fractional condensation did not completely separate **3** from small amounts (ca. 10% by ^1H NMR) of unidentified impurities.

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Registry No. 1, 72525-56-5; **2**, 72525-57-6; **3**, 72525-58-7; *t*-Bu(Me_3Si)$NSiMe_2H$, 72525-59-8; Me(Me_3Si)$NSiMe_2H$, 72525-60-1; *t*-BuN($SiMe_2H$)$_2$, 72525-61-2; *t*-Bu(Me_3Si)$NSiMe_2Cl$, 72525-62-3; *t*-BuN($SiMe_2Cl$)$_2$, 72525-63-4; (Me_3Si)$_2NSiMe_2H$, 17067-57-1; (Me_3Si)$_2NSiMe_2Cl$, 1586-72-7; Me_3SiN($SiMe_2H$)$_2$, 16642-71-0; Me_3SiN($SiMe_2Cl$)$_2$, 18790-09-5; *t*-BuN(H)$SiMe_2H$, 18182-35-9; Me_2SiHCl, 1066-35-9; *t*-Bu(Me_2SiH)NLi, 72525-64-5; Me(Me_3Si)NLi, 10568-44-2; *t*-Bu(Me_3Si)NLi, 18270-42-3; *t*-Bu(Me_3Si)NH, 5577-67-3; BCl_3, 10294-34-5.

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Fluorosilicate Equilibria in Sodium Chloride Solutions from 0 to 60 °C[†]

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A potentiometric method employing quinhydrone and solid-state fluoride electrodes was used to observe the free hydrogen ion and the free fluoride ion concentrations in equilibrium experiments in aqueous solutions at 0–60 °C. In dilute silicic acid solutions the predominant reaction can be expressed as $Si(OH)_4(aq) + 4H^+ + 6F^- \rightleftarrows SiF_6^{2-} + 4H_2O$. The logarithm of the equilibrium quotient has values of 31.610, 29.980, and 28.23 at 0, 25, and 60 °C in 1 *m* NaCl (molal units). There is evidence for the existence of small amounts of additional species with fewer fluorides under certain conditions. The absence of a regular sequence of species from the array $Si(OH)_{4-x}F_y^{x-y}$ is proven by an analysis of the results. The average number of fluoride ions complexed by millimolal silicic acid approaches 6.0 in 0.01 *m* fluoride as the pH is reduced to 3 or lower in titration experiments. Simultaneously the average number of hydrogen ions consumed approaches 4.0.

Introduction

There is considerable interest in the detailed chemistry of dilute solutions that occur naturally and in practical processes. The fluoride concentrations in geothermal brines are commonly found in the range 10^{-3}–10^{-4} *m*.[2a] The interactions that occur between fluoride ion and silicic acid in dilute solutions are poorly understood. The only species in aqueous solution whose identity is well-known[2b] from Raman and NMR spectroscopy is SiF_6^{2-}, an octahedral ion. Also, a common means for preparation of salts of hexafluorosilicic acid is by precipitation from aqueous solution. However, there are no definitive equilibrium data involving this species with other dissolved species of silica.

There are indeed a large number of conceivable species of the type $Si(OH)_{4-x}F_y^{x-y}$ which might occur and must be considered if a complete description of even dilute solutions is to be made. For the analogous system[3-5] B–F, a sequence of species has been observed including BF_4^-, BF_3OH^-, $BF_2(OH)_2^-$, and probably $BF(OH)_3^-$ in dilute solutions, all of which involve replacement of a hydroxide ion from tetrahedral $B(OH)_4^-$. There have been several reports[6-11] describing equilibria of SiF_6^{2-} with other fluorosilicates or with $Si(OH)_4$, but none of these studies present conclusive data. Silica can be dissolved in relatively concentrated H_2SiF_6 solutions to attain SiO_2 concentrations well beyond the solubility of amorphous silica, indicating the formation of additional species. Several authors[11,12] have suggested the presence of species such as SiF_5^- and SiF_4(aq) to account for such observations. In this paper we have employed precision potentiometric methods for the examination of the complexing behavior in dilute (0.001 *m*) silicic acid solutions in 1 *m* NaCl.

Experimental Section

Materials. A stock solution of about 5.2 *m* NaCl prepared from Fisher Scientific Co. analyzed reagent was purified by acidifying with hydrochloric acid to pH 3.5 and sparging with H_2 to remove CO_2. After sparging, the solution was again neutralized with a small amount of carbonate-free NaOH solution.

A stock solution of 0.25 *m* NaF and 0.75 *m* NaCl was prepared from recrystallized NaF (J. T. Baker Chemical Co.) and the above NaCl stock solution. The recrystallized NaF was dried at 150 °C.

Stock solutions of 1 *m* NaOH, 1 *m* HCl, and approximately 0.5 *m* Si(IV), the same solutions employed and described in our silicic acid equilibrium studies,[13] were employed together with the two above stock solutions to prepare the required cell solutions, reference solutions, and titrant solution. Quinhydrone (Eastman Kodak Co.) was added as a solid to the cell-solution aliquot and reference-solution aliquot when these solutions were introduced into the electrode compartments of the cell, giving a concentration of approximately 0.003 *m*. The silicic acid concentration used in these experiments was about 0.001 *m*, which is believed to be below the saturation level for amorphous silica in these experiments. Should the solubility be exceeded by a small amount in the pH range of these experiments, it is well-known[14] that polymerization of the $Si(OH)_4$ is very slow under these conditions.

Potentiometric Cells. The potentiometric-cell assembly was similar to that described previously for the study of fluoride complexes of beryllium.[15] However, for most of this work quinhydrone electrodes were used in place of hydrogen electrodes. The cell consisted of an

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(1) (a) Oak Ridge National Laboratory. (b) Depauw University.
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all-Teflon vessel with several ports for platinum electrodes, the lanthanum fluoride solid-state electrode, gas inlets, and titrant inlets. Quinhydrone (QH) was added to each compartment to make the final concentration about 0.003 *m*. The assembly was submerged in a constant-temperature (±0.01 °C) bath, and both solutions were purged with hydrogen gas for 45 min before beginning a titration. The cell representation is shown by (I). Reference compartment B contained

$$\begin{array}{r|l||l|l} & \text{soln A} & \text{soln B} & \\ \mathrm{LaF_3\ and\ QH, Pt} & \begin{array}{l}(1-a-c)\ m\ \mathrm{NaCl}\\ a\ m\ \mathrm{NaF}\\ 0.001\ m\ \mathrm{Si(OH)_4}\\ c\ m\ \mathrm{HCl}\end{array} & \begin{array}{l}(1-d)\ m\ \mathrm{NaCl}\\ d\ m\ \mathrm{HCl}\end{array} & \mathrm{Pt, QH} \end{array} \qquad \text{(I)}$$

a solution of 0.005 *m* HCl in 1.0 *m* NaCl, and this composition remained unchanged during the experiments. The concentration of NaF was varied from 0.001 to 0.009 *m* at 0, 25, and 60 °C. A titrant containing HCl and the medium salt was added by means of a syringe microburet to vary the acidity from the nearly neutral condition to pH 2. The reference for the fluoride electrode was the initial fluoride concentration in the outer compartment (adjusted for any small amount of HF that might be present). Equilibrium was established rapidly, usually within 3 min.

Free H^+ and F^- Concentration Measurements. A high concentration of electrolyte was used to control the medium and the ionic activity coefficients. The difference in potential between the two quinhydrone electrodes is given by eq 1 where r refers to the solution in the reference

$$\Delta E_H = (RT/F) \ln \frac{[H^+]_r}{[H^+]} - \Sigma D_i([i]_r - [i]) \qquad (1)$$

compartment (B), [i] represents the molality of the ith ionic component, and the coefficients D_i are derived from the Henderson equation for liquid junction potentials (see ref 15). The approximation was made that $D_{Cl^-} = D_{F^-} = D_{HF_2^-}$ and that $D_{HF} = 0$. Since the concentration of silicic acid in these studies was always 1/1000th of that of the medium salt, the fluorosilicates were not included in the liquid junction calculation.

In an analogous manner, the fluoride concentration was calculated from the potential of the fluoride electrode vs. the reference hydrogen electrode. In this case the potential between the lanthanum fluoride electrode and the reference electrode was observed, but the difference from the initial value was used to calculate the fluoride concentration for each point, i.e.

$$\Delta E_F = -(RT/F) \ln \frac{[F]_r}{[F^-]} - \Sigma D_i([i]_r - [i]) \qquad (2)$$

where r refers to the initial solution in the titration.

Data Analysis. For modeling the data in terms of assumed chemical equilibria, it is convenient to define two quantities, $\bar{n}_F$ and $\bar{n}_H$, which represent the average number of fluoride ions and hydrogen ions involved in the general reaction

$$\mathrm{Si(OH)_4} + x\mathrm{H^+} + y\mathrm{F^-} \overset{Q_{xy}}{\rightleftharpoons} \mathrm{Si(OH)_{4-x}F_y{}^{x-y}} + x\mathrm{H_2O} \qquad (3)$$

These quantities are derived for each data point from the relationships

$$\bar{n}_H = (m_H - [H^+] - [HF] - [HF_2^-] + [OH^-])/m_{Si} \qquad (4)$$

$$\bar{n}_F = (m_F - [F^-] - [HF] - 2[HF_2^-])/m_{Si} \qquad (5)$$

where m_H, m_F, and m_{Si} are stoichiometric molalities of hydrogen ion, fluoride ion, and silicon, respectively. Previously published values for the equilibrium quotients[15] for HF and HF_2^- and for the ionization quotient for water[16] were used.

Values for the $\bar{n}$ quantities were also computed from a least-squares fit to the data for assumed schemes of chemical equilibria:

$$\bar{n}_H(\mathrm{calcd}) = \frac{\Sigma x[\mathrm{Si(OH)_{4-x}F_y{}^{x-y}}]}{m_{Si}} = \frac{\Sigma x Q_{x,y}[\mathrm{Si(OH)_4}][H^+]^x[F^-]^y}{m_{Si}} \qquad (6)$$

$$\bar{n}_F(\mathrm{calcd}) = \frac{\Sigma y[\mathrm{Si(OH)_{4-x}F_y{}^{x-y}}]}{m_{Si}} = \frac{\Sigma y Q_{x,y}[\mathrm{Si(OH)_4}][H^+]^x[F^-]^y}{m_{Si}} \qquad (7)$$

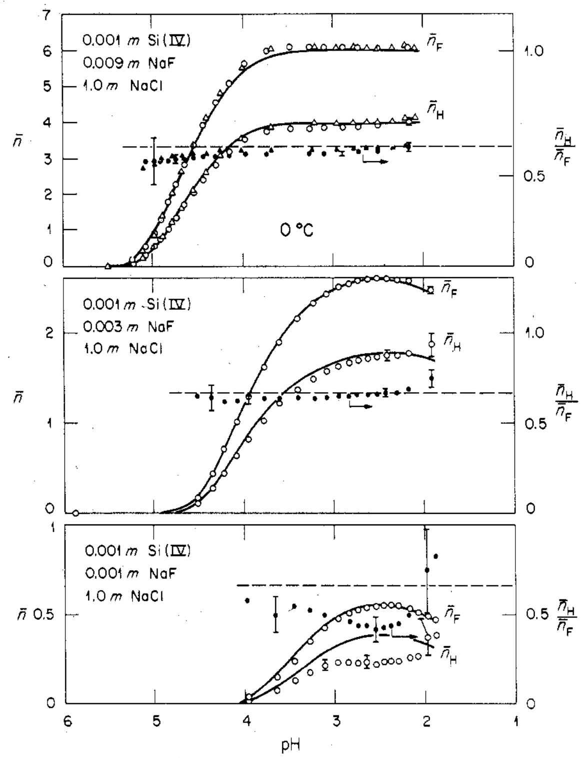

Figure 1. Equilibria emf data on the Si^{IV}–F^- system in 1 *m* NaCl at 0 °C. $\bar{n}_F$ and $\bar{n}_H$ (left ordinate) are shown as a function of pH at three concentrations of fluoride ion. Ratios of $\bar{n}_H/\bar{n}_F$ (filled symbols) are shown on the right ordinate. The experimental uncertainties are shown where they are significantly larger than the symbols used. The curves are calculated on the basis of the scheme of species giving the best fit: $Si(OH)_4$, SiF_6^{2-}, and $Si(OH)F_4^-$ (the minor species).

The summations include all the fluorosilicates assumed to be present. The silicic acid concentration is not determined experimentally but is derived from the material balance expression for silicon, i.e.

$$m_{Si} = [\mathrm{Si(OH)_4}] + \Sigma Q_{x,y}[\mathrm{Si(OH)_4}][H^+]^x[F^-]^y \qquad (8)$$

The equilibrium quotients ($Q_{x,y}$) were adjusted by means of a general least-squares computer program to give the best fit to the data.

Results

Potentiometry. The results of experiments in which acid was titrated into an essentially neutral $Si(OH)_4$ solution containing varying amounts of fluoride are summarized in Table I. Constant signals are obtained in a few minutes after each addition. Most of the data were obtained over the pH range 2–6. The temperature was held at 0, 25, and 60 °C. At 60 °C we confirmed the interference of HF_2^- with the response of the lanthanum fluoride electrode observed previously.[15] For this reason we have only analyzed data at 0 and 25 °C in detail for the identity of species present (as discussed later).

Inspection of Figures 1 and 2 shows that, when sufficient fluoride is present, constant values of $\bar{n}_F$ and $\bar{n}_H$ are obtained, i.e., 6 and 4, respectively. Also, plotted on the right ordinate is the ratio $\bar{n}_H/\bar{n}_F$. Within the computed error limits this value is equal to 2/3 over the entire range of the data, showing the predominance of the SiF_6^{2-} species. Some increase in this ratio is indicated at the lowest fluoride concentrations. The shift of the curves to greater acidities with increasing temperatures reflects the weaker stability of the complex as defined by eq 3.

Analysis of Species. Because of the obvious predominance of SiF_6^{2-} in some of these experiments, we attempted to find any one or more species which, included with SiF_6^{2-}, would account for the data. In this analysis those species Si-

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[16] R. H. Busey and R. E. Mesmer, *J. Solution Chem.*, **5**, 147 (1976).

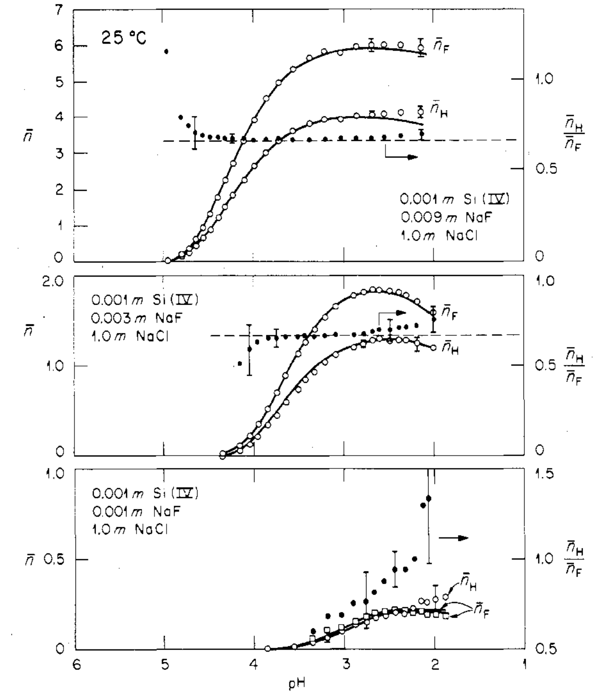

Figure 2. Equilibria emf data on the Si^{IV}–F system in 1 *m* NaCl at 25 °C. $\bar{n}_F$ and $\bar{n}_H$ (left ordinate) are shown as a function of pH at three concentrations of fluoride ion. Ratios of $\bar{n}_H/\bar{n}_F$ (filled symbols) are shown on the right ordinate. The experimental uncertainties are shown where they are significantly larger than the symbols used. The curves are calculated from the sequence of species giving the best fit of the data: $Si(OH)_4$, SiF_6^{2-}, and $Si(OH)_2F_2(aq)$ (the minor species).

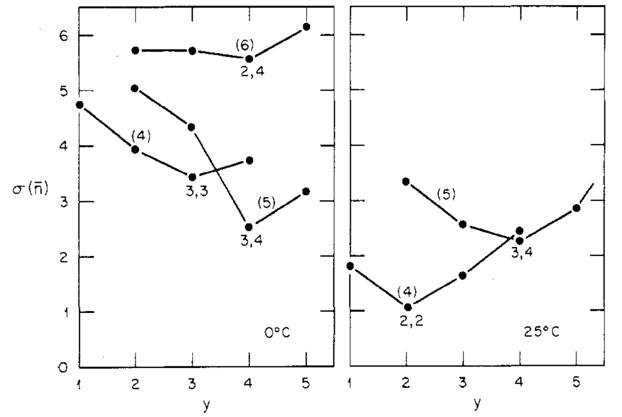

Figure 3. Variation of the agreement factor $\sigma(\bar{n})$ with the value of y for the minor species, $Si(OH)_{4-x}F_y^{x-y}$, combined with $Si(OH)_4$ and SiF_6^{2-} in the fit of all the data at 0 and 25 °C. The values of x and y are indicated as x,y below the best value of $\sigma(\bar{n})$ obtained for the series of species for a constant coordination number (in parentheses) or $4 - x + y$. The points for a given series are joined by lines for clarity.

$(OH)_{4-x}F_y^{x-y}$, abbreviated as (x,y), were considered in which the silicon was coordinated with 4, 5, or 6 ligands, excluding H_2O, i.e., all species for which $(4 - x) + y$ (or the number of OH^- plus F^- ligands) equals 4, 5, or 6. The agreement factors[17] obtained at 0 and 25 °C from all the data are shown in Figure 3 in which $\sigma(\bar{n})$ is plotted as a function of y in the species. The series of species for a given value of $(4 - x) + y$ are joined by a solid line. The best fit at 25 °C was obtained with the $Si(OH)_2F_2(aq)$ species, and at 0 °C a better fit was obtained with the $Si(OH)F_4^-$ species. The stability constants for the formation of these species by equilibrium 3 are given in Table II.

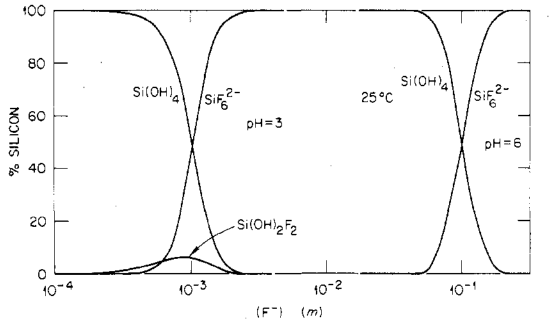

Figure 4. Distribution of fluorosilicates as a function of free-fluoride concentration. Results are shown for two values of pH in 1 *m* NaCl at 25 °C.

We are unable from these data alone to uniquely define the composition of the minor species contributing at the low fluoride concentrations. Because of the pH region of occurrence of these minor complexes (their inherent instability), the high concentrations of F^-, HF, and HF_2^- contribute to the large uncertainty in $\bar{n}$ values which are calculated.

Comparison with Other Data. From the pH and free-fluoride measurements of Crosby[18] on dilute solutions of H_2SiF_6, we have calculated a value for the logarithm of the equilibrium constant for the formation of SiF_6^{2-} in eq 3 of 30.8 ± 0.5 in dilute solutions. In 1931, Kubelka and Pristoupil[19] carried out a titration experiment in which the following stoichiometry was assumed in order to calculate the free-fluoride concentration and the H^+ was measured with a hydrogen electrode:

$$yH_2SiF_6 + xNaOH \rightarrow ((6y - x)/4)Na_2SiF_6(s) + ((x - 2y)/4)SiO_2(s) + yH_2O + 6((x - 2y)/4)/NaF \quad (9)$$

These data lead to a value of 10^{29} for the quotient for the formation of SiF_6^{2-} in eq 3. Considerable uncertainty, possibly 1 log unit, should be assigned to this result.

From our value of the equilibrium quotient for the formation of SiF_6^{2-} from $Si(OH)_4$ (eq 3), we can demonstrate that the experiments of Plakhotnik and Kotlyar[10] were not correctly interpreted. They determined the solubility of K_2SiF_6 in acidic solutions, assuming only SiF_6^{2-} and SiF_5^- were present in solution. At the low concentrations of dissolved silicon, relatively high concentrations of silicic acid would have also occurred.

Figure 4 illustrates the free-fluoride concentration needed to produce SiF_6^{2-} at pH 3 and 6 at 25 °C in 1 *m* NaCl. At temperatures near 25 °C, we can calculate that solutions with 0.001 *m* free fluoride contain a ratio of $[SiF_6^{2-}]/[Si(OH)_4]$ less than 0.01 when the pH is greater than 3.5. Likewise, at higher temperatures the pH at which this condition is obtained occurs at a still lower pH. The change in enthalpy for the formation of SiF_6^{2-} in eq 3 is −23.72 kcal/mol of $Si(OH)_4$ at 25 °C, on the basis of a constant ΔC_p of 59.4 cal/K.

We cannot draw a close analogy between the silicon(IV) and boron(III) systems because of the difference in coordination number between the pairs SiF_6^{2-}–$Si(OH)_4$ and BF_4^-–$B(OH)_4^-$. There is no regular sequence of fluoro complexes for Si(IV) as was observed for B(III). This likely can be attributed to the change in coordination number that occurs as fluoride is replaced by hydroxide or oxide ligands on silicon.

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(17) The agreement factor $\sigma(\bar{n})$ was computed from $\sigma(\bar{n}) = [(\sum w(\bar{n}_H - \bar{n}_H(\text{calcd}))^2) + \sum w(\bar{n}_F - \bar{n}_F(\text{calcd}))^2/(N_o - N_v)]^{1/2}$ where N_o and N_v are the number of observations and the number of variables, respectively. The weights w were assigned by propagation of the errors of the observables.

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(19) P. Kubelka and V. Pristoupil, *Z. Anorg. Allg. Chem.*, **197**, 391 (1931).

Table I. Potentiometric Data on Fluorosilicate Solutions in 1 *m* NaCl

$\bar{n}_H$	$\bar{n}_F$	$m_{Si} \times 10^3$	$[H^+]^*$	$[F^-]^*$
		0°C		
0.000	0.000	1.000	6.751E-7	9.613E-3
0.142	0.236	0.999	5.997E-6	9.331E-3
0.349	0.587	0.997	8.384E-6	8.955E-3
0.563	0.942	0.996	1.032E-5	8.580E-3
0.800	1.348	0.994	1.243E-5	8.154E-3
1.068	1.808	0.992	1.495E-5	7.673E-3
1.403	2.338	0.990	1.838E-5	7.121E-3
1.732	2.861	0.988	2.259E-5	6.578E-3
2.088	3.421	0.985	2.838E-5	5.996E-3
2.440	3.970	0.983	3.609E-5	5.427E-3
2.836	4.593	0.980	4.909E-5	4.778E-3
3.222	5.174	0.977	6.990E-5	4.162E-3
3.547	5.671	0.975	1.048E-4	3.614E-3
3.792	6.031	0.972	1.859E-4	3.132E-3
3.868	6.127	0.969	3.398E-4	2.806E-3
3.877	6.136	0.966	5.444E-4	2.534E-3
3.882	6.133	0.963	7.855E-4	2.282E-3
3.908	6.132	0.957	1.279E-3	1.896E-3
3.931	6.131	0.951	1.878E-3	1.572E-3
3.974	6.134	0.940	3.192E-3	1.141E-3
4.094	6.106	0.912	6.877E-3	6.421E-4
0.000	0.000	0.999	1.307E-6	3.296E-3
0.118	0.181	0.998	3.026E-5	3.058E-3
0.287	0.448	0.996	4.505E-5	2.768E-3
0.449	0.720	0.995	6.055E-5	2.480E-3
0.641	1.021	0.994	8.257E-5	2.160E-3
0.825	1.307	0.992	1.119E-4	1.856E-3
1.037	1.629	0.990	1.642E-4	1.511E-3
1.229	1.909	0.988	2.435E-4	1.205E-3
1.385	2.170	0.986	3.869E-4	9.109E-4
1.505	2.342	0.984	5.844E-4	7.050E-4
1.581	2.452	0.981	8.260E-4	5.647E-4
1.641	2.521	0.979	1.120E-3	4.643E-4
1.681	2.566	0.976	1.462E-3	3.898E-4
1.706	2.594	0.973	1.872E-3	3.314E-4
1.734	2.611	0.969	2.376E-3	2.827E-4
1.746	2.621	0.965	3.018E-3	2.401E-4
1.760	2.619	0.959	3.863E-3	2.033E-4
1.762	2.603	0.950	5.148E-3	1.678E-4
1.792	2.580	0.939	6.815E-3	1.380E-4
1.882	2.490	0.903	1.203E-2	9.277E-5
0.000	0.000	1.000	7.229E-6	1.011E-3
0.025	0.042	0.999	1.079E-4	9.141E-4
0.078	0.157	0.997	2.237E-4	7.577E-4
0.138	0.266	0.996	3.550E-4	6.191E-4
0.188	0.357	0.994	5.273E-4	5.017E-4
0.219	0.431	0.992	7.658E-4	4.017E-4
0.235	0.478	0.990	1.065E-3	3.294E-4
0.237	0.509	0.987	1.399E-3	2.770E-4
0.234	0.530	0.985	1.793E-3	2.351E-4
0.241	0.543	0.981	2.251E-3	2.020E-4
0.230	0.549	0.978	2.760E-3	1.763E-4
0.239	0.554	0.973	3.438E-3	1.511E-4
0.245	0.552	0.969	4.104E-3	1.336E-4
0.247	0.548	0.963	4.990E-3	1.163E-4
0.265	0.532	0.951	6.694E-3	9.490E-5
0.278	0.518	0.940	8.379E-3	8.053E-5
0.375	0.498	0.923	1.077E-2	6.656E-5
0.392	0.473	0.905	1.347E-2	5.623E-5

$\bar{n}_H$	$\bar{n}_F$	$m_{Si} \times 10^3$	$[H^+]^*$	$[F^-]^*$
		25°C		
0.000	0.000	1.000	9.861E-7	9.608E-3
0.046	0.039	0.999	1.095E-5	9.475E-3
0.151	0.190	0.998	1.566E-5	9.278E-3
0.270	0.357	0.997	1.895E-5	9.078E-3
0.445	0.622	0.996	2.290E-5	8.776E-3
0.666	0.953	0.994	2.766E-5	8.405E-3
0.924	1.333	0.992	3.309E-5	7.985E-3
1.234	1.787	0.990	4.031E-5	7.486E-3
1.533	2.251	0.988	4.867E-5	6.979E-3
1.853	2.731	0.985	5.958E-5	6.452E-3
2.272	3.356	0.982	7.830E-5	5.764E-3
2.648	3.917	0.979	1.029E-4	5.135E-3
3.021	4.480	0.976	1.402E-4	4.488E-3
3.338	4.940	0.973	1.951E-4	3.918E-3
3.603	5.334	0.970	2.775E-4	3.384E-3
3.806	5.648	0.966	4.217E-4	2.856E-3
3.926	5.821	0.963	6.209E-4	2.435E-3
3.929	5.771	0.958	9.515E-4	2.090E-3
4.034	5.970	0.953	1.406E-3	1.641E-3
4.067	5.992	0.946	2.098E-3	1.291E-3
4.076	5.999	0.939	2.919E-3	1.032E-3
4.127	5.983	0.928	4.358E-3	7.650E-4
4.137	5.916	0.907	7.365E-3	4.986E-4
0.000	0.000	0.999	4.542E-7	3.298E-3
0.000	0.037	0.998	4.444E-5	3.145E-3
0.063	0.122	0.997	7.034E-5	2.999E-3
0.137	0.230	0.996	9.191E-5	2.847E-3
0.227	0.360	0.995	1.134E-4	2.682E-3
0.347	0.530	0.994	1.449E-4	2.466E-3
0.465	0.708	0.993	1.812E-4	2.248E-3
0.603	0.905	0.991	2.310E-4	2.005E-3
0.750	1.143	0.989	3.149E-4	1.708E-3
0.850	1.271	0.988	3.801E-4	1.542E-3
0.940	1.413	0.986	4.805E-4	1.350E-3
1.041	1.553	0.984	6.278E-4	1.152E-3
1.127	1.668	0.982	8.361E-4	9.685E-4
1.215	1.794	0.977	1.315E-3	7.271E-4
1.249	1.833	0.974	1.682E-3	6.194E-4
1.289	1.853	0.971	2.125E-3	5.300E-4
1.312	1.855	0.968	2.505E-3	4.751E-4
1.292	1.843	0.962	3.339E-3	3.905E-4
1.300	1.820	0.956	4.171E-3	3.345E-4
1.291	1.788	0.950	5.008E-3	2.946E-4
1.261	1.725	0.938	6.685E-3	2.395E-4
1.214	1.599	0.917	9.889E-3	1.804E-4
0.000	0.000	1.000	3.41E-5	1.018E-3
-0.006	0.014	0.999	1.414E-4	9.264E-3
0.011	0.039	0.997	2.724E-4	8.270E-4
0.044	0.072	0.995	4.317E-4	7.239E-4
0.076	0.111	0.993	6.264E-4	6.237E-4
0.105	0.151	0.991	9.221E-4	5.154E-4
0.139	0.182	0.988	1.287E-3	4.261E-4
0.153	0.201	0.985	1.698E-3	3.587E-4
0.175	0.213	0.981	2.195E-3	3.022E-4
0.192	0.217	0.976	2.833E-3	2.531E-4
0.204	0.218	0.971	3.619E-3	2.112E-4
0.200	0.212	0.965	4.533E-3	1.782E-4
0.229	0.208	0.956	5.684E-3	1.484E-4
0.272	0.207	0.948	6.899E-3	1.255E-4
0.263	0.196	0.939	8.208E-3	1.086E-4
0.278	0.190	0.928	9.844E-3	9.227E-5
0.292	0.179	0.908	1.285E-2	7.202E-5

$\bar{n}_H$	$\bar{n}_F$	$m_{Si} \times 10^3$	$[H^+]^*$	$[F^-]^*$
		60°C		
0.000	0.000	1.000	5.460E-6	9.497E-3
-0.004	-0.060	0.999	1.608E-5	9.320E-3
-0.003	-0.077	0.997	2.809E-5	9.086E-3
0.040	-0.059	0.996	4.010E-5	8.833E-3
0.129	0.108	0.994	5.205E-5	8.469E-3
0.276	0.321	0.992	6.554E-5	8.060E-3
0.473	0.611	0.989	8.194E-5	7.573E-3
0.724	0.994	0.987	1.039E-4	6.978E-3
1.000	1.406	0.983	1.318E-4	6.354E-3
1.286	1.835	0.980	1.699E-4	5.692E-3
1.551	2.237	0.976	2.187E-4	5.054E-3
1.798	2.607	0.973	2.854E-4	4.427E-3
2.025	2.939	0.969	3.819E-4	3.799E-3
2.219	3.225	0.965	5.211E-4	3.190E-3
2.366	3.423	0.960	7.273E-4	2.622E-3
2.469	3.535	0.955	1.006E-3	2.141E-3
2.541	3.550	0.948	1.525E-3	1.629E-3
2.577	3.453	0.940	2.323E-3	1.213E-3
2.619	3.237	0.928	3.522E-3	8.934E-4
2.728	2.718	0.903	6.523E-3	5.544E-4
0.000	0.000	0.999	1.674E-5	3.203E-3
-0.002	-0.022	0.998	4.988E-5	3.046E-3
0.009	-0.034	0.996	9.685E-5	2.839E-3
0.005	-0.034	0.994	1.477E-4	2.639E-3
0.022	-0.014	0.993	2.101E-4	2.416E-3
0.063	0.033	0.990	3.031E-4	2.136E-3
0.108	0.086	0.988	4.232E-4	1.857E-3
0.149	0.163	0.985	5.896E-4	1.565E-3
0.194	0.212	0.982	8.056E-4	1.310E-3
0.214	0.240	0.979	1.107E-3	1.076E-3
0.240	0.246	0.975	1.472E-3	8.888E-4
0.243	0.237	0.971	1.912E-3	7.381E-4
0.241	0.212	0.966	2.450E-3	6.145E-4
0.215	0.176	0.961	3.114E-3	5.112E-4
0.230	0.152	0.956	3.822E-3	4.325E-4
0.238	0.119	0.949	4.824E-3	3.554E-4
0.263	0.082	0.939	6.225E-3	2.842E-4
0.361	0.031	0.914	9.734E-3	1.871E-4
0.000		0.998	1.321E-5	9.939E-4
0.014		0.998	8.882E-5	8.952E-4
0.014		0.997	2.057E-4	7.716E-4
0.012		0.995	3.420E-4	6.647E-4
0.021		0.993	5.128E-4	5.665E-4
0.038		0.991	7.602E-4	4.664E-4
0.049		0.988	1.073E-3	3.815E-4
0.060		0.985	1.474E-3	3.087E-4
0.068		0.981	1.971E-3	2.496E-4
0.075		0.977	2.578E-3	2.021E-4
0.078		0.973	3.173E-3	1.700E-4
0.084		0.968	3.872E-3	1.432E-4
0.092		0.960	4.967E-3	1.145E-4
0.111		0.951	6.383E-3	9.062E-5
0.126		0.939	8.096E-3	7.210E-5
0.226		0.912	1.215E-2	4.799E-5
0.000	0.000	0.997	2.172E-6	1.991E-2
-0.014	0.107	0.996	6.588E-6	1.971E-2
0.039	-0.054	0.994	1.126E-5	1.935E-2
0.182	0.133	0.993	1.484E-5	1.894E-2
0.392	0.431	0.990	1.807E-5	1.845E-2
0.695	0.849	0.988	2.205E-5	1.782E-2
1.089	1.428	0.983	2.711E-5	1.701E-2
1.615	2.196	0.979	3.453E-5	1.596E-2
2.198	3.033	0.974	4.539E-5	1.477E-2
2.804	3.905	0.968	6.404E-5	1.340E-2
3.225	4.484	0.961	9.446E-5	1.211E-2

*1E-5 = 1 × 10^{-5}

Table II. Stability Constants for Selected Schemes of Fluorosilicates Formed by Reaction 3

T, °C	SiF_6^{2-}	$Si(OH)_2F_2(aq)$	$Si(OH)F_4^-$	$\sigma(\bar{n})$
0	31.679 ± 0.005			5.68
0	31.610 ± 0.004		21.40 ± 0.02	2.56
25	29.994 ± 0.005			2.74
25	29.980 ± 0.002	11.09 ± 0.02		1.13
60	28.233 ± 0.011			1.33

The relative stabilities of SiF_6^{2-} and BF_4^- can be seen from the following relationship derived from results in this paper and ref 3:

$$\left(\frac{[BF_4^-]}{[B(OH)_3]}\right)^3 = 10^{-3}[H^+]\left(\frac{[SiF_6^{2-}]}{[Si(OH)_4]}\right)^2 \qquad (10)$$

The relationship is independent of the free-fluoride concentration and indicates that at pH 3, when half of the silicon is complexed as SiF_6^{2-}, the ratio $[BF_4^-]/[B(OH)_3]$ has a value of 0.01.

Additional information is needed to define the composition of species formed in relatively concentrated H_2SiF_6 solutions saturated with silica. In these solutions the ratio m_F/m_{Si} approaches about 5 in 40% H_2SiF_6, and this increases to about 5.3 in 0.02 *m* H_2SiF_6. This result in the more dilute solutions is consistent with our results, considering the difference in medium. We expect that Raman studies in the more concentrated solutions to which silica is added to H_2SiF_6 could yield helpful information on the nature of the species present.

Registry No. SiF_6^{2-}, 17084-08-1; $Si(OH)_2F_2$, 39630-76-7; $Si(OH)F_4^-$, 72541-63-0; $Si(OH)_4$, 10193-36-9; F^-, 16984-48-8.