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Fluoride Complexes of Beryllium(II) in Aqueous Media

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Received August 19, 1968

The stability of the beryllium fluoride complexes has been measured potentiometrically in 1 *m* NaCl at 0, 25, and 60° and in 1 *m* $NaClO_4$ at 25°. The potentiometric cell consisted of a solid-state fluoride electrode and two hydrogen electrodes. The HF and HF_2^- equilibria were determined in both media in order to demonstrate the reversibility of the electrode as well as to interpret beryllium fluoride equilibria in acidic solutions. Efforts were made to identify species of the type $Be_xF_y(OH)_z^{(2x-y-z)+}$ which might exist by varying the beryllium ion, fluoride ion, and hydrogen ion concentrations over wide limits. Only mononuclear species were observed and no mixed complexes were identified. The small differences seen in chloride and in perchlorate media are attributed to changes in activity coefficients. Four mononuclear complexes with $y = 1$–4 give an excellent fit to the data which cover ligand numbers up to 3.4. Omission of any one of the stepwise equilibria leads to large systematic deviations in the calculated ligand numbers. The over-all log Q values in 1 *m* NaCl at 25° are 4.900 ± 0.014, 8.662 ± 0.015, 11.450 ± 0.018, and 12.876 ± 0.022. The differences in successive stability constants are interpreted in terms of the statistical effects and the electrostatic interactions in a series of tetrahedral complexes. The over-all beryllium fluoride formation equilibria are slightly exothermic with enthalpies of −0.35 ± 0.32, −1.51 ± 0.28, −1.80 ± 0.34, and −2.26 ± 0.35 kcal/mol, respectively. The stability of the complexes results from the large positive entropies of 21.2 ± 1.1, 34.6 ± 1.0, 46.4 ± 1.1, and 51.3 ± 1.2 eu. The stability data confirm some previously reported nmr results and the Raman spectrum observed for a $(NH_4)_2BeF_4$ solution is consistent with a tetrahedral structure. A general correlation was found for the log Q values for the fluoride complexes of a large number of metal ions in terms of Z_+ and r_+, the charge and radius of the cation. The log Q for the over-all formation reaction for metal fluoride complexes is given by $\log Q_{1,y} = -0.46 - 1.1y + (0.48Z_+{}^2/r^+)$.

Introduction

Beryllium fluoride complexes are of particular interest because they involve the smallest divalent cation and the most electronegative anion. Also they are expected to appear as a complete series of species with fourfold coordination:[1] $Be(H_2O)_4{}^{2+}$, $BeF(H_2O)_3{}^+$, $BeF_2(H_2O)_2$, $BeF_3(H_2O)^-$, $BeF_4{}^{2-}$. These complexes are uniquely stable[2] among the fluoride complexes of the divalent cations. Precise equilibrium measurements in this system over a range of temperature would permit an interesting examination of the separate contributions of the entropy and enthalpy changes to the stability of each successive complex.

Previous equilibrium studies in this system, largely confined to 25°, have led to rather discordant results. For example, values reported for log Q_1 corresponding to the first stepwise formation reaction are 5.05,[3] 4.29,[4a] 5.64,[4b] 5.89,[5] 5.40,[6] 4.89,[7] 3.64,[8] and 4.71.[9] This lack of accord may be attributed mainly to the difficulties of the several indirect methods of measurement used for the studies of fluoride complexing. Until now the most widely used[10] and probably the most reliable such method has been that first employed by Brosset and Orring,[11] who used the ferric–ferrous electrode as an indirect measure of the fluoride ion activity. The pH at which the ferric ion hydrolyzes limits the region of utility of this electrode and precise measurement and control of the ratio of ferric ion to ferrous ion concentration presents a tedious experimental problem. The number of equilibria which must be accurately defined before the stabilities of the fluoride complexes of a given cation can be determined also limits the accuracy of stability quotients measured by this method.

In the present emf study of beryllium fluoride complexing, we employed the recently developed lanthanum fluoride solid-state electrode,[12] demonstrating it to be a suitable fluoride ion reversible electrode for precise physical–chemical measurements. Hydrogen electrodes—as indicator and reference electrodes—were also included in the cells used so that the hydrogen ion concentration as well as the fluoride concentration could be followed directly. Measurements were made in the range 0–60° in 1 *m* NaCl media and at 25° in 1 *m* $NaClO_4$ media. The purpose of the latter measure-

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[11] C. Brosset and G. Orring, *Svensk. Kem. Tidskr.*, **55**, 101 (1943).

[12] M. S. Frant and J. W. Ross, Jr., *Science*, **154**, 1553 (1966).

ments was to verify the absence of significantly stable chloride complexes. Although there have been no reports of fluoride complexes involving other ligands or fluoride bridges in aqueous solutions, the pH, the fluoride concentration, and the beryllium concentration were varied widely to detect the presence of mixed complexes and/or polynuclear complexes—$Be_xF_y(OH)_z^{(2x-y-z)+}$—if such are formed in appreciable amounts. Finally an attempt was made to examine the complexes formed in this system by Raman spectroscopy.

Experimental Section

Reagents.—All beryllium solutions were prepared from a source of very high-purity beryllium hydroxide which was previously used in a recent beryllium hydrolysis study.[13] The hydroxide was dissolved in a slight excess of acid and the free acid composition was determined in the previously employed manner.

Sodium chloride solutions were prepared by neutralization of reagent sodium hydroxide with reagent hydrochloric acid. These solutions were found to contain appreciably less fluoride ($<2 \times 10^5$ *m* fluoride in 1 *m* NaCl) than could be obtained by recrystallizing commercially available reagent sodium chloride.[14] Reagent quality $NaClO_4 \cdot H_2O$ was recrystallized once from water by evaporation of the solvent to recover about half of the salt. Carbon dioxide was removed from stock solutions of sodium chloride and sodium perchlorate by acidifying to pH 3, purging with N_2, and then neutralizing with reagent sodium hydroxide. Solutions prepared in the above manner contained less than 2×10^{-5} *m* fluoride and less than a 10^{-5} *m* concentration of other protolytic impurities.

Sodium hydroxide solutions containing less than 0.1 mol % carbonate were stored in paraffin-coated Pyrex vessels to minimize contamination by silicates. A large volume of stock solution of reagent hydrofluoric acid was prepared, purged with N_2, and stored in a heavy-walled polyethylene vessel.

High-purity hydrogen (>99.5%) was further purified by passage through a Serfass hydrogen purifier, Model C-15D, and saturated with water vapor over the appropriate salt solution before admittance to the potentiometric cells. This purifier, which diffuses the hydrogen through a palladium alloy, is capable of producing hydrogen containing less than 10 ppb impurities.

Commercial BeF_2 and NH_4F were used to prepare concentrated solutions for the Raman spectral measurements. A Cary Model 81 spectrometer was employed using laser and Hg lamp energy sources.

Potentiometric Cells.—The potentiometric circuit, previously described,[15] consisted primarily of a vibrating-reed electrometer and a K-3 potentiometer in series with the cell. The cell temperature was maintained at 25.0 and 60.0° (±0.02°) and at 0° (±0.05°). The apparatus illustrated in Figure 1 consisted of a Teflon vessel with a Pyrex cap constructed with several ground-glass inlets for introducing the hydrogen gas, the titrant, and the electrode leads. The cell representations in 1 *m* NaCl are given below. The internal Ag, AgCl|Cl⁻ electrode of the LaF_3 electrode (Orion Model 94-09) is not represented. Solution A contained both the LaF_3 electrode and a hydrogen electrode and solution B in the small inner compartment contained only a hydrogen electrode. The liquid junction (Figure 1) was a porous Teflon plug compressed to produce a satisfactorily low flow rate (about 0.002 g/cm head of water/hr). Agitation was provided in solution A both by bubbling gas and by a magnetic stirrer and in solution B by bubbling gas. The hydrogen gas was bubbled at a flow rate of about 50 cm³/min over the platinized platinum hydrogen electrodes. Loss of hydrogen fluoride from acidic solutions by transpiration was observed to be less than 0.5% during the course of an experiment at 60°. This result is consistent with the vapor pressures reported for HF in aqueous solutions by Brosheer, *et al.*[16]

$$\begin{array}{r|l||l|l} & \text{solution A} & \text{solution B} & \\ \text{LaF}_3 & (1-2a)\ m\ \text{NaCl} & (1-d)\ m\ \text{NaCl} & \\ \text{and} & a\ m\ \text{BeCl}_2 & d\ m\ \text{HCl} & \text{H}_2,\ \text{Pt} \\ \text{Pt, H}_2 & b\ m\ \text{HF} & & \\ & c\ m\ \text{NaF} & & \end{array}$$

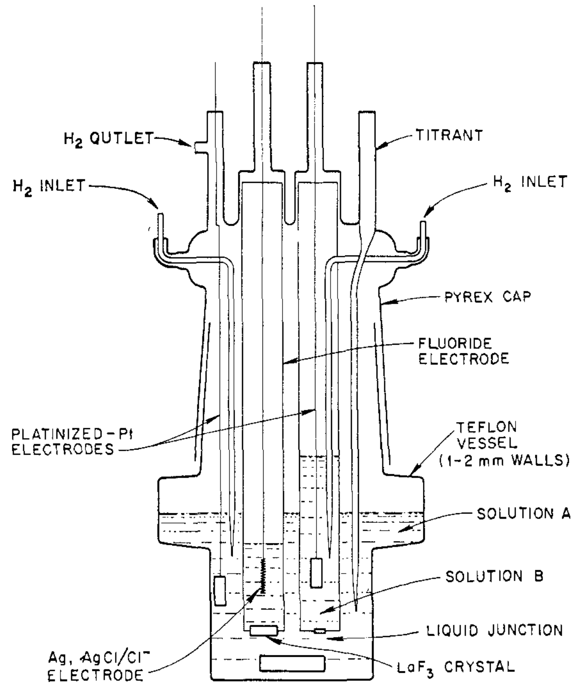

Figure 1.—Sketch of the potentiometric cell.

Corrections were made for the small drift in the fluoride electrode potential with time in the same manner employed previously for the glass electrode.[15] Approximately constant drift rates varying from a few tenths of a millivolt per hour to a few millivolts per hour were observed. The hydrogen electrodes attained constant potential within 30 min in all experiments and the fluoride electrode attained constant potentials or constant drift rates within a very few minutes after each addition except in some dilute solutions at 0.0° where up to 0.5 hr was required. Evidence for equilibrium in experiments on beryllium fluoride complexing was obtained not only by observing potentials until they became constant but also by conducting experiments in which the same $\bar{n}$ (ligand number) was attained at different acidities (Figure 4).

Results

Acidity Measurements.—The media were of very nearly constant ionic strength and constant composition and therefore activity coefficients could be neglected. The total *change* in potential between the hydrogen electrodes in the two solutions as titrant is added is given by

$$\sum \Delta E = (RT/\mathfrak{F}) \ln (h_r/h) + E_{LJ} \qquad (1)$$

E_{LJ} represents the corresponding change in liquid junction potential and h_r is a reference concentration

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[13] R. E. Mesmer and C. F. Baes, Jr., *Inorg. Chem.*, **6**, 1951 (1967).
[14] R. E. Mesmer, *Anal. Chem.*, **40**, 443 (1968).
[15] C. F. Baes, Jr., and N. J. Meyer, *Inorg. Chem.*, **1**, 780 (1962).
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of acid, at the beginning or the end of the titration experiment, to which the potential changes are referred. Experimentally observed values of E_{LJ} produced by changes in solution A in the absence of beryllium or fluoride were found to vary linearly with the hydrogen ion concentration as is predicted by the Henderson equation for such media.[15] In particular the Henderson equation for the liquid junction potential takes the form

$$E_{LJ} = -\sum(D_i(m_{i,r} - m_i)) \qquad (2)$$

wherein the coefficients D_i are given by

$$D_i = RT\lambda_i/(Z_i\mathfrak{F}\sum m_i\lambda_i) \qquad (3)$$

Here λ_i is the equivalent conductance of the ith ion and Z_i is the charge on the ion. Because the sum of the Na^+ and H^+ concentrations is constant in the absence of beryllium and the fluoride ions, the liquid junction potential is given by[15]

$$E_{LJ} = -(D_{H^+} - D_{Na^+})(h_r - h) \qquad (4)$$

The values for E_{LJ} calculated by eq 4 are in excellent agreement with the observed values; *e.g.*, the calculated value for $(D_{H^+} - D_{Na^+})$ is 61 mV m^{-1} compared with the observed value of 62 mV m^{-1}.

This excellent approximation of the liquid junction term was expected as a result of our previous work with similar glass junctions. Liquid junction potential corrections which ranged from 0 to 0.6 mV were made on all measurements by means of eq 2. In the presence of beryllium and fluoride ions the contribution of beryllium fluoride complexes to the liquid junction potentials was small owing to the low concentrations (less than 0.025 *m*) of total beryllium employed. The following approximations were made for the complexes

$$D_{BeF^+} \sim D_{Na^+},\ D_{BeF_2} \sim 0,\ D_{BeF_3^-} \sim D_{F^-},\ D_{BeF_4^{2-}} \sim D_{SO_4^{2-}}$$

The correct liquid junction term and the best set of formation quotients were calculated by successive approximations. The $-\log h$ columns in Tables I and II were determined from eq 1 in which the acidity of the solution A at the beginning of a titration was taken as h_r.

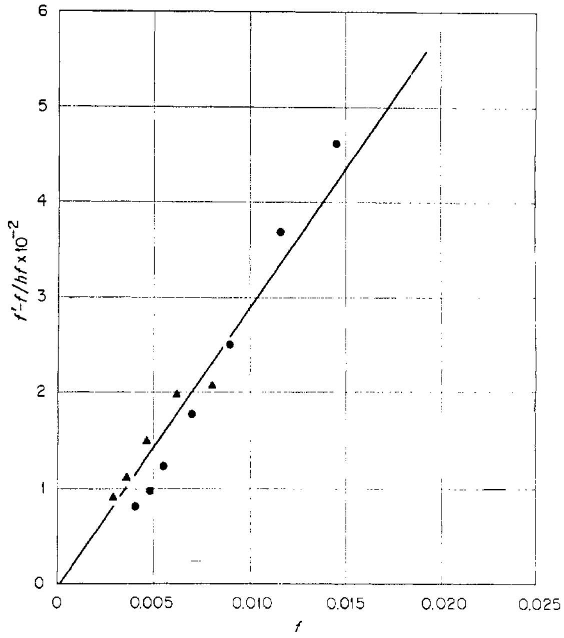

Figure 2.—Plot of the $(f' - f)/hf$ *vs.* f at 60° in 1 *m* NaCl for (●) 0.035 and (▲) 0.015 *m* fluoride solutions.

Fluoride Ion Measurements.—The solid-state fluoride electrode which was described in some detail previously[12,17] consists essentially of an internal Ag, AgCl|Cl$^-$ electrode in a solution containing fluoride ions on one side of a Eu^{2+}-doped LaF_3 single crystal. The potential of the electrode *vs.* a reference electrode is given by

$$E = E' - (RT/\mathfrak{F}) \ln a_{F^-} \qquad (5)$$

where the free fluoride ion activity is measured. The value of E' depends on the potential of the internal Ag, AgCl|Cl$^-$ electrode, the potential of the reference electrode, the activity of fluoride in the internal solution, and the liquid junction potential if any. The electrode exhibits Nernst behavior down to less than 10^{-7} *m* free fluoride in a fluoride-buffered solution in 1 *m* chloride.[14] The response of the electrode in acidic solutions was examined by measuring the hydrogen fluoride equilibria. The fluoride species known to exist in acidic aqueous solutions are F^-, HF, and HF_2^-.[9,18] The *changes* in potential occurring during a titration experiment when the potential of the fluoride electrode is measured against the hydrogen reference electrode are given by

$$\sum\Delta E = -(RT/\mathfrak{F}) \ln (f_r/f) - \sum D_i(m_{i,r} - m_i) \qquad (6)$$

where f_r is the reference concentration, a known fluoride concentration at the beginning or end of the titration (noting again that activity coefficients may be assumed constant). Fluoride ion concentrations thus obtained at 0 and 25° agree well with calculated values based on the measured hydrogen ion concentration and the assumed equilibria (to be discussed later). However, at 60° an apparent interference by HF_2^- ion exists. The interference led to a greater drift rate as well as a higher value for the measured fluoride concentration, f', compared with the fluoride concentration derived from hydrogen ion data, f. If the selectivity ratio α of the electrode for HF_2^- compared with F^- is defined by

$$f' = f + \alpha Q_{1,2}hf^2 \qquad (7)$$

then the slope a plot of $(f' - f)/hf$ *vs.* f (Figure 2) gives a value of 0.7 for α. In eq 7 $Q_{1,2}$ is the quotient for the formation of HF_2^- from H^+ and F^-. Because of the interference of HF_2^- ion, the fluoride ion concentration (f) used at 60° (Table I) was derived from the hydrogen ion concentration, h, and the assumed equilibria.

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(17) J. J. Lingane, *Anal. Chem.*, **39**, 881 (1967).

(18) H. N. Farrer and F. J. C. Rossotti, *J. Inorg. Nucl. Chem.*, **26**, 1959 (1964).

TABLE I

HYDROGEN FLUORIDE EQUILIBRIUM DATA IN 1 *m* NaCl AND 1 *m* $NaClO_4$

$m_f\times10^2$	$-\log h$	$-\log f^a$	$\bar{n}(H)_o$
25°, 1 *m* $NaClO_4$			
4.232	2.159	2.222	0.836
4.144	2.253	2.160	0.807
4.051	2.357	2.090	0.769
3.939	2.507	1.998	0.709
3.861	2.594	1.947	0.670
3.770	2.718	1.883	0.611
3.672	2.859	1.818	0.543
3.552	3.049	1.744	0.448
3.356	3.465	1.636	0.272
3.243	3.898	1.580	0.158
3.143	5.121	1.529	0.047
3.109	5.590	1.507	0.006
1.134	2.508	2.519	0.726
1.123	2.610	2.460	0.678
1.112	2.714	2.402	0.625
1.100	2.855	2.331	0.554
1.089	2.999	2.268	0.479
1.072	3.257	2.180	0.355
1.061	3.478	2.128	0.268
1.054	3.703	2.091	0.201
1.048	3.967	2.064	0.150
1.043	4.307	2.037	0.098
1.037	4.695	1.999	0.033
1.034	5.575	1.986	0.008
4.232	2.167	2.219	0.839
4.144	2.263	2.151	0.810
4.052	2.370	2.079	0.772
3.931	2.521	1.985	0.712
3.864	2.606	1.934	0.674
3.773	2.735	1.869	0.616
3.677	2.860	1.804	0.547
3.557	3.039	1.731	0.452
3.460	3.205	1.675	0.368
3.365	3.401	1.625	0.278
3.256	3.718	1.572	0.170
3.194	4.019	1.544	0.103
3.138	4.713	1.519	0.041
0°, 1 *m* NaCl			
3.401	2.144	2.191	0.789
3.286	2.310	2.085	0.721
3.195	2.462	1.997	0.652
3.105	2.630	1.910	0.570
3.028	2.791	1.840	0.489
2.944	2.998	1.768	0.389
2.864	3.248	1.705	0.284
2.790	3.603	1.651	0.178
2.729	4.430	1.609	0.083
1.778	2.342	2.326	0.744
1.751	2.449	2.263	0.691
1.724	2.577	2.194	0.626
1.696	2.722	2.121	0.547
1.665	2.914	2.042	0.445
1.635	3.136	1.973	0.337
1.607	3.431	1.912	0.224
1.584	3.889	1.864	0.124
1.568	5.014	1.829	0.049
1.562	5.369	1.812	0.018
25°, 1 *m* NaCl			
1.074	2.503	2.520	0.707
1.060	2.618	2.449	0.654
1.047	2.737	2.383	0.596
1.034	2.870	2.314	0.523
1.017	3.071	2.230	0.414
1.003	3.290	2.164	0.306
0.986	3.651	2.092	0.172
0.977	3.985	2.057	0.098
0.971	4.429	2.032	0.044
25°, 1 *m* NaCl			
3.652	2.184	2.237	0.821
3.555	2.294	2.165	0.785
3.444	2.432	2.077	0.733
3.325	2.592	1.989	0.662
3.218	2.745	1.910	0.587
3.134	2.877	1.852	0.519
3.011	3.093	1.772	0.409
2.894	3.352	1.703	0.290
2.793	3.689	1.649	0.177
2.690	4.742	1.597	0.051
60°, 1 *m* NaCl			
3.953	2.331	2.390	0.835
3.863	2.435	2.320	0.803
3.783	2.534	2.256	0.769
3.659	2.694	2.158	0.709
3.507	2.898	2.044	0.618
3.359	3.118	1.936	0.515
3.230	3.346	1.840	0.412
3.079	3.708	1.719	0.279
2.984	4.097	1.632	0.187
2.874	4.772	1.569	0.069
1.687	2.563	2.539	0.768
1.657	2.701	2.446	0.709
1.622	2.881	2.337	0.629
1.581	3.121	2.207	0.510
1.540	3.414	2.081	0.378
1.509	3.738	1.979	0.266
1.472	4.252	1.891	0.120

[a] Measured with fluoride electrode at 25° and 0°; derived from hydrogen ion data at 60°C.

TABLE II

BERYLLIUM FLUORIDE EQUILIBRIUM DATA IN 1 *m* NaCl AND 1 *m* $NaClO_4$

$m_b\times10^3$	$m_f\times10^2$	$-\log h$	$-\log f$	$\bar{n}_o$
25°, 1 *m* NaCl				
0.2224	0.1032	3.084	3.426	1.881
0.4132	0.0995	3.032	3.708	1.594
0.5865	0.0961	3.002	3.989	1.329
0.8014	0.0919	2.983	4.320	1.039
1.043	0.0872	2.971	4.615	0.793
1.355	0.0811	2.965	4.883	0.581
1.639	0.0756	2.961	5.064	0.452
1.906	0.0704	2.958	5.202	0.363
2.342	0.0619	2.952	5.389	0.261
1.567	4.372	5.750	1.418	3.462
2.887	4.204	5.741	1.494	3.430
4.126	4.046	5.711	1.578	3.386
5.167	3.914	5.596	1.660	3.332
6.031	3.804	5.544	1.738	3.268
7.268	3.647	5.488	1.873	3.168
8.270	3.520	5.428	2.008	3.065
9.545	3.357	5.320	2.223	2.888
10.52	3.233	5.227	2.429	2.717
11.52	3.106	5.115	2.667	2.509
13.15	2.899	4.861	3.076	2.140
14.56	2.719	4.603	3.409	1.840
1.224	1.040	2.315	2.814	2.504
2.085	1.016	2.216	3.022	2.262
2.946	0.9925	2.140	3.230	2.050
3.816	0.9684	2.086	3.439	1.839
4.899	0.9384	2.044	3.691	1.584
6.057	0.9064	2.019	3.953	1.342
7.101	0.8775	2.009	4.164	1.153
8.956	0.8262	2.005	4.475	0.890
11.38	0.7592	2.009	4.766	0.655
13.44	0.7021	2.015	4.950	0.515
16.76	0.6103	2.026	5.182	0.361
0.320	0.3488	2.735	2.951	2.403
1.808	0.3353	2.489	3.726	1.491
2.790	0.3264	2.437	4.206	1.085
3.810	0.3172	2.413	4.552	0.803
4.775	0.3084	2.396	4.773	0.632
5.872	0.2985	2.383	4.954	0.500
6.993	0.2883	2.369	5.094	0.407
8.603	0.2737	2.348	5.250	0.315
0.617	0.4218	2.608	3.020	2.322
1.163	0.4079	2.513	3.285	2.002
2.082	0.3844	2.421	3.765	1.523
2.770	0.3668	2.388	4.113	1.209
3.547	0.3469	2.377	4.431	0.934
4.438	0.3242	2.369	4.701	0.711
5.291	0.3024	2.362	4.893	0.561
6.031	0.2834	2.346	5.029	0.463
25°, 1 *m* NaCl				
0.813	1.868	5.761	1.794	3.181
1.661	1.823	5.729	1.887	3.152
2.670	1.769	5.692	2.021	3.057
3.521	1.724	5.637	2.163	2.943
4.219	1.687	5.581	2.306	2.826
4.994	1.646	5.477	2.501	2.662
6.083	1.588	5.274	2.832	2.368
7.017	1.539	4.995	3.143	2.089
8.241	1.473	4.671	3.518	1.751
10.18	1.371	4.264	3.969	1.336
25°, 1 m $NaClO_4$				
0.878	2.058	5.558	1.752	3.202
1.982	2.007	5.586	1.862	3.185
3.556	1.934	5.251	2.070	3.030
4.649	1.883	5.109	2.265	2.874
5.674	1.835	4.971	2.506	2.681
6.948	1.776	4.798	2.873	2.361
8.571	1.701	4.580	3.355	1.932
9.826	1.643	4.382	3.670	1.649
10.86	1.594	4.206	3.883	1.455
12.22	1.531	4.035	4.118	1.246
1.960	4.694	5.738	1.398	3.478
4.594	4.408	5.699	1.548	3.424
7.218	4.123	5.665	1.757	3.284
9.391	3.887	5.698	2.010	3.096
11.64	3.643	5.639	2.398	2.786
13.85	3.402	5.213	2.876	2.360
15.91	3.179	4.750	3.316	1.968
17.90	2.963	4.383	3.675	1.643
19.44	2.796	4.161	3.907	1.432
1.277	1.064	2.314	2.838	2.493
2.096	1.045	2.223	3.031	2.283
3.201	1.019	2.133	3.291	2.026
4.878	0.980	2.056	3.683	1.650
6.964	0.931	2.025	4.134	1.243
8.851	0.887	2.026	4.460	0.967
11.86	0.817	2.040	4.819	0.678
14.65	0.752	2.056	5.045	0.508
16.99	0.697	2.076	5.193	0.407
19.06	0.649	2.091	5.305	0.339
20.79	0.609	2.105	5.392	0.291
0.284	0.419	2.700	2.888	2.457
0.622	0.408	2.632	3.049	2.269
1.025	0.394	2.562	3.257	2.048
1.496	0.378	2.506	3.514	1.779
2.076	0.358	2.471	3.867	1.471
2.802	0.333	2.466	4.279	1.115
3.487	0.309	2.479	4.588	0.859
4.173	0.286	2.499	4.821	0.670
5.285	0.247	2.537	5.102	0.463
0°, 1 *m* NaCl				
3.538	0.9761	2.083	3.349	2.031
4.846	0.9399	2.033	3.701	1.680
6.294	0.8998	2.009	4.033	1.332
7.650	0.8623	2.003	4.307	1.084
9.007	0.8248	2.000	4.532	0.894
10.31	0.7888	2.004	4.700	0.752
11.34	0.7601	2.007	4.811	0.661
1.347	1.889	6.966	1.836	3.191
2.639	1.859	7.473	1.983	3.098
3.826	1.831	7.445	2.158	2.966
5.055	1.802	7.132	2.397	2.770
6.361	1.771	6.667	2.723	2.486
7.545	1.743	6.150	3.051	2.192
8.592	1.718	5.736	3.326	1.945
9.857	1.689	5.334	3.614	1.688
2.247	4.445	5.854	1.436	3.440
4.536	4.317	6.186	1.557	3.396
6.992	4.179	7.329	1.727	3.295
10.01	4.010	7.440	2.027	3.066
12.61	3.865	6.914	2.409	2.756
15.39	3.709	6.130	2.895	2.328
17.88	3.570	5.527	3.296	1.969
20.57	3.419	5.029	3.647	1.651
60°, 1 *m* NaCl				
1.281	0.4049	2.539	3.451	1.659
1.678	0.3947	2.486	3.640	1.533
2.221	0.3808	2.439	3.890	1.334
2.745	0.3674	2.414	4.122	1.149
3.497	0.3482	2.396	4.409	0.916
4.434	0.3243	2.390	4.696	0.699
5.366	0.3004	2.392	4.907	0.543
2.617	4.424	5.890	1.453	3.394
4.808	4.302	6.010	1.574	3.383
7.348	4.159	6.131	1.750	3.236
9.153	4.058	6.139	1.912	3.094
12.56	3.867	5.771	2.359	2.730
14.67	3.749	5.336	2.709	2.422
16.76	3.632	4.891	3.057	2.114
19.04	3.505	4.475	3.392	1.818
20.66	3.414	4.237	3.593	1.639
22.34	3.319	4.029	3.772	1.478
1.237	2.248	5.591	1.734	3.184
2.693	2.208	5.575	1.866	3.116
3.959	2.172	5.546	2.011	3.009
4.950	2.145	5.492	2.151	2.898
5.902	2.118	5.436	2.316	2.765
7.251	2.080	5.244	2.602	2.521
8.811	2.037	4.933	2.977	2.189
10.41	1.992	4.576	3.337	1.867
11.96	1.948	4.282	2.626	1.608

In the studies of beryllium fluoride complexing, low concentrations of free fluoride were employed at 60° to minimize the error from this source.

Data Analysis.—The nonlinear least-squares computer program previously used to treat beryllium hydrolysis data[13] was adapted for calculation of the formation quotients and their standard errors for the various fluoride species from the data of Tables I and II.

An observable quantity $\bar{n}(H)_o$, which represents the average number of H^+ ions bound per F^- ion in solution (as HF and HF_2^-), was defined for convenience in analyzing the hydrogen fluoride equilibria. It is given by

$$\bar{n}(H)_o = (m_h - h)/m_f \qquad (8)$$

where m_h and m_f are the total hydrogen ion and total fluoride ion concentrations, respectively. This was compared with the corresponding quantity derived from the assumed equilibria

$$\bar{n}(H)_c = [Q_{1,1}hf + Q_{1,2}hf^2]/m_f \qquad (9)$$

where $Q_{1,1}$ and $Q_{1,2}$ represent the formation of HF and HF_2^- from H^+ and F^-.

In the analysis of beryllium complexing data, the average number of fluorides bound per beryllium in solution, $\bar{n}_o$, was determined from the data by means of the expression

$$\bar{n}_o = (m_f - f)/m_b \qquad (10)$$

where m_f and m_b are, respectively, the total fluoride and total beryllium concentrations. A calculated value of this ligand number, $\bar{n}_c$, is given by the expression

$$\bar{n}_c = \sum yQ_{x,y}b^xf^y/m_b \qquad (11)$$

in which the formation quotients, $Q_{x,y}$, represent equilibria of the type

$$x\mathrm{Be}^{2+} + y\mathrm{F}^- = \mathrm{Be}_x\mathrm{F}_y^{(2x-y)+} \qquad (12)$$

and are defined by

$$Q_{x,y} = b_{x,y}/b^xf^y \qquad (13)$$

where $b_{x,y}$ represents the molal concentration of the complex ion $\mathrm{Be}_x\mathrm{F}_y^{(2x-y)+}$ and b is the concentration of the free beryllium. The value of b is computed for each point by successive approximations from the material balance expression corresponding to the assumed scheme of complex ions, *i.e.*

$$m_b = b + xQ_{x,y}b^xf^y \qquad (14)$$

As a measure of the agreement of $\bar{n}_c$ with $\bar{n}_o$ (or of $\bar{n}(H)_c$ and $\bar{n}(H)_o$) the agreement factor, $\sigma(\bar{n})$, is derived as

$$\sigma(\bar{n}) = [\sum W(\bar{n}_c - \bar{n}_o)^2/(N_o - N_v)]^{1/2} \qquad (15)$$

where N_o is the number of observations, N_v is the number of parameters varied in the calculation, and W is the weighting factor (taken as unity in this study).

Discussion

Hydrogen Fluoride Equilibria.—Most of the measurements of beryllium fluoride complex stability in this study were conducted in acidity ranges where the fluoride ion itself becomes protonated to some extent. Precise determination of the hydrogen fluoride equilibria in similar media is therefore essential to the correct analysis of the data. The formation quotients observed from the combined hydrogen ion concentration and fluoride ion concentration data at 0 and 25° and from the hydrogen ion concentration data alone at 60° are given in Table III. The goodness of fit of the data for all temperatures and the two media was shown by the agreement factors which ranged from 0.017 to 0.034. These formation quotients are consistent with previous results summarized in ref 9 and in the only instance where identical media were used[18] (1.0 *M* $NaClO_4$) the formation quotients for HF and HF_2^- agree within the estimated experimental error. Farrer and Rossotti[18] concluded that, in solutions with up to 1.0 *M* fluoride, only the species F^-, HF, and HF_2^- are present. The amount of HF_2^- present under the conditions of our experiments on beryllium fluoride complexing is small because fluoride concentrations of less than 0.01 *m* were used in pH regions where HF_2^- forms; *e.g.*, at 25° in 0.01 *m* fluoride solution with 10^{-3} *m* hydrogen ion concentration only 5% of the fluoride exists as HF_2^-.

Beryllium Fluoride Complexes.—The beryllium, fluoride, and hydrogen ion concentrations were varied over wide ranges to identify the significant species of the type $Be_xF_y(OH)_z^{(2x-y-z)+}$ where *z* can be positive or negative representing complexes containing hydroxide ions or hydrogen ions (as would be the case if HF or HF_2^- were a ligand). In experiments at 25° in 1 *m* NaCl the concentration ranges investigated were: beryllium concentrations from 2×10^{-4} to 1.7×10^{-2} *m;* total fluoride concentrations from 6×10^{-4} to 4.4×10^{-2} *m;* free fluoride concentrations from 1.6×10^{-6} to 1.0×10^{-2} *m.* The maximum value of $\bar{n}$ obtained was 3.46.

Figure 3 shows clearly that *x*, the number of beryllium ions in the complexes, is unity since for polynuclear complexes a series of approximately parallel curves for different beryllium ion concentrations is expected. This conclusion is also verified by the excellent fit of all of the data at the three temperatures to the curves which were calculated for schemes containing only mononuclear species. The complete absence of fluoride bridges is surprising in view of the strong tendency of OH^- to form bridges in aqueous solution.

The absence of OH^- or ligands containing hydrogen ions was very sensitively determined in experiments carried out in which $BeCl_2$ or $Be(ClO_4)_2$ solutions (with very small amount of free acid present) were added to approximately neutral sodium fluoride solutions in the 1 *m* chloride or perchlorate media. Under these conditions, any small amount of bound OH^- or H^+ would have produced an easily detectable change in pH. The small pH changes which occurred vividly illustrate that at $\bar{n} \geqslant 1.5$ the amount of hydroxide complexed is less than 0.5% of the beryllium complexed. These data as well as the previous work by us[13] show that hydrolysis at these very low concentrations of free beryllium ion is negligible. (In such experiments, the highest values of $\bar{n}$, *ca.* 3.4, were attained and uncertainties due to errors in the formation quotients for the hydrogen fluoride species are minimal.)

Although our experiments give no evidence for the existence of mixed complexes involving hydroxide and fluoride ions, one might expect their appearance at higher pH regions and at higher concentrations of beryllium. We did not extend our work to these regions because of expected hydroxide interference with the fluoride electrode.[12] The principal hydrolysis product of beryllium ion in this neutral region, $Be_3(OH)_3^{3+}$, is probably a ring structure and it seems likely, therefore, that if a mixed complex is formed, it would be an addition product of this species. A substitution product would probably have a chain structure since fluoride shows little tendency to be bidentate, and chain structures, in our opinion, are less stable than ring structures among hydrolysis products.

The lines (dotted, dashed, and solid) drawn in Figure 3 represent $\bar{n}_c$ calculated by least-squares analysis for three different schemes of complexes. The BeF^{2-} species was included in all three to account for $\bar{n}_0$ above 3.0 and this species was combined with BeF^+ and BeF_2 in one case and BeF^+ and BeF_3^- in the other. The omission of either BeF_2 or BeF_3^- from the current scheme produces large systematic deviations in $\bar{n}_c$. The corresponding effect is obtained if BeF^+ is omitted from the scheme of four species. The three species schemes give an agreement factor of *ca.* 0.2, whereas with the four-species scheme a value of 0.03 is obtained. This clearly demonstrates that none of the four species can be omitted.

Distribution of Beryllium Fluoride Species.—The formation quotients with their standard errors for the over-all equilibria are given in Table III. The goodness of fit of the data for all of the temperatures and the two media was shown by the agreement factors which ranged from 0.02 to 0.03 (less than 1% of the maximum

Table III

Logarithms of Stability Constants for Fluoride Equilibria in 1.0 *m* Chloride and 1.0 *m* Perchlorate Media

	1.0 *m* chloride			1.0 *m* perchlorate
	0.0°	25.0°	60.0°	25.0°
		$Be^{2+} + yF^- = BeF_y^{(2-y)+}$		
1	4.944 ± 0.032	4.900 ± 0.014	4.904 ± 0.030	4.989 ± 0.016
2	8.796 ± 0.028	8.662 ± 0.015	8.595 ± 0.027	8.796 ± 0.017
3	11.530 ± 0.033	11.450 ± 0.018	11.250 ± 0.032	11.610 ± 0.019
4	12.999 ± 0.034	12.876 ± 0.022	12.659 ± 0.033	13.048 ± 0.024
		$H^+ + yF^- = HF_y^{(1-y)+}$		
1	2.758 ± 0.020	2.887 ± 0.009	3.183 ± 0.011	2.928 ± 0.009
2	3.75 ± 0.22	3.87 ± 0.11	4.62 ± 0.07	3.79 ± 0.13

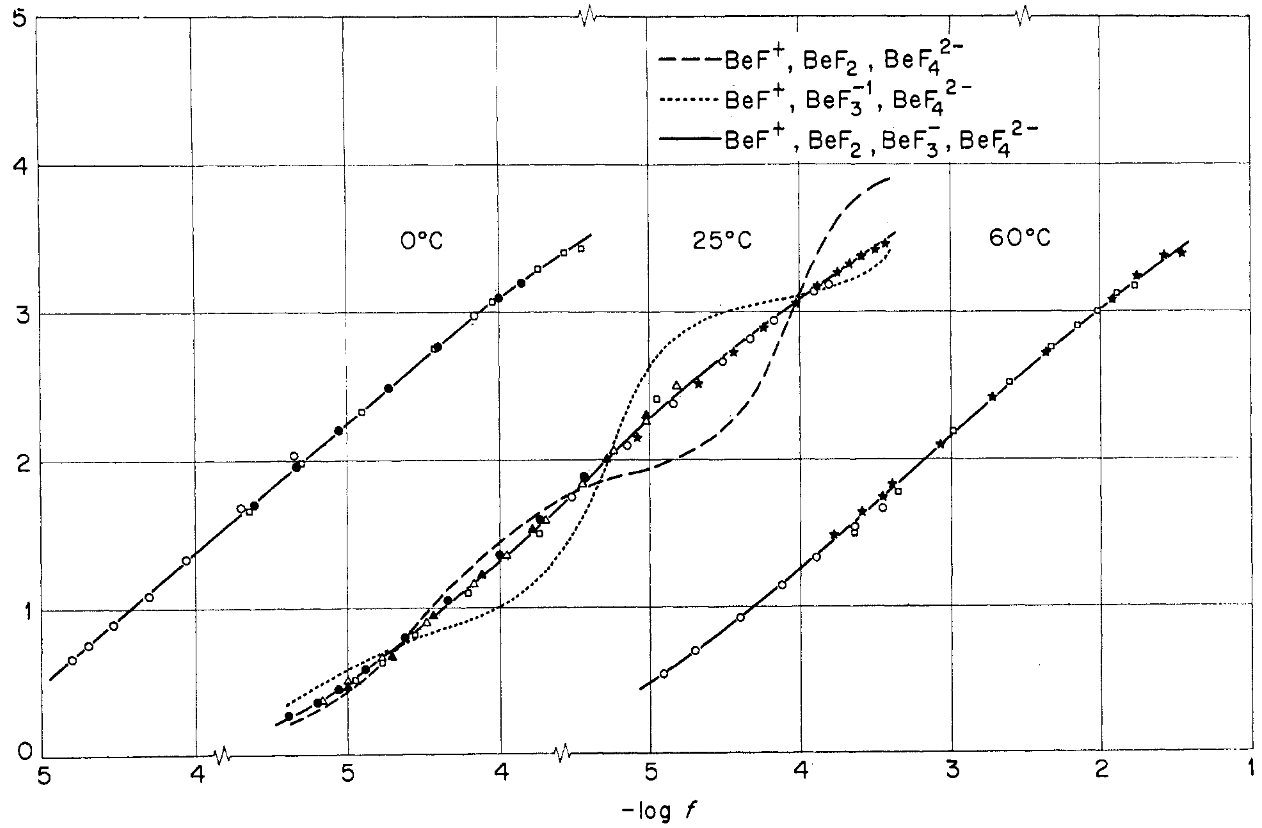

Figure 3.—The average number of fluorides complexed per beryllium, $\bar{n}_0$, as a function of $-\log f$ from experiments of Table II in 1 *m* NaCl at 0, 25, and 60° (the different symbols represent different experiments of Table II).

value of $\bar{n}$ attained). None of the previously reported studies was made in media identical with those used here. However, the work of Yates[3] on the first three equilibria in 0.5 *M* $NaClO_4$—log Q_1 = 5.05, log Q_2 = 8.82, and log Q_3 = 11.78 (Q_3 being poorly determined because the maximum $\bar{n}$ attained by Yates was only 2.0)—is most consistent with those reported here at 25°.

Figure 4 illustrates the distribution of species at 25° as a function of $-\log f$. It is important to note that this plot is independent of the total beryllium concentration (only mononuclear species are present) and the pH, the distribution being specified completely by the free fluoride concentration. The maximum attainable amounts of the species are 64% BeF^+, 58% BeF_2, 70% BeF_3^-, and 100% BeF_4^- (in concentrated fluoride solutions). It is noteworthy that the lowest maximum is attained for the neutral species.

This distribution confirms the recent interpretation of F^{19} spectra of BeF_4^{2+} and BeF_3^- by Kotz, *et al.*[19] They reported the spectrum of 1 *M* $(NH_4)_2BeF_4$ in water and observed two quartets with similar coupling constants, one representing about 80–85% of the signal and the other 15–20% of the signal. The major peaks were attributed to BeF_4^{2-} and the minor quartet was attributed to BeF_3^-. Our data indicate that 15% of the beryllium is present as BeF_3^- in a 1 *M* solution of $(NH_4)_2BeF_4$ supporting the spectral assignments made by Kotz, *et al.* The temperature dependence of the nmr spectrum indicated rapid fluoride exchange between species. This is consistent with our observation of the rapid equilibration in the system.

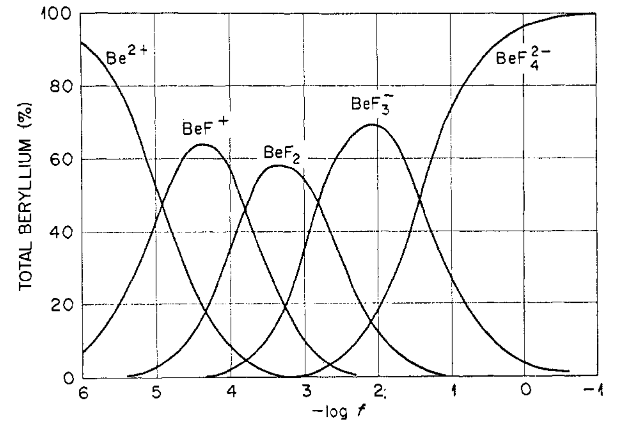

Figure 4.—Distribution of beryllium fluoride complexes as a function of $-\log f$ at 25° in 1 *m* NaCl.

Absence of Beryllium Chloride Complexes.—From our data in both chloride and perchlorate media at 25° in Table III, it is evident that the amount of beryllium complexing by chloride is very small. An accurate calculation of the formation quotient for $BeCl^+$ is not possible because of the unavailability of activity coeffi-

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(19) J. C. Kotz, R. Schaeffer, and A. Clouse, *Inorg. Chem.*, **6**, 620 (1967).

cient data for the species involved in the two media. However, in the absence of this information we will note that the HF formation quotient increases by only 0.04 ± 0.02 log unit in going from 1 *m* NaCl to 1 *m* $NaClO_4$. For these same media log Q_1 for BeF^+ increases by only 0.09 ± 0.03 unit. In view of the small magnitude of these differences and the uncertainties which must be assigned, as well as the likelihood that greater activity coefficient changes might be expected for BeF^+ formation than for HF formation, the assignment of any significantly large value for the formation quotient for $BeCl^+$ is not warranted by our data. Hardy, *et al.*,[7] assigned a value of 0.22 for this formation quotient without allowing for activity coefficient changes in 1 *M* HCl and 1 *M* HNO_3. From their data and those reported here we can only conclude that $BeCl^+$ is indeed a very weak complex.

There is a strong argument for the formation of outer-sphere complexes between beryllium and chloride based on the ionic radii. The waters on $Be(H_2O)_4{}^{2+}$ are essentially touching and to introduce the 30% larger Cl^- ion in place of one water requires a lengthening of all the Be^{2+}–H_2O distances or a reduction of the coordination number of Be^{2+}. Both of these processes are energetically highly unfavorable. Outer-sphere complexes of rather low stability might result which have a beryllium to chloride distance of 5 Å. The 10^5- to 10^6-fold differences in the stabilities of the beryllium fluoride and beryllium chloride complexes could not be accounted for simply in electrostatic terms by the difference in the $(r_+ + r_-)$ sum if inner-sphere complexes were formed in both cases.

Raman Spectra.—To obtain information on the bonding and structure of the $BeF_4{}^{2-}$ ion, the Raman spectrum of a 3.0 *m* solution of $(NH_4)_2BeF_4$ in 2.6 *m* NH_4F was examined. Relatively weak peaks were observed at 543 and 800 cm^{-1} which we assign to ν_1 and ν_3 for a tetrahedral species. These positions are generally consistent with the trends seen[20] for CF_4 and $BF_4{}^-$. There can be little doubt that the $BeF_4{}^{2-}$ is an inner-sphere complex as all of the physical evidence suggests and the very weak Raman intensities observed would be expected for a weakly polarizable ionic species such as $BeF_4{}^{2-}$. Very broad, low-intensity peaks occur in the lower wave number region, 300–400 cm^{-1}, where ν_2 and ν_4 are expected to occur.

Thermodynamic Properties.—The log values of the ratios of stepwise *Q* values [log (Q_1/Q_2) is represented by 1:2] are: at 0° (1:2) 1.09, (2:3) 1.12, and (3:4) 1.27; at 25° (1:2) 1.14, (2:3) 0.97, and (3:4) 1.36; and at 60° (1:2) 1.21, (2:3) 1.03, and (3:4) 1.26. The trend for successive ratios is slightly irregular in that 2:3 is smallest at each temperature and 3:4 is greatest.

A part of these ratios is attributable to the statistical effect of the changes of symmetry numbers of the product and reactant species. Based on tetrahedral geometry for all beryllium species, the log values of the ratios calculated for the statistical effect are (1:2) 0.57, (2:3) 0.65, and (3:4) 0.57. The corresponding observed values are 1.15 ± 0.2 indicating that additional effects must be considered in order to account for the magnitude of the observed ratios.

Considering that each complex is a tetrahedron, we should be able to approximate its coulombic energy in terms of the interaction of F^- and H_2O at the vertices with the central Be^{2+} ion and with one another along the tetrahedral edges. There are five such pairwise interactions: Be^{2+}–F^- (bf), Be^{2+}–H_2O (bw), F^-–F^- (ff), F^-–H_2O (fw), and H_2O–H_2O (ww). Considering the interactions for each complex

$Be(H_2O)_4{}^{2+}$	0bf + 0fw + 4bw + 6ww + 0ff
$BeF(H_2O)_3{}^+$	1bf + 3fw + 3bw + 3ww + 0ff
$BeF_2(H_2O)_2$	2bf + 4fw + 2bw + 1ww + 1ff
$BeF_3(H_2O)^-$	3bf + 3fw + 1bw + 0ww + 3ff
$BeF_4{}^{2-}$	4bf + 0fw + 0bw + 0ww + 6ff

and the differences between the interactions for successive complexes

$$BeF(H_2O)_3{}^+ - Be(H_2O)_4{}^{2+} \qquad 1bf + 3fw - 1bw - 3ww + 0ff$$

$$BeF_2(H_2O)_2 - BeF(H_2O)_3{}^+ \qquad 1bf + 1fw - 1bw - 2ww + 1ff$$

$$BeF_3(H_2O)^- - BeF_2(H_2O)_2 \qquad 1bf - 1fw - 1bw - 1ww + 2ff$$

$$BeF_4{}^{2-} - BeF_3(H_2O)^- \quad 1bf - 3fw - 1bw - 0ww + 3ff$$

we see that the differences in these differences—which contribute to the ratio of the successive stepwise *Q* values—are a constant equal to ff + ww − 2fw. These are all repulsive terms and if, as seems likely, the F^-–F^- term plus the H_2O–H_2O term is greater than twice the F^-–H_2O term, then it is expected that the coulombic energy of successive complexes should decrease in such a way as to make a constant contribution to log $(Q_\nu/Q_{\nu+1})$. This, along with the statistical effect, could account for the essential features of the successive complex stabilities. (The coulombic interactions, as well as the statistical effects to be considered in the case of the octahedral complexes of aluminum fluoride, are much more complicated because of the possible distribution of isomers as discussed briefly by King and Gallagher.[21]) With this model the nearly regular variation of log *Q* for the successive stepwise reactions would be expected to be reflected in the ΔH and ΔS values for the reactions. Considering the estimated uncertainties of these quantities (1σ), the data in Table IV show a reasonably regular variation with the possible exception of step 2 in which BeF_2 is formed.

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(20) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, New York, N. Y., 1963, p 106.

(21) E. L. King and P. K. Gallagher, *J. Phys. Chem.*, **63**, 1073 (1959).

TABLE IV

THERMODYNAMIC PROPERTIES FOR STEPWISE EQUILIBRIA OF BERYLLIUM FLUORIDE SPECIES IN 1.0 m CHLORIDE AT 25°

$$BeF_{y-1}^{(3-y)+} + F^- = BeF_y^{(2-y)+}$$

	Log Q_y	ΔH, kcal	ΔS, eu
1	4.900 ± 0.014	-0.35 ± 0.32	21.2 ± 1.1
2	3.762 ± 0.016	-1.16 ± 0.24	13.3 ± 0.8
3	2.788 ± 0.017	-0.29 ± 0.23	11.8 ± 0.8
4	1.426 ± 0.020	-0.46 ± 0.25	5.0 ± 0.9

The ΔH and ΔS values in Table IV were derived from the temperature coefficient data assuming constant ΔC_p for the association reactions and the estimated errors were calculated by the propagation of error method. The stepwise association reactions are all slightly exothermic with heats less than -1.5 kcal/mol and the entropy changes are positive, 21 eu for the first association step and 5 eu for the fourth step. The agreement of these results with the ΔH and ΔS values obtained by Yates[3] for the first stepwise association for beryllium fluoride is excellent. However, Yates obtained a small positive heat for the second step and he was unable to derive thermodynamic data for the later steps because of the low $\bar{n}$ obtained experimentally and the scatter of data.

The ΔH and ΔS for the formation of HF from H^+ and F^- are 2.75 ± 0.18 kcal/mol and 22.5 ± 0.6 eu and for the formation of HF_2^- from the ions are 5.2 ± 1.9 kcal/mol and 35 ± 7 eu. The values 2.6 kcal/mol and 22 eu have been reported from calorimetric measurements in 0.5 M $NaClO_4$[11,22] for the association of HF. The ΔS for the first stepwise beryllium fluoride complex is the same as for the HF formation equilibrium but the heat is slightly exothermic for the former and endothermic for the latter reaction. For $AlF_y^{(3-y)+}$ complexes Hepler, *et al.*,[22] observed stepwise heats which varied regularly from 1.15 to -1.55 kcal/mol.

King and Gallagher[21] pointed out that for a given reaction there is a relationship between ΔS (corrected for statistical effects) and ΔZ^2, suggesting that the entropy of the ions is related to Z^2 of the ions. ΔS was given by $[12.8 - 2.9\Delta Z^2]$ for stepwise formation reactions for the aluminum fluoride complexes. For the beryllium fluoride complexes the relationship obtained for ΔS is $[11.2 - 1.8\Delta Z^2]$ with an average deviation of about 1 eu, approximately the estimated error. The significance of this correlation is not known but it may result because ΔZ^2 is a simple function of y, the number of fluorides on the complex for either of these cases.

The stability of the first beryllium fluoride complex far exceeds that predicted from Bjerrum's equation ($K \sim 40$) and the additional stability is due largely to the entropy term. This effect, found in other systems, is commonly attributed to desolvation, *i.e.*, the release of water from the complex ion. In general the reaction can be represented as shown in eq 16

$$Be(H_2O)_4^{2+} + yF(H_2O)_z^- = Be(H_2O)_{(4-y)}F_y(H_2O)_a^{(2-y)+} + (y + zy - a)H_2O \quad (16)$$

where the number of moles of water released $y + zy - a \geq 2$ because sites are made available on both the cation and anion to produce an inner-sphere complex. Depending on the unknown structure of the $F(H_2O)_z^-$ the number of waters freed in eq 16 might vary as more fluorides are crowded around the beryllium ion. This effect would also be reflected in the ratio of the successive Q values.

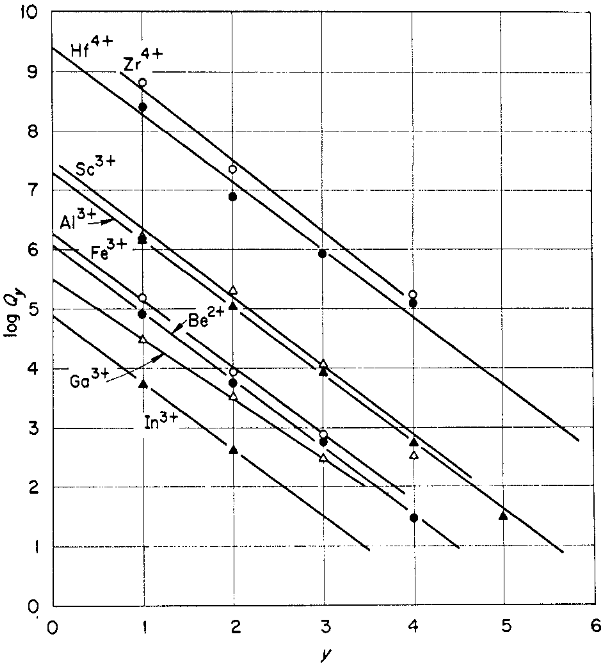

Figure 5.—Correlation of stepwise formation quotients for several +2, +3, and +4 cations with y, the number of fluorides in the complex (or the number of the steps in stepwise equilibria).

Correlations of Stabilities of Fluoride Complexes.—Figure 5 shows that for the systems for which the most reliable data are available[23] the $\Delta \log Q_y$ values for stepwise fluoride complex reactions are well represented by

$$\Delta \log Q_y = -1.1\Delta y \quad (17)$$

where y is the number of fluorides in the complex formed (or the number of the step). We have also found that an excellent empirical correlation is obtained if log Q_1 for the fluoride complexes of the 28 metal ions for which the most reliable fluoride complexing data are available is plotted as a function of Z_+^2/r_+ (see Figure 6), where Z_+ and r_+ are the charge and radius[24] of the cation. Log Q_1 values can be pre-

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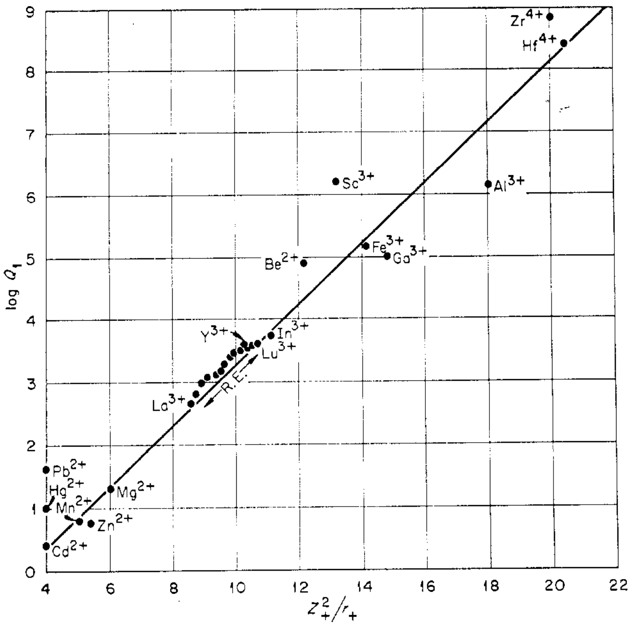

Figure 6.—Correlation of log Q_1 for the first stepwise fluoride complex with Z_+^2/r_+ for 28 +2, +3, or +4 cations where Z_+ and r_+ refer to the cation.

dicted with an average deviation of 0.3 log unit for the 28 examples shown in Figure 7 from the relationship

$$\log Q_1 = -1.56 + (0.48Z_+{}^2/r_+) \qquad (18)$$

(A somewhat poorer correlation (Figure 7) was found between log Q_1 and $Z_+/(r_+ + r_-)$ which might be expected from a simple coulombic picture of the ion association reaction.) From eq 17 and 18, we may write the following expression which should approximate the over-all formation quotient of any given fluoride complex $MF_y{}^{(n-y)+}$

$$\log Q_{1,y} = -0.46 - 1.1y + (0.48Z_+{}^2/r_+) \qquad (19)$$

These correlations are remarkable in view of the wide variations in cation size and charge represented in the systems compared and in view of the uncertainty of the cation sizes in solution.

One limiting factor on the formation of fluoride complexes with cations of high charge and small size is the competing tendency of the cations to hydrolyze even at high acidities in water. One would predict, however, from eq 19 very strong fluoride complexes for Si(IV) and B(III); and, even with their strong tendency for hydrolysis to form oxy anions, indeed very stable fluoride complexes, $SiF_6{}^{2-}$ and $BF_4{}^-$, are formed.[2]

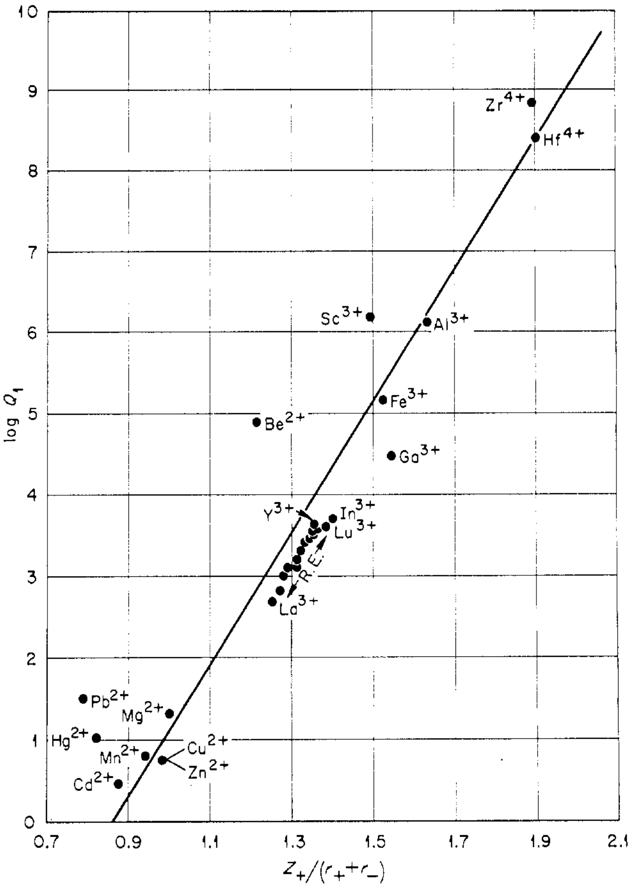

Figure 7.—Correlation of log Q_1 for the first stepwise fluoride complex with $Z_+/(r_+ + r_-)$, where Z_+ and r_+ refer to the cation and r_- to the anion.

Acknowledgment.—The authors gratefully acknowledge the assistance of G. M. Begun of the Chemistry Division for recording the Raman spectra of $(NH_4)_2BeF_4$ solutions and also helpful discussions with F. H. Sweeton of the Reactor Chemistry Division on data analysis. Research for this article was sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corp.