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by

ELIZABETH W. BAUMANN

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DETERMINATION OF STABILITY CONSTANTS OF HYDROGEN AND ALUMINUM FLUORIDES WITH A FLUORIDE-SELECTIVE ELECTRODE*

by

ELIZABETH W. BAUMANN

Savannah River Laboratory
E. I. du Pont de Nemours and Co.
Aiken, South Carolina 29801

Abstract—Stability quotients for the hydrogen-fluoride and aluminum-fluoride systems in NH_4NO_3 were determined from measurements of free fluoride ion concentration by the lanthanum fluoride membrane electrode. Stability quotients at 0.5, 0.3, 0.1, and 0.01 M ionic strength were extrapolated to infinite dilution through the Debye-Hückel equation to obtain thermodynamic stability constants at 25°C for HF, HF_2^-, AlF^{2+}, AlF_2^+, AlF_3, and AlF_4^-.

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INTRODUCTION

The lanthanum fluoride membrane electrode[1], which responds specifically and theoretically to changes of fluoride ion activity in solution, is a new tool for potentiometric investigation of metal-fluoride complexes[2,3]. An earlier fluoride-responsive electrode, the reversible lead amalgam-lead fluoride electrode, was used by Broene and DeVries[4] to investigate the hydrogen-fluoride system. Uncomplexed fluoride has also been determined indirectly from changes in hydrogen ion concentration or from potential changes in the ferrous-ferric couple[5].

The ability to directly determine free fluoride ion concentration (or mean activity) simplifies gathering and interpretation of experimental data for studies of metal complexes. In this work, the new lanthanum fluoride electrode was used to measure free fluoride ion in an investigation of the hydrogen-fluoride and aluminum-fluoride systems in NH_4NO_3. Stability quotients obtained at 0.5 M corroborate the classic work of Brosset and Orring[5]. Additional data at ionic strengths down to 0.01 M were extrapolated to infinite dilution to obtain thermodynamic stability constants.

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1. M. S. Frant and J. W. Ross, Jr., Science 154, 1553 (1966).
2. K. Srinivasan and G. A. Rechnitz, Anal. Chem. 40, 509 (1968).
3. R. E. Mesmer and C. F. Baes, Jr., Beryllium Fluoride Complexes in 1 M NaCl and 1 M $NaClO_4$. 156th American Chemical Society National Meeting, September 1968.
4. H. H. Broene and T. DeVries, J. Am. Chem. Soc. 69, 1644 (1947).
5. C. Brosset and J. Orring, Svensk Kem. Tidskr. 55, 101 (1943).

EXPERIMENTAL

Reagent-grade chemicals were used. Solutions were made in deionized water. Glass volumetric ware was used to prepare solutions, but solutions were stored in polyethylene to avoid prolonged contact with glass.

Standard NaF solutions were prepared from NaF that was dried several hours at 120°C. HF and HNO_3 were standardized by titration to pH 7 with standard NaOH. NH_4F was prepared by precise neutralization of the standardized HF with NH_4OH. $Al(NO_3)_3$ solutions were standardized by titrating the acid displaced by a measured volume passed through a column of "Amberlite"* IR-120 in the hydrogen form.

The experimental solutions were determinate mixtures, equilibrated in a water bath at 25±0.1°C, of acid (HF or HNO_3) and fluoride (HF or NH_4F), plus $Al(NO_3)_3$ in the fluoroaluminate investigation. Ionic strengths of 0.5, 0.3, 0.1, or 0.01 M were maintained constant with NH_4NO_3. During measurement, the 50-ml solutions were stirred in polypropylene beakers with "Teflon"**-coated magnetic stirring bars. In some cases a single solution was used for a single measurement, but in other cases, data were generated by titration of the initial solution with fluoride or aluminum.

The fluoride indicator electrode (Orion*** 94-09) was used with a saturated calomel reference electrode (Beckman**** 39170) that was protected from fluoride by a paraffin coating, save for the fiber

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*** Orion Research Incorporated, Cambridge, Mass.
**** Beckman Instruments, Inc., Fullerton, California

junction at the tip. Potentials were measured to ±0.1 mV with an Orion digital pH Meter, Model 801.

The electrodes were calibrated daily in standard solutions of fluoride (NH_4F or NaF) in the concentration range and at the ionic strength in NH_4NO_3 of the experiments. Experimental concentrations were calculated by the Nernst equation, which was obeyed over the range of concentrations used.

INTERPRETATION OF DATA

The experimental results were interpreted according to the Bjerrum formulation[6] in terms of $\bar{n}$, defined as the average number of fluoride ligands bound per complexing atom. This $\bar{n}$ can be expressed as a function of the free fluoride ion concentration, F, and the stability quotients, k_n, of the successively formed fluoride complexes with the atom M^{x+}:

$$\bar{n} = \frac{k_1F + 2k_1k_2F^2 + \cdots + nk_1k_2 \cdots k_nF^n}{1 + k_1F + k_1k_2F^2 + \cdots + k_1k_2 \cdots k_nF^n} . \qquad (1)$$

The stability quotient, k_n, is given in terms of the concentrations of the equilibrium components:

$$k_n = \frac{[(MF_n)^{x-n}]}{[(MF_{n-1})^{x-n-1}][F^-]} \qquad (2)$$

For the hydrogen system, $\bar{n}$ was calculated from the total fluoride and hydrogen ions added, F_T and H_T, and the measured free fluoride ion concentration, F:

6. J. Bjerrum, Metal Ammine Formation in Aqueous Solution. Theory of the Reversible Step Reactions, P. Haase and Son, Copenhagen (1941).

$$\bar{n}_H = \frac{F_T - F}{H_T} = \frac{(HF) + 2(HF_2^-)}{H_T} \qquad (3)$$

Stability quotients were calculated by fitting the experimental $\bar{n}$ and F values to Equation (1), as described below.

For the aluminum-fluoride system, which includes the hydrogen-fluoride equilibria, $\bar{n}_{Al}$ was calculated by

$$\bar{n}_{Al} = \frac{F_T - F - (HF) - 2(HF_2^-)}{Al_T} \qquad (4)$$

$$= \frac{F_T - F - \bar{n}_H H_T}{Al_T} \qquad (4a)$$

Values of $\bar{n}_H$ were calculated by Equation (1) for each experimental F using stability quotients determined for the hydrogen-fluoride system at the same ionic strength.

The experimental data were fitted by computer to Equation (1), using a method that numerically determines local minima of positive-valued differentiable functions of several variables[7]. Estimates were made for each set of stability quotients, $\prod_{n=1}^{n} k_n$, which were used for computation of the final values. The range of experimental data was not sufficient to define k_5 and k_6 experimentally; therefore the reasonable values of 30 and 3, were chosen for k_5 and k_6 to establish this end of the curve and improve the accuracy of the calculated k_4.

[7] W. C. Davidon, Variable Metric Method for Minimization. Argonne National Laboratory Report No. ANL 5990, (1959).

RESULTS AND DISCUSSION

Stability Quotients

Bjerrum formation curves for the hydrogen-fluoride and aluminum-fluoride systems in 0.5, 0.3, 0.1, and 0.01 M NH_4NO_3 are presented in Figures 1 and 2, where the ordinates have been individualized to avoid overlap of the curves. The fitted curve is drawn through each set of data. The fit was evaluated through the $\bar{n}$ residuals; the standard deviation was 0.05 or below for every curve, and the sum of the residuals was always less than 0.1, indicating that the fit was satisfactory.

Experimental data in Tables 1 and 2 illustrate the concentration ranges of the several components.

Computed stability quotients are given in Tables 3 and 4, where they are compared with those obtained by Brosset in 0.53 M NH_4NO_3. On the basis of the known experimental errors and the fitting of the curves, relative precisions of these quotients are estimated to be 5 to 10%.

Experimental results were not consistent at higher fluoride concentrations, for definition of k_5 and k_6. Fluoride values were sometimes high, suggesting that HF_2^- may interfere with electrode response, but this could not be demonstrated conclusively. In the complicated fluoroaluminate system, the formation of species other than those postulated could also have caused the irregularities.

Stability Constants

The stability quotients obtained at the four ionic strengths provide the basis for calculation of thermodynamic stability constants (K_n) in both the hydrogen-fluoride and aluminum-fluoride systems by extrapolation to infinite dilution. The Debye-Huckel equation was used, with 1.5 as a reasonable factor to account for the ion size parameter. The fitting was done through the constant C of the linear term.

$$\log K_n = \log k_n - \frac{\Delta Z_n^2 (0.511) \sqrt{\mu}}{1 + 1.5 \sqrt{\mu}} + C\mu \qquad (5)$$

where

$$\Delta Z_n^2 = \sum (\text{charge})^2_{\text{products}} - \sum (\text{charge})^2_{\text{reactants}} \qquad (6)$$

which comes from the Debye-Hückel formulation; for example, in the aluminum system, $\Delta Z_1^2 = -6$.

Results are given in Tables 5 and 6, together with published stability constants. The stability constants in the hydrogen system were determined directly by Broene and DeVries[4]. Those of the aluminum system are Brosset's[5] data converted to infinite dilution by numerical corrections used by Paul[9] for other polyvalent metal fluoride complexes. The present extrapolations agree remarkably well with the published values. The fact that the experimental data at the four ionic strengths fall into the proper sequence for extrapolation by the Debye-Hückel equation lends validity to these measurements by the lanthanum fluoride electrode.

9. A. D. Paul. University of California Radiation Laboratory Report No. UCRL 2926, (1955).

Acknowledgement—The help of W. L. Pillinger, who furnished the basic computer program and adapted it to our needs, is gratefully acknowledged.

Table 1. Experimental Data: Hydrogen-Fluoride System

Concentration (mM)			
F_T	H_T	F	$\bar{n}$
In 0.5 M NH_4NO_3			
0.978	9.902	0.137	0.085
1.953	9.883	0.295	0.168
4.761	19.630	0.422	0.221
5.000	20.612	0.417	0.223
5.000	20.612	0.409	0.223
2.924	9.863	0.475	0.248
3.891	9.844	0.680	0.326
4.854	9.825	0.930	0.399
4.854	9.825	0.900	0.402
9.433	19.445	1.109	0.428
10.00	20.612	1.080	0.433
5.335	9.816	1.070	0.434
5.814	9.806	1.220	0.468
6.292	9.797	1.410	0.498
6.770	9.788	1.580	0.530
7.722	9.768	2.000	0.586
8.670	9.749	2.450	0.638
9.615	9.731	2.950	0.685
9.615	9.731	2.800	0.700
18.518	19.085	4.091	0.756
20.00	20.612	4.170	0.768
20.00	20.612	4.100	0.771
24.93	22.14	6.559	0.830
27.272	18.738	10.271	0.907
In 0.3 M NH_4NO_3			
0.294	5.876	0.0320	0.045
0.587	5.871	0.119	0.080
0.590	4.420	0.151	0.099
1.172	5.859	0.253	0.157
0.597	0.994	0.381	0.217
0.597	0.829	0.411	0.224
1.754	5.848	0.403	0.231
0.597	0.664	0.440	0.236
0.598	0.504	0.472	0.250
0.598	0.339	0.511	0.257
2.335	5.836	0.577	0.301

Table 1. (Continued)

Concentration (mM)			
F_T	H_T	F	$\bar{n}$
1.478	2.96	0.586	0.301
2.913	5.825	0.773	0.367
2.913	5.82	0.768	0.369
3.488	5.814	1.003	0.427
4.062	5.803	1.257	0.483
2.941	2.941	1.429	0.514
4.633	5.792	1.533	0.535
5.202	5.780	1.812	0.586
5.769	5.769	2.176	0.623
5.77	5.77	2.162	0.625
4.390	2.927	2.494	0.648
7.177	5.742	3.150	0.701
5.825	2.912	3.693	0.732
8.571	5.714	4.185	0.768
9.953	5.687	5.325	0.814
8.654	2.885	6.249	0.834
25.21	22.69	6.090	0.843
11.32	5.66	6.533	0.846
11.32	5.660	6.522	0.847
25.64	17.95	9.500	0.899
16.67	5.56	11.57	0.917
26.09	13.04	13.76	0.946
16.822	2.804	14.10	0.971
26.79	5.357	21.02	1.077
In 0.1 M NH_4NO_3			
0.0706	0.0706	0.0699	0.053
0.0940	0.0940	0.0872	0.072
0.1904	0.0906	0.178	0.132
0.232	0.232	0.195	0.160
0.289	0.289	0.234	0.189
0.400	0.400	0.310	0.224
0.509	0.509	0.377	0.261
1.183	2.959	0.390	0.268
0.720	0.720	0.503	0.302
0.998	0.998	0.669	0.329
1.772	2.953	0.650	0.380
1.342	1.342	0.797	0.406
1.780	1.780	0.968	0.456

Table 1. (Continued)

Concentration (mM)			
F_T	H_T	F	$\bar{n}$
2.358	2.947	0.960	0.474
1.993	1.993	1.046	0.475
In 0.01 M NH_4NO_3			
0.0921	0.6004	0.0543	0.063
0.1838	1.199	0.0796	0.087
0.1840	0.6919	0.1044	0.115
0.1988	0.1988	0.1671	0.160
0.3668	1.3797	0.1531	0.155
0.3972	1.518	0.1568	0.158
0.2754	0.7831	0.1506	0.159
0.2136	0.2136	0.1755	0.178
0.3976	1.013	0.2014	0.194
0.3672	0.8742	0.1940	0.198
0.5491	1.560	0.2218	0.210
0.4585	0.9650	0.2347	0.232
0.3980	0.5070	0.2763	0.240
0.7307	1.7396	0.2872	0.255
0.4263	0.4263	0.3063	0.281
0.5502	0.5502	0.3830	0.304
0.6382	0.6382	0.4182	0.345
0.8492	0.8492	0.5140	0.395
1.059	1.059	0.6025	0.431
1.477	1.477	0.7580	0.487
1.892	1.892	0.8926	0.528

Table 2. Experimental Data: Aluminum-Fluoride System

Concentration (mM)				
R_T	H_T	Al	F	$\bar{n}$
In 0.5 M NH_4NO_3				
9.174	4.760	13.762	0.00112	0.666
1.000	5.153	1.250	0.00200	0.793
9.259	4.804	11.574	0.00152	0.799
9.259	4.804	11.574	0.00180	0.799
4.900	19.908	4.902	0.00360	0.989
9.345	4.848	9.345	0.00276	0.999
9.416	4.885	7.533	0.00544	1.247
9.469	4.913	6.155	0.01189	1.530
9.505	4.931	5.228	0.02510	1.797
2.500	5.153	1.250	0.03640	1.870
9.525	4.942	4.762	0.04117	1.963
9.525	4.942	4.762	0.04247	1.962
9.540	4.949	4.293	0.0758	2.147
9.560	4.960	3.824	0.1360	2.353
9.578	4.969	3.352	0.2448	2.569
5.000	5.153	1.250	0.4430	2.675
18.182	18.867	4.546	0.5340	2.757
9.597	4.979	2.879	0.4373	2.778
41.667	17.293	12.500	0.5690	2.895
20.361	18.878	4.525	0.7379	2.918
19.610	19.908	4.902	0.4510	2.939
9.615	4.988	2.404	0.7450	2.980
9.615	4.988	2.403	0.7235	3.003
41.840	17.365	11.510	0.7960	3.027
22.523	18.695	4.504	1.0075	3.058
42.017	17.439	10.504	1.130	3.158
9.634	4.998	1.927	1.217	3.171
24.663	18.611	4.484	1.349	3.175
42.192	17.512	9.493	1.629	3.284
26.786	18.528	4.464	1.771	3.289
28.889	18.446	4.444	2.300	3.394
74.630	15.100	18.660	2.000	3.416
42.372	17.586	8.474	2.367	3.411
30.973	18.364	4.425	2.961	3.487
42.553	17.661	7.447	3.520	3.522
33.040	18.284	4.405	3.771	3.573
75.760	15.330	15.150	5.650	3.795

Table 2. (Continued)

Concentration (mM)				
F_T	H_T	Al	F	$\bar{n}$
In 0.3 M NH_4NO_3				
0.600	5.153	1.250	0.00040	0.478
1.000	5.153	1.250	0.00159	0.794
1.500	5.153	1.250	0.00268	1.190
1.470	2.940	1.220	0.00460	1.193
1.760	2.940	1.220	0.00870	1.420
2.050	2.940	1.220	0.01567	1.640
2.350	2.930	1.220	0.02720	1.856
2.500	5.153	1.250	0.03056	1.884
2.640	2.930	1.220	0.0481	2.042
3.000	5.153	1.250	0.0593	2.179
2.927	2.927	1.220	0.0812	2.196
3.216	2.923	1.218	0.1251	2.334
3.794	2.918	1.216	0.2397	2.560
4.369	2.913	1.214	0.396	2.726
5.000	5.153	1.250	0.388	2.765
4.942	2.907	1.211	0.598	2.846
5.760	4.320	1.200	0.713	2.955
6.000	5.153	1.250	0.626	2.986
5.797	2.899	1.208	0.958	3.002
8.570	4.290	1.190	2.033	3.302
10.000	5.153	1.250	2.274	3.562
20.000	5.153	2.500	6.064	3.844
In 0.1 M NH_4NO_3				
1.012	1.012	1.242	0.00089	0.813
1.214	1.214	1.242	0.00145	0.975
1.416	1.416	1.242	0.00275	1.135
1.618	1.618	1.242	0.00368	1.296
1.618	1.618	1.242	0.00401	1.295
1.820	1.820	1.242	0.00532	1.455
1.820	1.820	1.242	0.00574	1.453
2.022	2.022	1.241	0.00730	1.613
2.022	2.022	1.241	0.00827	1.610
2.022	2.022	1.241	0.01056	1.606
2.223	2.223	1.241	0.01230	1.762
2.223	2.223	1.241	0.01340	1.760
2.425	2.425	1.248	0.01950	1.895
2.425	2.425	1.241	0.02057	1.903

Table 2. (Continued)

Concentration (mM)				
F_T	H_T	Al	F	$\bar{n}$
1.015	1.015	0.498	0.02678	1.936
2.627	2.627	1.241	0.02787	2.044
2.828	2.828	1.240	0.04210	2.165
2.828	2.828	1.240	0.04996	2.144
3.029	3.029	1.240	0.06047	2.271
3.029	3.029	1.240	0.07455	2.232
3.231	3.231	1.240	0.08162	2.366
1.482	1.482	0.494	0.1250	2.450
3.634	3.634	1.239	0.1287	2.530
3.033	3.033	0.993	0.1568	2.526
4.036	4.036	1.239	0.1862	2.649
4.036	4.036	1.239	0.1934	2.627
2.028	2.028	0.498	0.2715	2.740
5.040	5.040	1.238	0.3226	2.909
4.040	4.040	0.992	0.3409	2.787
2.071	1.479	0.493	0.3350	2.837
6.041	6.041	1.236	0.4987	2.986
7.034	7.034	1.481	0.5231	2.893
6.041	6.041	1.236	0.5354	2.882
5.044	5.044	0.991	0.5354	2.912
3.017	3.017	0.497	0.5570	2.941
7.041	7.041	1.235	0.6952	2.961
6.048	6.048	0.990	0.7199	2.997
7.048	7.048	0.989	0.8952	3.055
10.019	10.019	1.476	0.9226	3.096
8.039	8.039	1.234	0.8111	3.124
10.029	10.029	1.231	1.105	3.191
12.012	12.012	1.229	1.374	3.240
13.986	13.986	1.227	1.618	3.288
15.953	15.953	1.224	1.847	3.324
19.844	19.844	1.462	2.039	3.308
18.108	18.108	1.222	2.084	3.351
19.863	19.863	1.219	2.279	3.338
21.807	21.807	1.217	2.474	3.349

Table 2. (Continued)

Concentration (mM)				
F_T	H_T	Al	F	$\bar{n}$
In 0.01 M NH_4NO_3				
1.000	5.153	2.500	0.00014	0.400
1.000	5.153	1.250	0.00046	0.797
2.500	5.153	2.500	0.00086	0.998
3.212	3.212	2.711	0.00150	1.182
3.218	3.218	2.223	0.00337	1.440
4.000	5.153	2.500	0.00515	1.585
2.022	2.022	1.241	0.00555	1.613
3.024	3.024	1.733	0.00836	1.723
3.225	3.225	1.732	0.01150	1.829
2.500	5.153	1.250	0.01560	1.912
5.000	5.153	2.500	0.01840	1.948
3.030	3.030	1.240	0.0581	2.237
3.030	3.030	1.240	0.0550	2.247
4.036	4.036	1.239	0.1682	2.572
7.500	5.153	2.500	0.1598	2.603
5.040	5.040	1.238	0.2968	2.756
5.000	5.153	1.250	0.2600	2.807
6.041	6.041	1.236	0.4247	2.884
7.041	7.041	1.235	0.5579	2.948
8.039	8.039	1.234	0.6795	3.015
10.000	5.153	2.500	0.496	3.028
10.029	10.029	1.232	0.908	3.120
12.011	12.011	1.229	1.132	3.163
13.896	13.896	1.227	1.344	3.156
15.952	15.952	1.224	1.517	3.273
17.912	17.912	1.222	1.711	3.262
19.863	19.863	1.219	1.887	3.271
23.743	23.743	1.215	2.2043	3.306
27.593	27.593	1.210	2.486	3.352
38.966	38.966	1.196	3.240	3.362

Table 3. Stability Quotients of Hydrogen-Fluoride System in NH_4NO_3 at 25°C

Ionic Strength, M	k_1	k_2
0.53[8]	658	3.9
0.5	692	5.0
0.3	742	3.7
0.1	878	6.8
0.01	1203	5.8

[8] C. Brosset, Svensk Kem. Tidskr. 54, 155 (1942).

Table 4. Stability Quotients of Aluminum-Fluoride System in NH_4NO_3 at 25°C

Ionic Strength, M	k_1	k_2	k_3	k_4
0.53[5]	1.36×10^6	1.04×10^5	7.16×10^3	5.50×10^2
0.5	1.21×10^6	8.53×10^4	4.85×10^3	3.18×10^2
0.3	1.96×10^6	9.38×10^4	5.32×10^3	3.15×10^2
0.1	2.49×10^6	1.56×10^5	8.10×10^3	2.66×10^2
0.01	4.47×10^6	2.73×10^5	8.41×10^3	2.38×10^2

Table 5. Stability Constants of Hydrogen-Fluoride System

	This Work		
	log K ±2σ*	C	Reference [4]
log K_1	3.164 ±.010	-0.05	3.17
log K_2	0.7 ±0.2	0	0.59

*σ is standard deviation of K_n, calculated from the four k_n values used in the extrapolation

Table 6. Stability Constants of Aluminum-Fluoride System

	This Work		
	log K ±2σ*	C	References [5,9]
log K_1	6.98 ±0.16	-0.4	7.00
log K_2	5.62 ±0.04	0	5.55
log K_3	4.05 ±0.10	0	4.23
log K_4	2.38 ±0.02	-0.2	2.74

*See footnote, Table V.

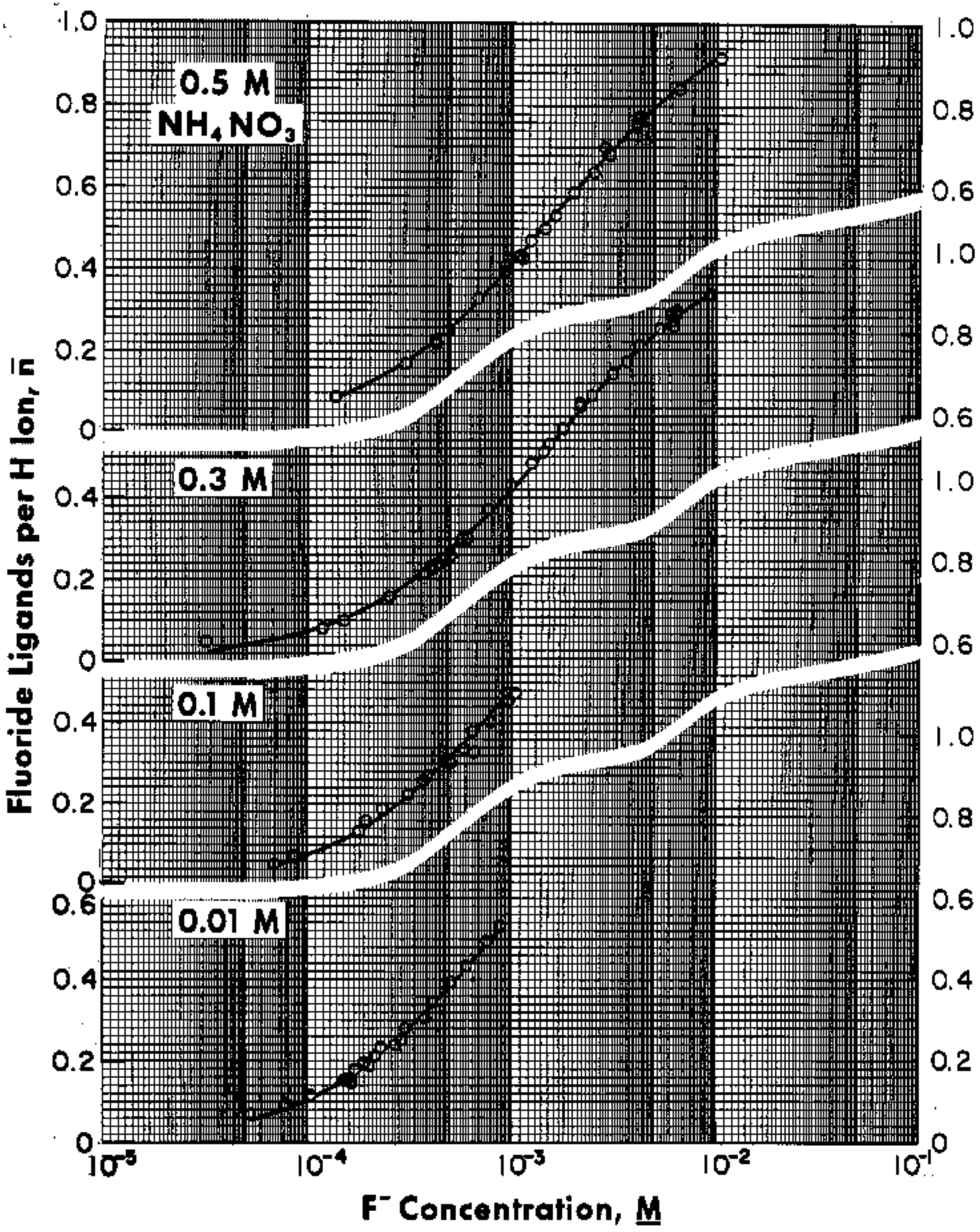

Fig. 1. Hydrogen-Fluoride System in NH_4NO_3.

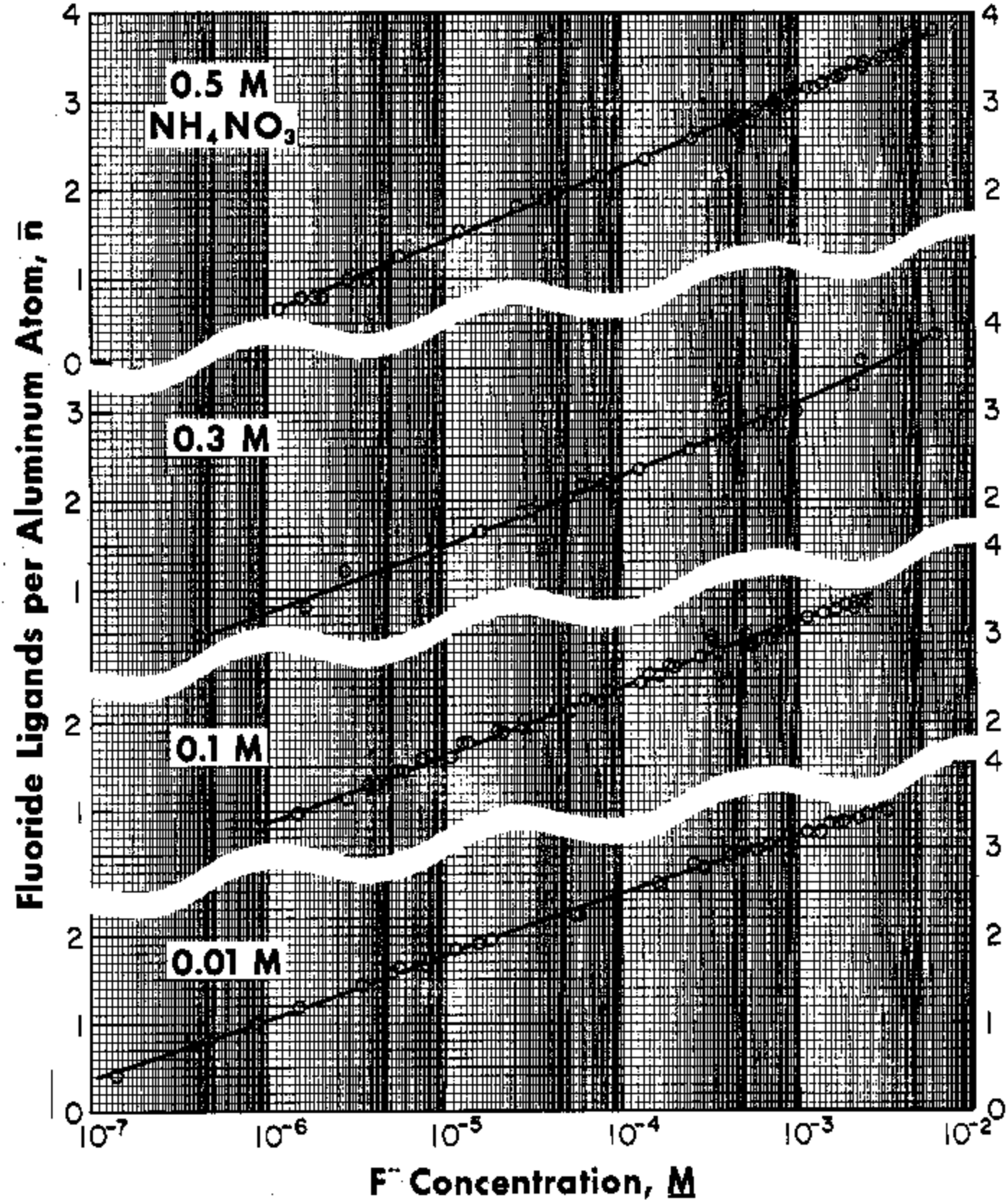

Fig. 2. Aluminum-Fluoride System in NH_4NO_3.