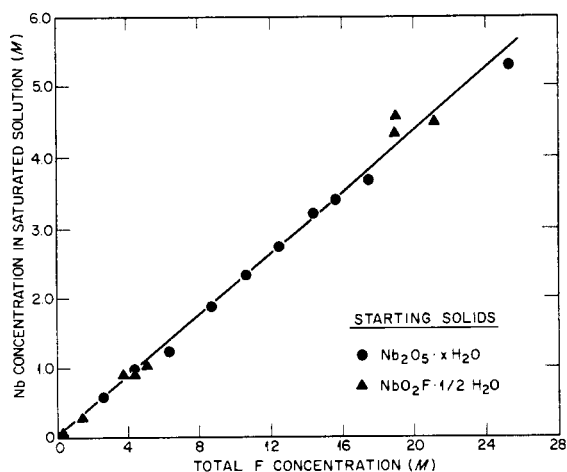[a] Free fluoride concentration in saturated solution less than 0.003 M.

Figure 1. Solubility of niobium in hydrofluoric acid solutions at 25° C.

Slope of line, 0.220, corresponding to F/Nb ratio of 4.54 in saturated solutions

Table II. Solubility of NbO_2F in Hydrofluoric Acid Solutions at 25° C.

(Samples equilibrated about 2 years)

	Saturated Solution				Composition of Solid Phase[a]		
Sample	Nb concn., M	F concn., M	F/Nb atom ratio	Density, g./ml.	Nb, wt. %	F, wt. %	F/Nb atom ratio
14	0.082	0.41	5.00	1.0144	60.4	12.7	1.03
15	0.145	0.67	4.62	1.0366	60.3	10.6	0.86
16	0.293	1.47	5.02	1.0448	59.5	11.9	0.98
17	0.932	3.89	4.17	...	52.2	13.6	1.28
18	0.921	4.42	4.80	...	...	...	...
19	1.06	4.58	4.32	...	57.4	12.6	1.07
20	1.06	5.01	4.74	...	...	...	...
21	4.60	19.0	4.12	...	60.9	13.8	1.11
22	4.50	21.2	4.71	...	...	...	...

[a] Solids were recovered by filtration, washed with water, and air-dried at room temperature. NbO_2F detected in each solid by x-ray diffraction analysis.
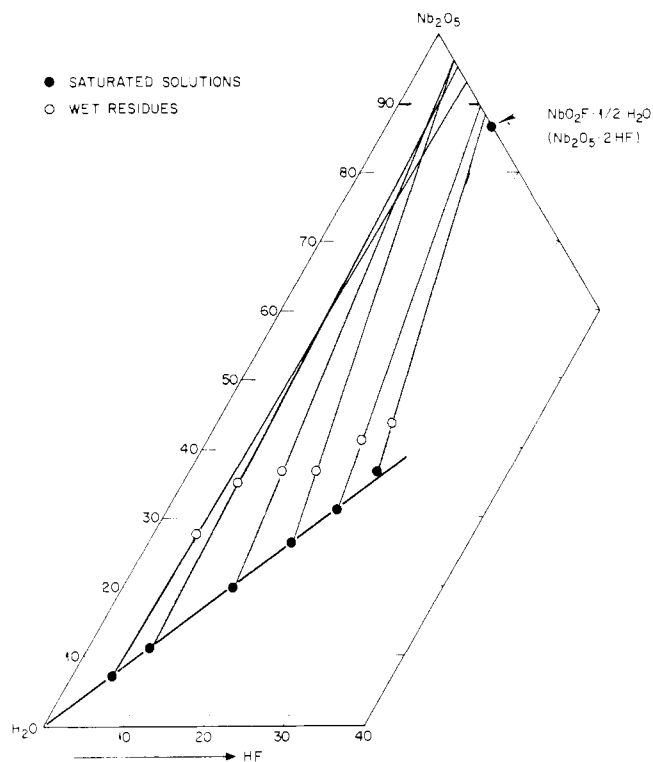
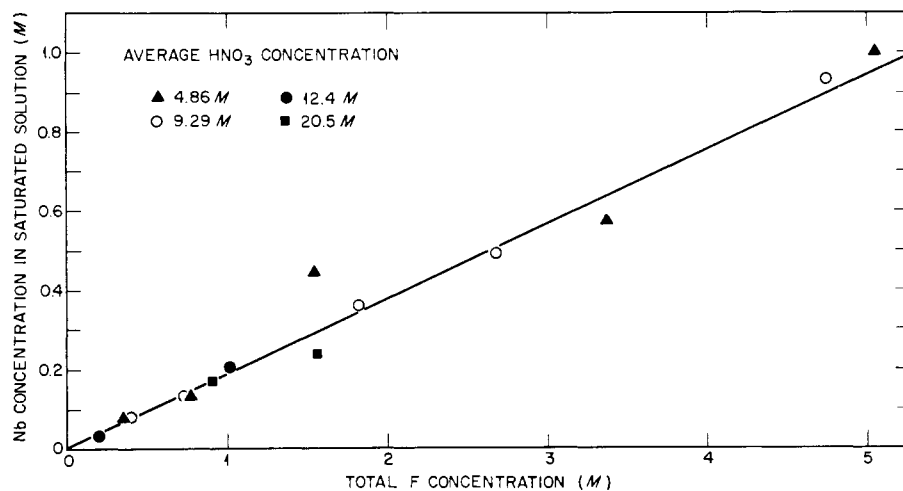Figure 2. Portion of Nb₂O₅-HF-H₂O system at 25° C.
Composition in weight %

Table III. Solubility of Niobic Oxide in Nitric
Acid–Hydrofluoric Acid Solutions at 25° C.

(Samples equilibrated about 1 year)

| Sample[a] | Concentration in Saturated Solution, M | | | F/Nb Atom Ratio |
	HNO₃	Nb	F	
23	5.35	0.087	0.353	4.07
24	4.93	0.138	0.758	5.49
25	4.94	0.449	1.58	3.51
26	4.68	0.572	3.37	5.89
27	4.42	1.02	5.06	4.96
Av.	4.86			
28	9.66	0.080	0.421	5.27
29	9.62	0.132	0.742	5.62
30	8.89	0.361	1.82	5.04
31	9.30	0.493	2.68	5.45
32	8.98	0.932	4.74	5.08
Av.	9.29			
33	12.4	0.031	0.200	6.45
34	12.5	0.204	1.03	5.05
Av.	12.4			
35	21.3	0.030	0.198	6.69
36	20.6	0.173	0.916	5.29
37	19.7	0.243	1.56	6.41
Av.	20.5			

[a] NbO₂F identified in each solid phase by x-ray diffraction analysis.

Figure 3. Solubility of Nb₂O₅·xH₂O in nitric acid-hydrofluoric acid solutions at 25° C.
Slope of line 0.189, corresponding to F/Nb atom ratio of 5.28 in saturated solutions

analyses. Not only was NbO₂F detected by x-ray analysis in each residue but also the chemical analyses, within experimental error, were those expected for NbO₂F · ½H₂O (Table II).

Only limited studies were made of the solubility of niobium compounds in HF-HNO₃ solutions. Data were obtained by equilibrating the hydrous oxide with solutions that initially were 0 to 20M in HNO₃ and up to 5M in HF. Over this concentration range, the niobium concentrations in the saturated solutions were again about one fifth the total fluorine concentrations (Table III, Figure 3). The dioxyfluoride was detected in each solid phase by x-ray diffraction analysis.

DISCUSSION

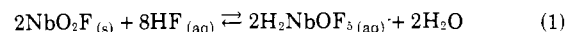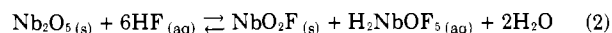The results of this study indicate that equilibration of either niobic oxide or niobium dioxyfluoride with hydro-

fluoric acid and hydrofluoric acid–nitric acid solutions at 25° C. results in solubilization of the niobium as the $NbOF_5^{-2}$ ion, since the F/Nb atom ratio in the saturated solution was always about 5 and direct analysis showed the free fluoride ion concentrations in the solutions to be negligibly low. Furthermore, the solid dioxyfluoride apparently is the thermodynamically stable solid phase. Thus, the equilibria involved are

$$2NbO_2F_{(s)} + 8HF_{(aq)} \rightleftarrows 2H_2NbOF_{5\,(aq)} + 2H_2O \qquad (1)$$

and

$$Nb_2O_{5\,(s)} + 6HF_{(aq)} \rightleftarrows NbO_2F_{(s)} + H_2NbOF_{5\,(aq)} + 2H_2O \qquad (2)$$

depending on the initial compound used. Hence, only when the dioxyfluoride is used for the equilibration does the composition of the solid phase remain constant. Reaction

of hydrofluoric acid solutions with the oxide is analogous to an acid-base reaction. When an excess of oxide is present, hydrofluoric acid is completely consumed according to the stoichiometry of Equation 2 and the solid phase becomes a mixture of the oxide and the dioxyfluoride.

The conclusion reached in this study, suggesting the $NbOF_5^{-2}$ ion as the primary niobium-containing species in 0 to $5M$ H_2NbOF_5 solutions, is the same as that arrived at by Nikolaev and Buslaev (9). Although the results of the present study are in good agreement with those of Nikolaev and Buslaev regarding the composition and densities of the saturated solutions, there is marked disagreement as to the composition of the equilibrium solid phase. Nikolaev and Buslaev, who equilibrated the hydrous oxide with hydrofluoric acid solutions and used the wet residue method to determine the solid phase, concluded that $Nb_2O_5 \cdot 2H_2O$ was the equilibrium solid phase. The dioxyfluoride was always present in the solid phases obtained in this study. This disparity in results is inexplicable unless it is assumed that Nikolaev and Buslaev used very large amounts of oxide relative to the amounts of hydrofluoric acid present in their samples. If this were the case, all the hydrofluoric acid could have been consumed without markedly depleting the amount of niobic oxide present.

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Solubility of Calcium Sulfate Dihydrate in the System NaCl–MgCl₂–H₂O from 28° to 70° C.

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Solubility data are presented for calcium sulfate dihydrate in the system NaCl–MgCl₂–H₂O for 28°, 38°, 50°, 70°, and 90° C. and in ranges of concentration up to 5.50 molal NaCl and 0.340 molal MgCl₂ in admixtures. Thermodynamic solubility products are given for calcium sulfate at 28°, 38°, 50°, 70°, and 90° C. Empirical equations describing the solubility of calcium sulfate dihydrate in these systems are also given.

THERE is widespread interest in the solubility of calcium sulfate dihydrate in solutions of various concentrations of sodium chloride and magnesium chloride and at various temperatures. Geologists and geochemists are interested because of gypsum and anhydrite conversion occurring in nature (1, 6, 11). Engineers involved in production of petroleum or water desalination are interested because of deposition of calcium sulfate scales. These scales are also a problem facing cooling tower operators (3). Solubility data for calcium sulfate in the simple solutions have been available in the literature for a long time but there has been no knowledge of the influence of mixtures of these salts on the solubility of calcium sulfate, particularly at temperatures above ambient. Some early work on gypsum solubility in water at different temperatures was done by Cameron (2) who measured gypsum solubility in sodium chloride solution at 23°, 30°, 52°, 70°, and 82° C. Shternina (10) measured the solubility of calcium sulfate in the presence of sodium chloride, magnesium chloride, sodium nitrate, magnesium nitrate, and ammonium chloride, but not in mixtures of these salts. Shternina formulated a method of calculating calcium sulfate solubility in these salt solutions at 25° C. which was based on the Debye-Hückel limiting law. Bock (1) determined the solubility of both anhydrite and gypsum in sodium chloride solutions at 25°, 30°, 40°, and 50° C. Denman (3) measured the solubility of gypsum in water and in dilute concentrations of sodium sulfate and a magnesium sulfate solution and formulated a calculation of calcium sulfate solubility based on ionic strength and activity coefficients. Solubility of calcium sulfate has been measured in concentrations of sodium chloride up to 4 molal at temperatures ranging from 40° to 200° C. and the Debye-Hückel theory applied as a method of calculating calcium sulfate solubility in these systems (5). Recently, solubilities of γ and β-hemihydrate, β-soluble anhydrite, and insoluble anhydrite have been measured (8). Zen (11) has measured the solubility of both gypsum and anhydrite at 35°, 50°, and 70° C., in various sodium chloride concentrations.

The solubility of calcium sulfate has been determined at temperatures of 28°, 38°, 50°, and 70° C. for sodium chloride molalities up to 5.5 and for admixtures with magnesium chloride between 0.01 and 0.325 molal.