Solubility of Molybdic Oxide and Its Hydrates in Nitric Acid, Nitric Acid–Ferric Nitrate, and Nitric Acid–Uranyl Nitrate Solutions

LESLIE M. FERRIS, Oak Ridge National Laboratory, Oak Ridge, Tenn.

URANIUM-MOLYBDENUM ALLOYS are proposed as fuels for several American nuclear power reactors (*2*). Processes for the recovery of uranium from nearly all types of spent fuel elements are based mainly on solvent extraction with tributyl phosphate from aqueous nitrate solutions (*3*). This approach is being considered for uranium-molybdenum alloy fuels. Knowledge of the solubility of molybdenum compounds in aqueous nitrate systems is, therefore, of value in developing processing methods. In previous work the solubilities of $MoO_3 \cdot H_2O$ (white) and $MoO_3 \cdot 2H_2O$ were determined in water (*20*) and the solubility of the white monohydrate was measured in nitric acid at 20° C. (*5*). In this investigation solubilities of hydrous molybdic oxide, $MoO_3(aq)$, in nitric acid at 26° C. and of the dihydrate and white monohydrate in water, nitric acid, and nitric acid–ferric nitrate solutions between 26° and 55° C. were determined. Solubilities at 26° C. in solutions containing uranyl nitrate were also obtained. The nitric acid and nitric acid–ferric nitrate solutions were of particular interest, since they can be used to dissolve alloys containing up to 10% molybdenum (*2*).

EXPERIMENTAL

Reagents. $MoO_3 \cdot 2H_2O$ was freshly precipitated before use by acidifying a solution of reagent grade sodium molybdate according to the procedure given by Freedman (*10*). Chemical, x-ray, and thermogravimetric analyses showed the yellow precipitate to be virtually pure dihydrate containing less than 0.04% sodium. The x-ray pattern was the same as that reported by Lindqvist (*16*).

Hydrous molybdic oxide, $MoO_{3(aq)}$, was prepared by digesting about 120 grams of reagent grade sodium molybdate with boiling 8*M* nitric acid for about 15 hours. The solid formed during this treatment appeared to be $Na_2O \cdot 10MoO_3 \cdot 18H_2O$. Analyses. Found: Na, 2.53; Mo, 54.88; calcd.: Na, 2.52, Mo, 52.55. The hydrated sodium molybdate was then digested for 5 hours in boiling 5*M* nitric acid. The final white solids exhibited an x-ray pattern identical with that of sublimed MoO_3. Analyses. H_2O, 3.3; Na, 0.04.

The yellow monohydrate was formed by heating the dihydrate in air for 1.5 hours at 103° C. Analyses. Found: Mo, 59.87; calcd.: Mo, 59.24. The x-ray pattern matched that obtained by Freedman (*9*).

The white monohydrate was prepared by heating the dihydrate in 1*M* nitric acid at 50° C. for 24 hours. The x-ray pattern was the same as that listed for molybdic acid by the ASTM (catalog No. 1-0125).

Uranyl nitrate, used in the preparation of one series of solutions, was recrystallized from water before use. All other chemicals were reagent grade. Distilled water was used in preparing the solutions.

Procedure. With the four-component systems, series of solutions having constant iron or uranium concentrations, but varying nitric acid concentrations, were prepared. In all cases, a few grams of freshly precipitated solid was placed in each of a series of stoppered borosilicate glass flasks and about 20 ml. of the desired solution was added. Each flask was shaken for about 3 weeks, although periodic analyses of the liquid phase showed that equilibrium was reached in a few hours. The samples were equilibrated in a water bath thermostatically controlled to ±0.25° C.

Analyses. Hydrogen ion, in the absence of uranium and iron, was titrated with standard base to the phenolphthalein end point. Iron, when present in the original solution, was removed by precipitation with potassium fluoride before the acid-base titration. Uranium was precipitated using potassium ferrocyanide (*19*) in saturated potassium nitrate solution and the hydrogen ion concentration determined with an automatic titrator.

Molybdenum was determined colorimetrically as the thiocyanate in ethyl acetate (*21*). Solutions containing no uranium were acidified with sulfuric acid, iron and thiocyanate were added, and the molybdenum was extracted into ethyl acetate prior to analysis. Uranium was separated from molybdenum by hexone extraction and determined colorimetrically as the thiocyanate (*18*). Iron was determined by phenanthroline colorimetric procedure (*7*).

Solubility in Water. The solubilities in water of the dihydrate at 26° C. and the white monohydrate at 40° and 55° C. (Figure 1) agree well with those expected from the data quoted by Seidell (*20*) for the dihydrate and the α-monohydrate, respectively. Alpha-$MoO_3 \cdot H_2O$ appears to be the same as the white monohydrate described by Freedman (*10*). Since the dihydrate rapidly converts to the monohydrate at temperatures above 40° C., previously reported data for the dihydrate (*20*) at the elevated temperatures probably were obtained from metastable solutions. Reconversion of the monohydrate to the dihydrate on cooling solutions from 55° to 26° C. did not occur within 3 weeks. Freedman (*8*) noted that this transition occurs very slowly in water at room temperature, and requires several weeks in 2*M* nitric acid even when the system is seeded with crystals of the dihydrate.

Solubility in Nitric Acid. Data were obtained with hydrous molybdic oxide and the dihydrate at 26° C. and the white monohydrate at 40° and 55° C. in solutions ranging in nitric acid concentration from 0 to 5*M*. The monohydrate was obtained when samples initially containing the dihydrate were heated to the higher temperatures. The solubilities of $MoO_{3(aq)}$ and $MoO_3 \cdot 2H_2O$ increased with increasing acid concentration to maximum values of about 0.05 and 0.12*M*, respectively, when the acid concentration was about 3*M* (Tables I and II; Figure 2). The fact that the solubilities pass through maxima at about 3*M* nitric acid was explained by Cannon (*5*) on the basis of Pryor and Evans' (*17*) theory of defect-controlled dissolution of oxides in acids. Cannon's data, obtained by equilibrating the white mono-

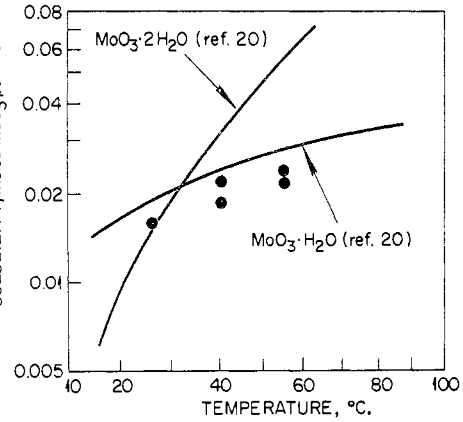

Figure 1. Solubility of molybdic oxide hydrates in water

● This investigation
Solid phases. At 26° C. $MoO_3 \cdot 2H_2O$
At 40° and 55° C. white $MoO_3 \cdot H_2O$

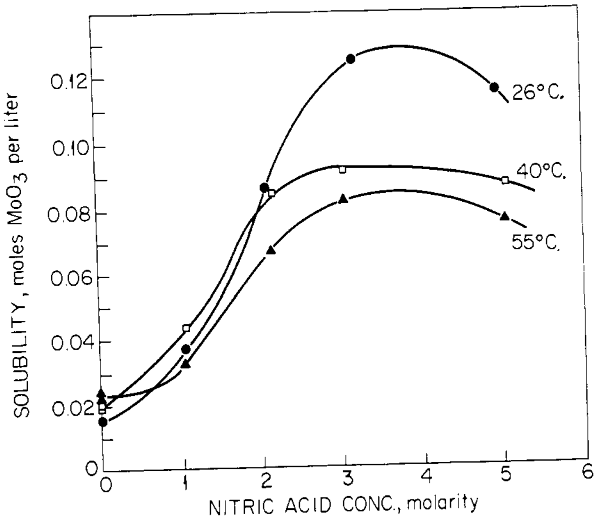

Figure 2. Solubility in nitric acid of $MoO_3 \cdot 2H_2O$ at 26° C. and of white $MoO_3 \cdot H_2O$ at 40° and 55° C.

Table I. Solubility of Molybdic Oxide in Nitric Acid Solutions at 26° C.

Nitric Acid Concn., Moles/L.	MoO_3 Solubility,[a] Mole/L.	Density of Satd. Solution, G./Ml.
0.11	0.0066	1.004
1.08	0.027	1.035
2.12	0.044	1.070
3.14	0.049	1.104
5.20	0.036	1.166

[a] Solid phase after equilibration: MoO_3.

Table II. Solubility in Nitric Acid Solutions of $MoO_3 \cdot 2H_2O$ at 26° C. and $MoO_3 \cdot H_2O$ (White) at 40° and 55° C.

26° C., $MoO_3 \cdot 2H_2O$ Concn., Moles/L.		40° C., $MoO_3 \cdot H_2O$ (White) Concn., Moles/L.		55° C., $MoO_3 \cdot H_2O$ (White) Concn., Moles/L.	
HNO_3	MoO_3 soly.	HNO_3	MoO_3 soly.	HNO_3	MoO_3 soly.
0.00	0.016	0.00	0.019	0.00	0.022
1.07	0.037	0.00	0.022	0.00	0.024
2.12	0.087	1.08	0.044	1.06	0.032
3.25	0.125	2.20	0.085	2.15	0.067
5.00	0.115	3.10	0.092	3.08	0.082
		5.10	0.087	5.10	0.076

Table III. Solubility of $MoO_3 \cdot 2H_2O$ in Nitric Acid–Uranyl Nitrate Solutions at 26° C.

Concentration, Moles/L.			Solid Phase, %	
HNO_3	U	MoO_3 Soly.	U	Mo
0.98	0.27	0.042	0.006	...
1.94	0.28	0.079	0.001	...
2.85	0.28	0.104	0.002	...
4.69	0.28	0.118	0.35 (?)	...
1.00	0.65	0.043	39.5	38.7
1.92	0.64	0.071	0.01	...
3.01	0.63	0.086	0.003	...
4.94	0.67	0.088	0.004	61.9
1.04	0.94	0.043	39.3	30.1
2.00	0.96	0.065	7.8	...
2.95	0.95	0.077	0.056	...
4.88	0.94	0.074	0.029	56.0[a]

[a] This solid was also shown by x-ray analysis to be white $MoO_3 \cdot H_2O$.

hydrate with nitric acid solutions, are in good agreement with those reported here for the dihydrate. While Cannon did not identify the solid phases present after equilibration, he noted that the solids in solutions having an acid concentration greater than 3*M* changed in color from white to yellow (the color of the dihydrate).

The solubility at 40° and 55° C. of the white monohydrate in water and dilute acid solutions was higher than that of the dihydrate at 26° C. and increased with increasing temperature; the opposite was true where the nitric acid concentration was greater than about 2*M* (Table II, Figure 2).

Since the solubilities are so low, densities of nitric acid–molybdic oxide solutions can be estimated from data for nitric acid (*11–15*).

Solubility in Nitric Acid–Uranyl Nitrate Solutions. Data were obtained at 26° C. by equilibration of the dihydrate with three series of nitric acid–uranyl nitrate solutions. In each series, the uranyl nitrate concentration was essentially constant, but the nitric acid concentration varied from 0 to 5*M*. The dihydrate, in contact with solutions of low acidity and having uranyl nitrate concentrations greater than about 0.6*M*, apparently was converted to an uranyl molybdate having the approximate composition $UO_3 \cdot 2MoO_3$ (Table III). The solid in equilibrium with all solutions in which the nitric acid concentration was greater than 3*M* was white (in contrast to the yellow-colored dihydrate) and appeared from chemical and x-ray analyses to be a monohydrate. In solutions where the nitric acid concentration was less than about 1.5*M*, the solubility was slightly higher in the presence of uranium, suggesting the formation of heteropolymolybdate species (Table III, Figure 3). The solubility decreased with increasing uranium concentration in solutions where the nitric acid concentration was greater than about 2*M*.

Since the molybdenum solubility is low, densities of the solutions may be estimated from data on the uranyl nitrate–nitric acid–water system (*4*).

Solubility in Nitric Acid-Ferric Nitrate Solutions. Data were obtained for the dihydrate at 26° and the white monohydrate at 40° and 55° C. As with solutions containing only nitric acid, the monohydrate was obtained when samples were heated to 40° C. In all solutions where the nitric acid concentration was less than 2*M*, the solubility increased with increasing iron concentration (Table IV, Figure 4), suggesting the formation of complex ions similar to the $(FeMo_6O_{21})^{-3}$ described by Baker and others (*1*). When the nitric acid concentration was greater than 3.5*M*, the solubility decreased with both increasing acid and iron concentration. Plots of the data obtained at 40° and 55° C. are similar to those shown in Figure 4. In solutions where the nitric acid concentration was less than about 2*M*, the solubility of the white monohydrate at 40° and 55° was higher than that of the dihydrate at 26° C. and increased with both temperature and increasing iron concentration. The opposite behavior was observed where the acid concentration was greater than about 3.5*M*.

A few additional experiments were performed to evaluate cursorily the solubility of the various hydrates of molybdic oxide in 3*M* nitric acid–0.95*M* ferric nitrate solution at 26° C. It appears that the solubility increases with increasing hydration of the oxide (Table V). The only phase change which occurred during the 3-week equilibration period was that of the yellow monohydrate to the white monohydrate.

The following equation for calculating approximately the densities of nitric acid–ferric nitrate–molybdic oxide solutions at 26° C. was derived from the published densities of nitric acid (*11–15*) and nitric acid–ferric nitrate (*6*) solutions:

$$d^2 = 0.0719(HNO_3) + 0.425(Fe) + 0.994$$

where density is given in grams per milliliter; nitric acid and ferric nitrate concentration in moles per liter. Molybdenum, in concentrations up to 0.1*M*, had a negligible effect on the density.

ACKNOWLEDGMENT

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Wilson, W.R. Laing, and R.L. Sherman of the ORNL Analytical Chemistry Division.

Table IV. Solubility in Nitric Acid–Ferric Nitrate Solutions of $MoO_3 \cdot 2H_2O$ at 26° C. and of $MoO_3 \cdot H_2O$ at 40° and 55° C.

Temp., ° C.	Concentration, Moles/L.		
	HNO_3	Iron	MoO_3 soly.
26, solid phase, apparently $MoO_3 \cdot 2H_2O$ (see Table V)	0.39	0.22	0.068
	0.96	0.22	0.070
	1.86	0.21	0.104
	2.78	0.21	0.123
	4.60	0.22	0.096
	0.42	0.45	0.176
	0.93	0.45	0.104
	1.81	0.43	0.115
	2.65	0.45	0.132
	4.58	0.45	0.088
	0.48	0.67	0.277
	0.91	0.68	0.134
	1.73	0.67	0.122
	2.60	0.69	0.113
	4.45	0.69	0.078
	0.53	0.90	0.394
	0.94	0.90	0.192
	1.71	0.89	0.134
	2.63	0.90	0.100
	4.45	...	0.071
40, solid phase, $MoO_3 \cdot H_2O$ (white)	0.68	0.23	0.092
	0.95	0.23	0.074
	2.03	0.24	0.106
	2.99	0.24	0.109
	4.95	0.24	0.081
	0.44	0.47	0.145
	0.98	0.49	0.145
	1.94	0.49	0.123
	2.98	0.49	0.119
	4.79	0.49	0.072
	0.86	...	0.322
	0.94	0.73	0.208
	1.90	0.73	0.136
	2.92	0.73	0.128
	4.80	0.74	0.057
	0.54	0.93	0.356
	0.96	0.97	0.294
	1.83	0.94	0.134
	2.85	0.95	0.132
	4.75	0.97	0.059
55, solid phase, $MoO_3 \cdot H_2O$ (white)	0.68	0.23	0.095
	0.97	0.24	0.076
	1.92	0.24	0.100
	2.90	0.24	0.104
	4.70	0.24	0.086
	0.38	0.47	0.092
	1.06	0.48	0.182
	1.86	0.49	0.123
	2.80	0.49	0.115
	4.55	0.49	0.079
	1.00	0.71	0.212
	1.86	0.68	0.134
	2.73	0.72	0.124
	4.40	...	0.053
	0.58	0.93	0.352
	0.90	0.94	0.267
	1.78	0.96	0.171
	2.70	0.91	0.153
	4.58	0.94	0.060

Table V. Solubility of Molybdic Oxide Hydrates in 3*M* Nitric Acid–0.95 *M* Ferric Nitrate at 26° C.

Solid Phase		Solution Concentration, Moles/L.		
Orig.	After equil.	Fe	HNO_3	MoO_3 soly.
MoO_3 (Merck reagent)	MoO_3	0.95	2.95	0.042
$MoO_{3(aq)}$	MoO_3	0.96	2.95	0.042
$MoO_3 \cdot H_2O$ (yellow)	$MoO_3 \cdot H_2O$ (white)	0.95	2.98	0.081
$MoO_3 \cdot 2H_2O$	$MoO_3 \cdot 2H_2O$	0.95	2.95	0.104

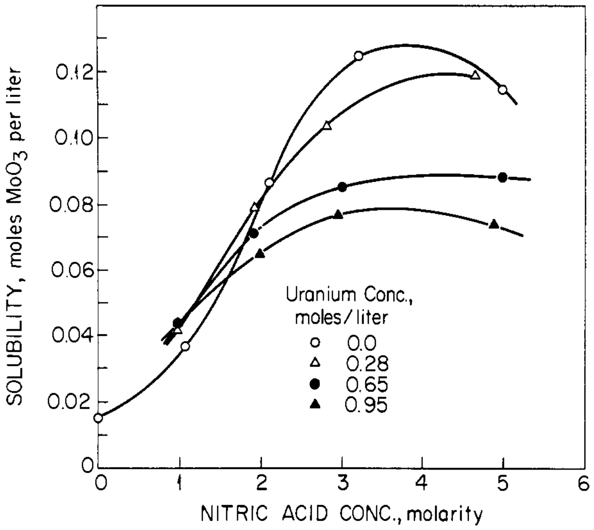

Figure 3. Solubility of $MoO_3 \cdot 2H_2O$ in nitric acid–uranyl nitrate solutions at 26° C.

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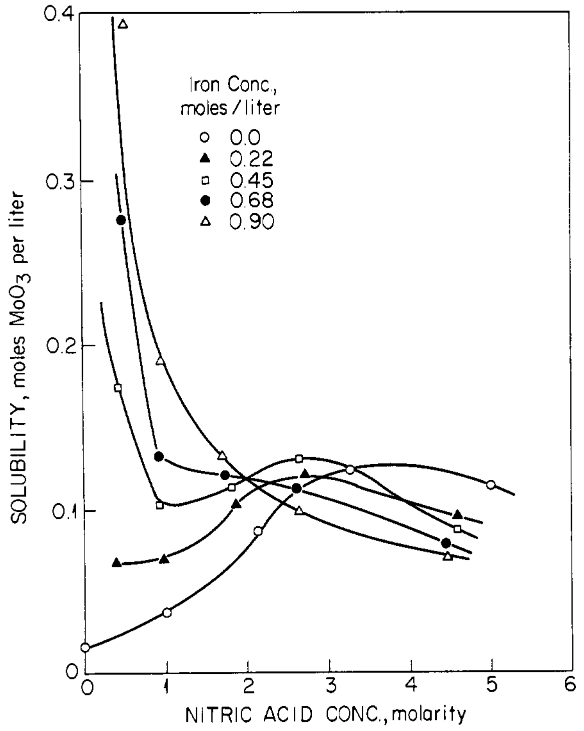

Figure 4. Solubility of $MoO_3 \cdot 2H_2O$ in nitric acid–ferric nitrate solutions at 26° C.

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Solubility of Boron Trifluoride in Liquid Hydrogen Fluoride

R.J. MIKOVSKY[1], S.D. LEVY[2], and A.L. HENSLEY, Jr., Research and Development Department, American Oil Co., Whiting, Ind.

MIXTURES of boron trifluoride in hydrogen fluoride have been used to catalyze a variety of Friedel-Crafts reactions including alkylation, isomerization, and disproportionation; they have also been used to effect separation and purification processes (*6*). Despite these varied uses, little has been reported about the composition of the catalyst phase.

The acidic nature of these catalysts depends largely on the concentration of BF_3. Such highly acidic systems are susceptible to deactivation and to dilution by the solution of basic material during the course of the reaction. These effects make the definition of the catalyst composition highly involved, and the determination of the solubility of BF_3 in HF then represents only a starting point.

In previous studies (*2, 3, 4*), the solubility of BF_3 was calculated by performing a mass balance; the experimental conditions ranged between 0° and 43° C. and 0 and 180 p.s.i. of BF_3. The present work involves the chemical analysis of the acid phase formed at 24°, 49°, and 98° C. and between 0 and 1000 p.s.i. of BF_3. Most practical catalysts would be formed under these conditions.

EXPERIMENTAL

The HF was anhydrous and of 99.9 mole % minimum purity; the BF_3 was of 99.0 mole % minimum purity. The solutions were prepared in a Hastelloy-B stirred autoclave.

To the closed reactor was added about 200 cc. of undistilled HF. The vessel was brought to temperature and the vapor pressure of HF was recorded. Boron trifluoride was added and the mixture was stirred 20 to 30 minutes to establish equilibrium. The difference between the total pressure and the vapor pressure of HF gave the BF_3 pressure. A small quantity of the liquid phase was withdrawn through a metering valve at the bottom of the reactor into methanol chilled in solid CO_2 and acetone; the sample was stored at this temperature until it was analyzed. The reactor was then pressured with more BF_3 or depressured by venting, and the stirring and sampling procedure was repeated. Usually, five or six samples were obtained in this manner from one charge of HF.

Determination of the mole fraction of BF_3 was based on hydrolysis in the presence of calcium:

$$2BF_3 + 6H_2O + 3Ca^{+2} \rightarrow 6H^+ + 2H_3BO_3 + 3CaF_2 \downarrow$$

This reaction produces three hydrogen ions and one molecule of boric acid for each molecule of BF_3. The HF content of the sample is equivalent to the strong-acid titer, A, minus three times the boric acid titer, B; the BF_3 content is equivalent to the boric acid titer. The mole fraction of BF_3 is then given by $B/(A-2B)$.

The analysis was started by transferring a small sample of the alcoholic $HF\text{-}BF_3$ solution to a 150-ml. beaker containing 70 ml. of $1M$ calcium chloride, which had been cooled to 0° C. and adjusted to the methyl red end point. The resulting solution was titrated back to the methyl red end point with $0.5M$ potassium hydroxide; this neutralization established part of the strong-acid titer. The temperature was then raised and maintained at 95° C. to hydrolyze the BF_3 more rapidly. During the hydrolysis, the pH was maintained between one and four, which required neutralization to the methyl red end point at 10-minute intervals

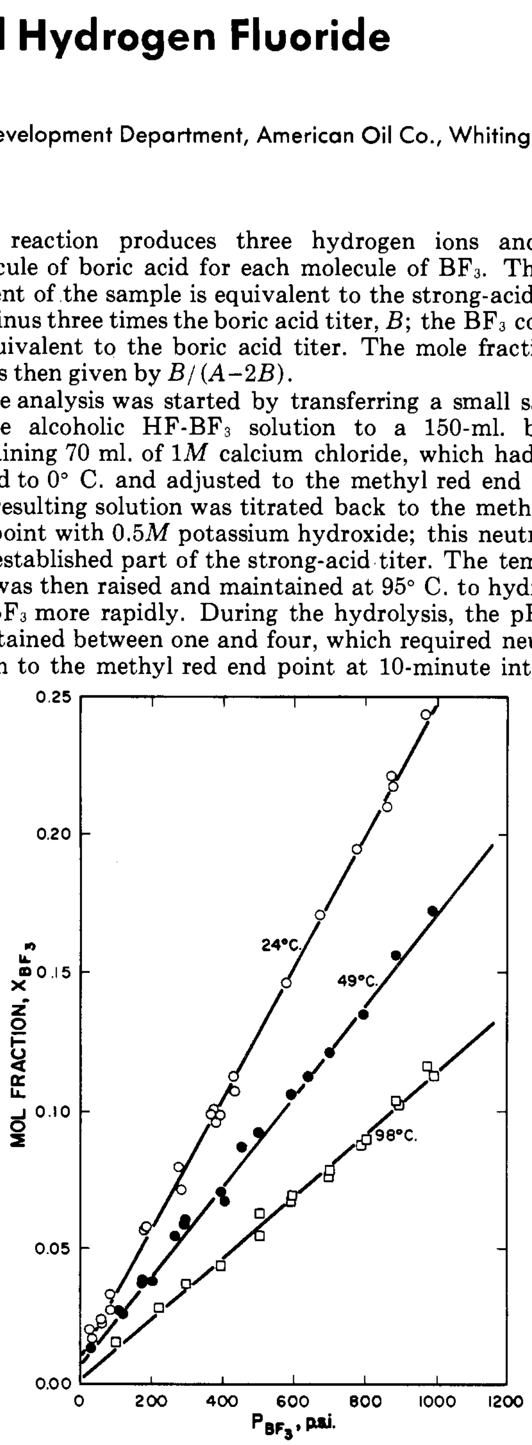

Figure 1. Isotherms for solubility of BF_3 in HF

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[1] Present address, 9 Budd Blvd., Woodbury, N. J.

[2] Present address, American Cyanamid Co., 1937 West Main St., Stamford, Conn.