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Ionization Equilibria of Silicic Acid and Polysilicate Formation in Aqueous Sodium Chloride Solutions to 300 °C

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The ionization behavior of silicic acid and polysilicate formation in basic solutions have been studied by precise potentiometry using titration techniques in a hydrogen-electrode concentration cell. Polysilicate formation was studied in 1 *m* NaCl solutions at temperatures from 60 to 290 °C and at Si(IV) concentrations 0.005–0.05 *m*. At the lowest silica concentration only mononuclear species occur over wide temperature and pH ranges. At hydroxyl numbers from about 0.7 to 1.0 (average charge per silicon) small polysilicates which equilibrate rapidly occur at higher Si(IV) concentrations. Polysilicate formation decreases with increasing temperature. The equilibrium quotient for the most significant reaction, $Si(OH)_4(aq) + OH^- \rightleftarrows SiO(OH)_3^- + H_2O$, has been precisely determined from 0.1 to 5.0 *m* NaCl and to about 300 °C. Values of the logarithm of the equilibrium quotient for the reaction are 3.96 and 2.20 at 50 and 300 °C in 1 *m* NaCl and 4.32 and 2.26 at the same two temperatures in 5 *m* NaCl. An analytical expression from which the thermodynamic quantities for the reaction can be computed is presented. The small effect of salt concentration is interpreted as evidence for little or no sodium ion complexing.

Introduction

The crust of the earth is composed of principally silicates and silica in the form of rocks, clays, sands, and soils as are the common inorganic building materials—cement, mortar, brick, glass, and ceramics. Most silicates are relatively insoluble except for the alkali metal silicates, but complex chemistry is exhibited by dissolved silicates particularly in basic solutions. Because of the sluggishness of the processes at certain compositions of silicate solutions and the numerous reports on the behavior encountered, even the simple equilibrium

$$Si(OH)_4(aq) + OH^- \rightleftarrows SiO(OH)_3^- + H_2O \qquad (1)$$

has escaped determination to the extent that most other such simple equilibria are now defined particularly under hydrothermal conditions.

Recent work of Seward[1] has provided what are probably the most reliable measurements of the ionization quotient of silicic acid by use of borate buffers to determine and control the pH in solubility studies on quartz from 150 to 350 °C. However, his use of literature values for the borate equilibria for application in another medium, the possibility of the existence of borate–silicate species, extension of these studies to temperatures well beyond the region of measurement of the borate equilibria, and the manner of extrapolation to infinite dilution raise doubts about his conclusions. We also question the postulation of sodium silicate complexes to account for the salt effects observed.

In what are less reliable estimates, Ryzhenko[2] experimentally determined the first and second ionization constants for silicic acid from conductance measurements on sodium silicate hydrolysis from 50 to 250 °C at the saturation vapor pressure.

Attainable silicic acid concentrations in solution are too low to establish the structure of the neutral species (believed to be $Si(OH)_4$) but ample Raman evidence[3-5] has been reported pointing to the tetrahedral configuration of the anions $SiO(OH)_3^-$ and $SiO_2(OH)_2^{2-}$. Bilinski and Ingri[6] have demonstrated that in 1 *m* $NaClO_4$ at 25 °C only mononuclear species of silica exist below silica concentrations of 0.001 *m*. Indeed, there appears to be a consensus among the numerous investigators of the solubility of amorphous silica that the species in equilibrium with the solid is monomeric $Si(OH)_4(aq)$. Invariably, however, when a solution is supersaturated with respect to amorphous silica, polymerization proceeds until colloidal solutions are produced, equilibrium sometimes requiring months depending on the degree of supersaturation and other conditions. These observations are generally based on use of the molybdate method[7] for detecting monomeric silica as the 1:12 heteropoly silicomolybdate species by spectrophotometry. Other evidence for such polymerization behavior stems from techniques of cryoscopy, light scattering, and chromatography.[5]

The detailed potentiometric work of Ingri[8] at 25 °C in 0.5 *m* NaCl has indicated the presence of small polynuclear anionic species $Si_4(OH)_{18}^{2-}$ (or $Si_4O_6(OH)_6^{2-}$) in equilibrium with $Si(OH)_4(aq)$, $SiO(OH)_3^-$, and possibly $SiO_2(OH)_2^{2-}$ at silica concentrations up to 0.08 *m* and at hydroxyl numbers generally above 0.7. Aveston[9] interpreted ultracentrifugation results at slightly higher concentrations in terms of somewhat larger species. As part of our work we will analyze the original data of Ingri in terms of alternative equilibrium models to test the statistical uniqueness of the assignment given.

In this paper we present the results of the use of potentiometric titration procedures to study the region of polynuclear silicate formation at temperature to 300 °C in a sodium chloride medium. After establishing from these measurements the concentrations below which polynuclear species formation is insignificant, experiments to examine the first ionization reaction as a function of salt concentration up to 5 *m* NaCl and to 300 °C were made. Using mathematical models which have proven adequate for numerous other ionization equilibria, the data were smoothed and thermodynamic parameters derived.

Experimental Section

Materials. Stock solutions of about 5.0 *m* NaCl prepared from Fischer Scientific Co. analyzed reagent were purified by acidifying with hydrochloric acid to pH 3.5–4.0 and sparging with N_2 or H_2 to remove CO_2. After sparging, the solutions were again neutralized with a small amount of carbonate-free NaOH solution.

The NaOH stock solutions were prepared from Fischer Scientific Co. 50% NaOH solutions and were standardized against potassium biphthalate. All base solutions (including those containing silica) were stored in either paraffin-lined glass vessels or polyethylene bottles under H_2 or N_2. The storage containers were equipped with delivery tubes which permitted solution transfer with minimum contact with air.

The silicic acid stock solution was prepared from J. T. Baker Chemical Co. silicic acid powder reagent by dissolution in strong NaOH solution in a Teflon beaker. The silicic acid powder sample was purified of any surface-adsorbed carbonate by suspending it in a small amount of dilute HCl solution and sparging the solution with N_2. The desired amount of 50% NaOH was then introduced to dissolve the silicic acid. When dissolution of the silicic acid was complete, water and NaCl stock solution were added to give the desired composition (approximately 0.5 *m* Si(IV), 0.2 *m* NaCl, and 0.8 *m* NaOH) which was stored under N_2 in a Teflon beaker inside a desiccator. The silicon content of the silicic acid powder was determined by ignition of samples to SiO_2 at approximately 1050 °C.

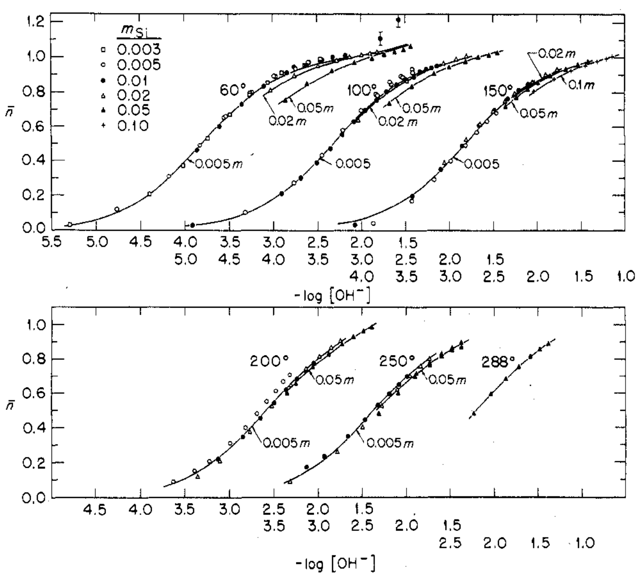

Figure 1. The effect of silicon concentration and temperature on the hydrolysis of silicic acid, $Si(OH)_4(aq)$, in 1 *m* NaCl. The approximate silicon concentrations are indicated and the curves were calculated from the equilibrium quotients given in Table V with $Si_4(OH)_{18}^{2-}$ the assumed polynuclear species.

The 1 *m* HCl stock solution was prepared from J. T. Baker Chemical Co. ultrahigh-purity hydrochloric acid (Ultrex). It was standardized against the 1 *m* NaOH stock solution using weight burets together with a syringe microburet and a Beckman Research pH meter to obtain the equivalence point.

All requisite solutions for this study were prepared from the above stock solutions. Ultrahigh-purity H_2 (99.999%) from J. T. Baker Chemical Co. was used throughout this research.

Potentiometric Apparatus and Techniques. The potentiometric apparatus has been described in detail previously.[10] Air was removed from the cell at the beginning of each experiment by successively pressurizing with H_2 to 500 psi and venting to the atmosphere. This operation was repeated four times before the final addition of H_2 for the equilibration. When required, titrant was added to the cell through a platinum capillary by a hand-operated volumetric pump (Ruska Instrument Corp. Model 2200 with a Zircaloy vessel).

Corrections for the small amount of water vaporized from the solutions to the gas phase at the higher temperatures were applied to the data. The correction amounted to less than 1% at 295 °C since the gas-to-liquid volume ratio was small in both cell compartments.

Potentiometric Measurements. The cell representation is

$$\mathrm{Pt,H_2}\left|\begin{array}{l} a\ m\ \mathrm{NaCl}\\ b\ m\ \mathrm{Si(IV)}\\ c\ m\ \mathrm{NaOH}\end{array}\right\|\left.\begin{array}{l} a\ m\ \mathrm{NaCl}\\ d\ m\ \mathrm{NaOH}\\ \end{array}\right|\mathrm{H_2,Pt} \tag{2}$$

The electrode compartment on the right contains the reference electrode. In these experiments the concentration of NaCl *a m* was varied from 0.1 to 5 *m*, and the NaOH content *d* was 0.005, 0.01, and 0.01 when *a* was 0.1, 0.25, and 0.5, respectively, and was 0.02 with $a > 0.5$. The solution on the left, contained in the larger outer compartment of the cell, had an initial NaOH-to-silicon concentration ratio $c/b \sim 1.7$ with *b* varying from 0.003 to 0.05.

In the titration experiments where the objective was to determine the species present, the NaCl concentration was kept at 1.0 *m*. At sufficiently low silica concentration and/or high temperatures, acid was added until $\bar{n} \leq 0.1$ ($\bar{n}$ is the average number of OH^- ions bound per silicic acid molecule). For higher silica concentrations and lower temperatures, additions of titrant were made and potentials observed until silica precipitation occurred (as manifested by drifting potentials) which terminated the observations for that run. Data were obtained from titrations from 60 to 288 °C and are summarized in Table I and Figure 1.

There was evidence of transient behavior following the addition of acid to the silicate solutions. The potential of the cell indicated that immediately following the addition of titrant the pH of the solution became too low and then slowly increased to the equilibrium value. The emf was usually within a millivolt of the final value in 2 min and then approached equilibrium with a half-life of about 3 min. This unusual behavior was more prominent in the more dilute silica solutions and at the lower temperatures (60–150 °C).

Table I. Potentiometric Data on Silicic Acid Solutions in 1 *m* NaCl[a]

$\bar{n}$ × 10	m_{Si} × 10^2	log [OH⁻]
	60.0°	
9.571	0.2997	2.640
9.344	0.2978	2.748
9.096	0.2960	2.889
8.585	0.2941	3.055
7.850	0.2923	3.267
6.707	0.2905	3.490
5.317	0.2887	3.745
3.727	0.2870	4.018
2.042	0.2853	4.397
0.285	0.2836	5.297
9.892	0.4712	2.462
9.726	0.4662	2.593
9.443	0.4614	2.764
8.884	0.4566	2.984
7.929	0.4519	3.262
6.497	0.4473	3.556
9.857	0.4717	2.459
9.727	0.4668	2.591
9.417	0.4620	2.755
8.911	0.4572	2.975
7.982	0.4526	3.247
6.586	0.4480	3.537
4.907	0.4436	3.833
3.091	0.4392	4.181
2.152	0.4371	4.403
1.204	0.4349	4.764
10.093	0.9426	2.173
10.024	0.9231	2.318
9.846	0.9091	2.451
9.583	0.8955	2.622
9.125	0.8822	2.842
8.346	0.8694	3.098
7.259	0.8569	3.356
5.987	0.8448	3.604
4.627	0.8330	3.867
10.05	0.9426	2.170
11.14	0.9324	1.778
12.18	0.9225	1.578
12.96	0.9127	1.441
13.32	0.9032	1.336
14.10	0.8939	1.256
14.42	0.8847	1.186
14.88	0.8758	1.128
15.18	0.8670	1.078
15.60	0.8584	1.034
16.03	0.8500	0.994
10.28	2.172	1.822
10.20	2.158	1.905
10.08	2.144	2.001
10.00	2.130	2.130
10.298	2.172	1.823
10.214	2.158	1.906
10.107	2.144	2.004
9.974	2.130	2.125
9.792	2.116	2.282
9.496	2.102	2.494
8.947	2.089	2.758
8.094	2.076	3.030
10.635	5.426	1.447
10.447	5.341	1.525
10.321	5.260	1.622
10.169	5.180	1.740
9.929	5.104	1.882
9.657	5.029	2.077
9.214	4.956	2.336
8.473	4.886	2.616
7.506	4.818	2.862
	100.0°	
9.286	0.4714	2.427
8.992	0.4664	2.538
8.589	0.4615	2.674
7.875	0.4567	2.824
6.950	0.4520	3.004
5.741	0.4474	3.210
9.090	0.4718	2.416
8.852	0.4668	2.528
8.451	0.4619	2.660
7.823	0.4571	2.814
6.947	0.4524	2.999
5.766	0.4479	3.208
4.335	0.4434	3.449
2.730	0.4390	3.763
0.996	0.4346	4.312
9.482	0.9430	2.137
9.414	0.9335	2.195
9.313	0.9238	2.260
9.174	0.9143	2.333
8.844	0.9050	2.399
8.728	0.8959	2.500
8.414	0.8870	2.599
8.025	0.8782	2.708
7.530	0.8696	2.824
6.948	0.8612	2.949
6.276	0.8530	3.080
5.529	0.8449	3.214
4.726	0.8369	3.357
3.880	0.8291	3.513
3.002	0.8215	3.690
2.097	0.8139	3.907
0.232	0.7993	4.909
10.066	2.368	1.808
9.889	2.345	1.922
9.656	2.323	2.067
9.288	2.301	2.256
8.644	2.280	2.492
6.353	2.238	3.031
10.266	5.534	1.453
10.138	5.436	1.551
9.992	5.342	1.669
9.763	5.251	1.814
9.441	5.162	2.002
9.068	5.098	2.173
8.316	5.015	2.423
7.330	4.935	2.680
	150.0°	
7.172	0.5583	2.368
6.792	0.5521	2.459
6.312	0.5461	2.564
5.672	0.5402	2.681
4.894	0.5344	2.816
3.983	0.5288	2.977
2.903	0.5232	3.168
1.697	0.5178	3.424
0.383	0.5125	3.864
8.496	0.9919	2.093
8.121	0.9698	2.202
7.644	0.9488	2.331
6.960	0.9286	2.479
6.048	0.9092	2.652
4.891	0.8907	2.854
3.509	0.8729	3.095
1.953	0.8558	3.421
0.262	0.8393	4.076
	150.0°	
9.720	1.1318	1.518
9.592	1.1067	1.555
9.561	1.0828	1.596
9.452	1.0379	1.683
9.396	1.0065	1.757
9.258	0.9770	1.838
9.091	0.9492	1.930
8.851	0.9230	2.037
8.642	0.9063	2.119
9.225	1.0676	1.508
9.154	1.0435	1.546
9.131	1.0204	1.587
9.082	0.9984	1.630
9.052	0.9773	1.676
8.864	0.9282	1.803
8.764	0.9064	1.873
8.674	0.8890	1.939
8.529	0.8722	2.012
8.304	0.8560	2.091
9.280	2.291	1.773
9.024	2.264	1.900
8.596	2.239	2.056
7.938	2.214	2.252
7.480	2.201	2.365
6.924	2.189	2.488
6.136	2.174	2.645
5.230	2.160	2.812
3.888	2.141	3.056
9.543	5.467	1.412
9.330	5.348	1.519
9.119	5.234	1.656
8.784	5.125	1.826
8.421	5.051	1.969
7.655	4.949	2.210
7.017	4.890	2.358
6.521	4.851	2.448
9.764	5.518	1.422
9.583	5.396	1.535
9.324	5.280	1.673
8.949	5.169	1.848
8.549	5.094	1.993
8.177	5.042	2.108
7.732	4.990	2.234
7.199	4.940	2.362
10.093	10.900	1.141
9.973	10.644	1.206
9.792	10.280	1.316
9.562	9.941	1.448
9.248	9.624	1.609
8.782	9.326	1.804
8.089	9.046	2.028
	200.0°	
7.135	0.4732	2.321
6.671	0.4683	2.396
6.142	0.4634	2.481
5.537	0.4586	2.578
4.831	0.4540	2.690
4.016	0.4494	2.824
3.100	0.4450	2.994
2.060	0.4406	3.227
1.490	0.4384	3.390
0.889	0.4363	3.625
	200.0°	
7.768	0.9462	2.049
7.356	0.9262	2.139
6.863	0.9070	2.241
6.238	0.8886	2.358
5.478	0.8709	2.495
4.550	0.8539	2.656
3.459	0.8375	2.857
2.203	0.8218	3.131
9.073	2.174	1.752
8.711	2.150	1.861
8.180	2.126	1.989
7.455	2.102	2.140
6.480	2.080	2.317
5.247	2.057	2.526
3.769	2.035	2.777
2.102	2.014	3.111
1.217	2.003	3.360
9.851	5.447	1.397
9.592	5.333	1.492
9.298	5.223	1.605
8.861	5.118	1.733
8.316	5.017	1.888
7.561	4.919	2.064
6.587	4.826	2.256
6.015	4.780	2.352
	250.0°	
6.965	0.9897	1.994
6.523	0.9676	2.088
5.973	0.9466	2.195
5.298	0.9264	2.320
4.471	0.9071	2.469
3.503	0.8886	2.660
2.364	0.8708	2.929
1.731	0.8622	3.129
7.992	1.971	1.741
7.571	1.949	1.844
6.990	1.928	1.965
6.234	1.907	2.108
5.255	1.886	2.282
4.027	1.866	2.498
2.554	1.846	2.789
0.876	1.827	3.318
8.697	4.931	1.377
8.577	4.818	1.488
8.187	4.710	1.605
7.682	4.607	1.746
6.954	4.508	1.908
6.008	4.414	2.097
4.822	4.323	2.315
8.863	4.926	1.386
8.609	4.817	1.486
8.278	4.712	1.602
7.766	4.612	1.734
7.120	4.517	1.893
	288.1°	
0.8852	4.944	1.384
0.8562	4.830	1.483
0.8121	4.720	1.593
0.7557	4.616	1.720
0.6851	4.516	1.869
0.5935	4.420	2.039
0.4814	4.328	2.234

[a] $\bar{n}$ is the average number of OH^- ions bound per silicon in solution and m_{Si} is the silicon molality.

In the experiments where the objective was to determine the equilibrium quotient for reaction 1 (Q_{11}) as a function of temperature and ionic strength, the concentration of silica was 0.005 *m* and the alkalinity was adjusted so that at 150 °C the $\bar{n}$ was approximately 0.55. This concentration was judged to eliminate significant shifts due to polymerization based on the extensive measurements in 1 *m* NaCl. We anticipate a small ΔV for reaction 1 since ΔZ^2 (the difference of the sums of the squares of the charges of the products and reactants) is zero and no attempt was made to measure the effect of pressure on this process since only small pressure increases are possible with the apparatus. The emf was then observed as a function of temperature. The calculated values of the equilibrium quotient are summarized in Table II and Figure 2.

Data Reduction and Analysis. The potential *E* for the cell (2) is given by the expression

$$E = (RT/F)\ln([\mathrm{OH^-}]/[\mathrm{OH^-}]_\mathrm{r}) - \Sigma D_\mathrm{i}([\mathrm{i}]_\mathrm{r} - [\mathrm{i}]) \tag{3}$$

where $[OH^-]$ denotes the molal concentration of hydroxide ion, [i] denotes the concentration of each ionic species in the solution including the hydroxide ion, and the subscript r refers to the reference solution. The liquid junction potentials are given by the term on the right containing D_i which are calculated from the Henderson equation.[10] The limiting equivalent conductances at high temperatures required for the calculation of D_i were obtained from Quist and Marshall.[11] The approximation that the equivalent conductance of $SiO(OH)_3^-$

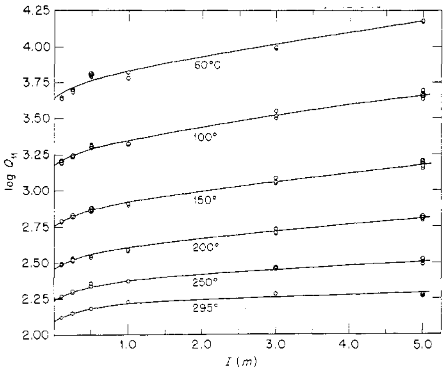

Figure 2. Log Q_{11} as a function of ionic strength and temperature. The curves were drawn using eq 9.

Table II. Data for Log Q_{11} as a Function of Temperature and Ionic Strength in NaCl Solutions

t°C	$m_{Si}\times 10^2$	$\bar{n}$	log Q_{11}
		I = 0.100	
60.05	0.4998	0.6424	3.643
100.0	0.5000	0.5622	3.200
150.0	0.5004	0.4546	2.791
199.95	0.5012	0.3608	2.491
99.9	0.5000	0.5619	3.199
149.9	0.5004	0.4542	2.790
200.0	0.5011	0.3601	2.489
250.2	0.5020	0.2884	2.268
295.05	0.5012	0.2416	2.120
60.15	0.4998	0.6415	3.637
100.05	0.5000	0.5606	3.193
150.15	0.5004	0.4521	2.782
200.05	0.5012	0.3584	2.484
		I = 0.250	
60.0	0.4998	0.6492	3.687
59.9	0.4998	0.6483	3.680
99.95	0.5001	0.5702	3.233
150.0	0.5005	0.4636	2.819
199.95	0.5013	0.3699	2.518
250.0	0.5022	0.2998	2.302
295.0	0.5014	0.2511	2.149
60.1	0.4999	0.6496	3.690
100.0	0.5000	0.5727	3.245
150.0	0.5004	0.4667	2.830
200.0	0.5011	0.3725	2.526
60.0	0.4999	0.6497	3.691
59.95	0.4999	0.6490	3.685
100.0	0.5000	0.5708	3.236
150.0	0.5004	0.4634	2.819
200.0	0.5011	0.3683	2.513
250.05	0.5017	0.2959	2.290
		I = 0.500	
60.0	0.5027	0.8298	3.796
100.0	0.5029	0.7231	3.297
150.0	0.5033	0.5889	2.856
100.0	0.5026	0.7224	3.303
150.0	0.5031	0.5879	2.860
200.0	0.5038	0.4712	2.541
60.0	0.5022	0.8263	3.803
59.85	0.5022	0.8241	3.790
100.0	0.5024	0.7185	3.296
149.95	0.5029	0.5844	2.854
199.95	0.5036	0.4686	2.539
250.0	0.5044	0.3912	2.339
250.05	0.5049	0.4011	2.356
295.0	0.5039	0.3352	2.182
60.0	0.4866	0.6804	3.791
59.85	0.4866	0.6803	3.790
100.0	0.4867	0.6019	3.318
149.9	0.4871	0.4910	2.881
60.0	0.4863	0.6780	3.790
59.9	0.4863	0.6776	3.787
100.0	0.4865	0.5993	3.315
150.0	0.4868	0.4881	2.877
		I = 1.00	
60.0			3.818[b]
100.0			3.324[b]
200.0			2.591[b]
250.0			2.370[b]
288.1			2.250[b]
100.0	0.5045	0.6020	3.325
100.0	0.5045	0.6023	3.326
60.0	0.5043	0.6755	3.780
100.0	0.5045	0.6008	3.319
150.0	0.5050	0.4957	2.894
200.1	0.5060	0.4000	2.583
60.05	0.5043	0.6754	3.779
150.0	0.5051	0.4994	2.907
		I = 3.00	
100.1	0.4866	0.6420	3.551
150.0	0.4871	0.5448	3.087
200.0	0.4881	0.4432	2.732
250.0	0.4894	0.3568	2.464
60.0	0.4863	0.7012	3.995
59.9	0.4863	0.7005	3.988
100.0	0.4866	0.6367	3.503
150.0	0.4871	0.5369	3.048
200.0	0.4880	0.4362	2.704
100.0	0.4867	0.6383	3.517
150.0	0.4872	0.5383	3.056
200.0	0.4882	0.4370	2.708
250.0	0.4895	0.3570	2.462
295.0	0.4898	0.2965	2.280
		I = 5.00	
100.0	0.4874	0.6695	3.652
150.0	0.4882	0.5741	3.167
200.0	0.4895	0.4709	2.795
60.0	0.4872	0.7252	4.175
100.0	0.4875	0.6708	3.664
100.15	0.4875	0.6667	3.637
150.0	0.4882	0.5702	3.153
200.0	0.4895	0.4656	2.780
250.0	0.4917	0.3712	2.488
100.0	0.4871	0.6691	3.667
150.0	0.4878	0.5768	3.187
200.0	0.4891	0.4745	2.813
250.0	0.4913	0.3808	2.521
296.1	0.4933	0.2979	2.271
296.1	0.4933	0.2996	2.276
60.1	0.4870	0.7236	4.181
100.0	0.4873	0.6727	3.688
150.0	0.4880	0.5811	3.203
200.0	0.4893	0.4781	2.824
250.0	0.4915	0.3831	2.526
296.0	0.4934	0.3010	2.280
100.0	0.4861	0.6621	3.695
150.0	0.4868	0.5708	3.199
199.95	0.9880	0.4676	2.814

[a] Q_{11} is the molal equilibrium quotient for reaction (1), I is the ionic strength, m_{Si} is the silicon molality, and $\bar{n}$ is the ligand number.
[b] Derived from data of Table 1.

equals that of Cl$^-$ was used, with a large allowance (20%) for error from this assumption in the error analysis. The differences ([i]$_r$ − [i]) were all small compared to the ionic strength and as a result the maximum liquid junction potentials were 0.5 mV.

The data were analyzed and interpreted according to the treatment presented previously for similar studies.[12,13] The ligand number, $\bar{n}$, or the average number of OH$^-$ ions bound to a silicon atom, was derived from the data using the equation

$$\bar{n} = ([\mathrm{H^+}] + m_{\mathrm{OH^-}} - [\mathrm{OH^-}])/m_{\mathrm{Si}} \quad (4)$$

where $m_{\mathrm{OH^-}}$ and m_{Si} are the stoichiometric concentrations of base and total silicon in solution. The OH$^-$ concentration in the solution was obtained by a reiterative solution of eq 3. The H$^+$ concentration, a small or negligible contribution to $\bar{n}$ in this study, was obtained from the observed value of the dissociation quotient for water in NaCl media.[14]

The analysis of the data from more concentrated silica solutions (Table I) in terms of polymeric species was performed by the usual procedure. (1) A sequence of equilibria

$$x\mathrm{Si(OH)_4(aq)} + y\mathrm{OH^-} \overset{Q_{x,y}}{\rightleftharpoons} \mathrm{Si}_x(\mathrm{OH})_{4x+y}{}^{y-} \quad (5)$$

was assumed, corresponding to a scheme of hydrolysis products. (2) Trial values of the corresponding equilibrium quotients, $Q_{x,y}$, were used to calculate a value of $\bar{n}$ for each data point by means of the expression

$$\bar{n}_c = (\Sigma y Q_{x,y}[\mathrm{Si(OH)_4}]^x[\mathrm{OH^-}]^y)/m_{\mathrm{Si}} \quad (6)$$

The free silicic acid concentration was obtained by reiterative solution of the material balance equation

$$[\mathrm{Si(OH)_4}] = m_{\mathrm{Si}} - \Sigma x Q_{x,y}[\mathrm{Si(OH)_4}]^x[\mathrm{OH^-}]^y \quad (7)$$

and eq 6. (3) The $Q_{x,y}$ values were adjusted until the best agreement was obtained between calculated and observed $\bar{n}$ values for all the data.

This data analysis calculation was made using a least-squares computer program originally employed by Rush, Johnson, and Kraus.[15] The interpretation is based upon the assumption that the most probable scheme of hydrolysis products is that scheme containing a minimum number of species, $\mathrm{Si}_x(\mathrm{OH})_{4x+y}{}^{y-}$, which suffice to account for all the data within the limits of the estimated error.

Weighting of Data. The data used in the above least-squares analysis were weighted according to the assigned experimental errors. Estimated errors were assigned to 17 independently measured quantities involved in solution makeup and in volume, potentiometric, and temperature measurements. The effect of these errors on $\bar{n}$ for each data point was obtained by numerical differentiation in the computer program used to calculate the experimental data. Weights (W) were then obtained for use in the least-squares procedure by summing all 17 variances which could then be calculated to obtain the variance in $\bar{n}$ for each point.

The agreement factor defined by the equation

$$\sigma(\bar{n}) = [\Sigma(W(\bar{n} - \bar{n}_c)^2/(N_o - N_v))]^{1/2} \quad (8)$$

was used as the criterion for the scheme tested. The weight W is the reciprocal of the variance for the data point and $(N_o - N_v)$ is the difference in the number of observations and the number of variables. The $\sigma(\bar{n})$ would be unity when the weights are accurately estimated and the data fit the model exactly (with the assignment of unit weight, $\sigma(\bar{n})$ is the standard error of the data points).

Discussion of Results

Mononuclear Silicates. There is evidence from early potentiometric and spectral work that silicic acid ionizes one, two, or three protons in successively more basic solutions to give $\mathrm{SiO(OH)_3}^-$, $\mathrm{SiO_2(OH)_2}^{2-}$, and $\mathrm{SiO_3(OH)}^{3-}$. There is Raman evidence[3-5] for the tetrahedral structure of the first two and x-ray evidence exists for the tetrahedral $\mathrm{SiO_2(OH)_2}^{2-}$ in alkali and alkaline-earth silicate compounds.[16]

We have made precise measurements of the first ionization of Si(OH)$_4$(aq) and have obtained more approximate estimates of the second ionization reaction in 1 m NaCl as shown later in Table V. The first ionization was also determined as a function of NaCl concentration to 5 m in the experiments summarized in Table II where generally 0.005 m Si(IV) solutions with $\bar{n}$ values from about 0.5 to 0.7 were examined from 60 to 295 °C. Because hydroxide solutions were used

Table III. Thermodynamic Quantities at Saturation Pressure for $Si(OH)_4 + OH^- = SiO(OH)_3^- + H_2O$ in NaCl Media

t °C	log Q_{11}	ΔH cal mole^{-1}	ΔS cal deg^{-1} mole^{-1}	ΔC_p cal deg^{-1} mole^{-1}
		$I = 0.0$		
0	4.662 ± 0.049	−7510 ± 330	−6.17 ± 1.02	11.8 ± 2.6
25	4.168 ± 0.033	−7220 ± 270	−5.14 ± 0.80	11.8 ± 2.6
50	3.767 ± 0.025	−6920 ± 210	−4.19 ± 0.61	11.8 ± 2.6
75	3.438 ± 0.022	−6630 ± 160	−3.31 ± 0.44	11.8 ± 2.6
100	3.165 ± 0.022	−6330 ± 110	−2.49 ± 0.31	11.8 ± 2.6
125	2.937 ± 0.022	−6040 ± 90	−1.72 ± 0.24	11.8 ± 2.6
150	2.746 ± 0.021	−5740 ± 120	−1.01 ± 0.28	11.8 ± 2.6
175	2.585 ± 0.021	−5450 ± 160	−0.33 ± 0.38	11.8 ± 2.6
200	2.448 ± 0.022	−5150 ± 220	0.31 ± 0.49	11.8 ± 2.6
225	2.332 ± 0.024	−4860 ± 280	0.92 ± 0.61	11.8 ± 2.6
250	2.233 ± 0.027	−4560 ± 340	1.50 ± 0.73	11.8 ± 2.6
275	2.149 ± 0.031	−4270 ± 400	2.05 ± 0.84	11.8 ± 2.6
300	2.078 ± 0.037	−3970 ± 470	2.58 ± 0.96	11.8 ± 2.6
		$I = 0.5$		
0	4.793 ± 0.045	−7540 ± 330	−5.68 ± 1.02	11.5 ± 2.6
25	4.297 ± 0.026	−7260 ± 270	−4.67 ± 0.81	11.4 ± 2.6
50	3.893 ± 0.014	−6970 ± 210	−3.75 ± 0.61	11.4 ± 2.6
75	3.562 ± 0.010	−6690 ± 160	−2.91 ± 0.44	11.3 ± 2.6
100	3.286 ± 0.010	−6400 ± 110	−2.13 ± 0.30	11.2 ± 2.6
125	3.056 ± 0.010	−6120 ± 80	−1.40 ± 0.22	11.1 ± 2.6
150	2.861 ± 0.010	−5850 ± 100	−0.73 ± 0.24	11.1 ± 2.6
175	2.696 ± 0.010	−5570 ± 150	−0.10 ± 0.33	11.0 ± 2.6
200	2.556 ± 0.011	−5300 ± 200	0.50 ± 0.45	10.9 ± 2.6
225	2.436 ± 0.014	−5030 ± 260	1.05 ± 0.56	10.8 ± 2.6
250	2.333 ± 0.018	−4760 ± 320	1.58 ± 0.68	10.7 ± 2.6
275	2.245 ± 0.023	−4500 ± 380	2.07 ± 0.79	10.6 ± 2.6
300	2.169 ± 0.030	−4230 ± 440	2.54 ± 0.89	10.4 ± 2.6
		$I = 1.0$		
0	4.865 ± 0.046	−7570 ± 340	−5.45 ± 1.03	11.2 ± 2.5
25	4.367 ± 0.027	−7290 ± 270	−4.48 ± 0.81	11.1 ± 2.5
50	3.961 ± 0.016	−7020 ± 210	−3.59 ± 0.62	10.9 ± 2.5
75	3.627 ± 0.012	−6740 ± 160	−2.78 ± 0.45	10.8 ± 2.5
100	3.348 ± 0.012	−6480 ± 110	−2.04 ± 0.30	10.6 ± 2.5
125	3.115 ± 0.013	−6210 ± 80	−1.35 ± 0.21	10.5 ± 2.5
150	2.917 ± 0.013	−5950 ± 90	−0.72 ± 0.22	10.3 ± 2.5
175	2.749 ± 0.013	−5700 ± 130	−0.13 ± 0.31	10.1 ± 2.5
200	2.605 ± 0.013	−5450 ± 190	0.41 ± 0.41	9.9 ± 2.5
225	2.481 ± 0.015	−5200 ± 240	0.91 ± 0.53	9.7 ± 2.5
250	2.374 ± 0.018	−4960 ± 300	1.38 ± 0.64	9.5 ± 2.5
275	2.281 ± 0.023	−4720 ± 360	1.82 ± 0.74	9.3 ± 2.5
300	2.200 ± 0.029	−4490 ± 420	2.23 ± 0.85	9.1 ± 2.5
		$I = 3.0$		
0	5.072 ± 0.051	−7680 ± 340	−4.92 ± 1.03	9.9 ± 2.4
25	4.565 ± 0.031	−7440 ± 280	−4.06 ± 0.82	9.6 ± 2.4
50	4.150 ± 0.018	−7200 ± 220	−3.30 ± 0.64	9.2 ± 2.4
75	3.805 ± 0.012	−6980 ± 170	−2.63 ± 0.47	8.8 ± 2.4
100	3.516 ± 0.011	−6760 ± 120	−2.04 ± 0.33	8.3 ± 2.4
125	3.270 ± 0.011	−6560 ± 90	−1.52 ± 0.23	7.9 ± 2.4
150	3.059 ± 0.011	−6370 ± 80	−1.06 ± 0.20	7.3 ± 2.4
175	2.876 ± 0.011	−6200 ± 120	−0.67 ± 0.26	6.8 ± 2.4
200	2.717 ± 0.011	−6030 ± 160	−0.32 ± 0.36	6.2 ± 2.4
225	2.577 ± 0.012	−5880 ± 220	−0.02 ± 0.46	5.6 ± 2.4
250	2.452 ± 0.015	−5750 ± 270	0.23 ± 0.57	5.0 ± 2.4
275	2.341 ± 0.019	−5640 ± 330	0.43 ± 0.67	4.3 ± 2.4
300	2.241 ± 0.024	−5540 ± 380	0.59 ± 0.77	3.6 ± 2.4
		$I = 5.0$		
0	5.266 ± 0.059	−7800 ± 350	−4.45 ± 1.04	8.7 ± 2.4
25	4.750 ± 0.039	−7580 ± 300	−3.71 ± 0.84	8.1 ± 2.4
50	4.324 ± 0.026	−7390 ± 240	−3.08 ± 0.66	7.5 ± 2.4
75	3.968 ± 0.019	−7210 ± 190	−2.56 ± 0.51	6.8 ± 2.4
100	3.666 ± 0.015	−7050 ± 150	−2.12 ± 0.39	6.0 ± 2.4
125	3.407 ± 0.014	−6910 ± 130	−1.77 ± 0.32	5.2 ± 2.4
150	3.181 ± 0.013	−6790 ± 130	−1.49 ± 0.31	4.4 ± 2.4
175	2.984 ± 0.013	−6700 ± 160	−1.29 ± 0.37	3.5 ± 2.4
200	2.808 ± 0.013	−6620 ± 200	−1.14 ± 0.46	2.5 ± 2.4
225	2.651 ± 0.016	−6570 ± 260	−1.06 ± 0.56	1.5 ± 2.4
250	2.509 ± 0.020	−6550 ± 310	−1.03 ± 0.66	0.4 ± 2.4
275	2.379 ± 0.025	−6550 ± 370	−1.06 ± 0.77	−0.7 ± 2.4
300	2.259 ± 0.031	−6580 ± 440	−1.15 ± 0.89	−1.8 ± 2.4

Table IV. Equilibrium Quotients for the First Ionization of Silicic Acid in the Hydrogen Ion Form,[a] $Si(OH)_4(aq) \rightleftarrows SiO(OH)_3^- + H^+$

	$-\text{Log } Q_{11}{}^a$				
t, °C	$I = 0.0$	$I = 0.1$	$I = 1.0$	$I = 3.0$	$I = 5.0$
0	10.28	10.04	9.82	9.86	9.99
25	9.82	9.57	9.35	9.40	9.54
50	9.50	9.24	9.01	9.05	9.19
75	9.27	8.99	8.74	8.77	8.90
100	9.10	8.80	8.52	8.53	8.64
125	8.98	8.66	8.35	8.32	8.40
150	8.90	8.55	8.20	8.13	8.18
175	8.85	8.48	8.09	7.97	7.97
200	8.85	8.45	8.00	7.82	7.77
225	8.89	8.44	7.94	7.68	7.58
250	8.96	8.47	7.88	7.55	7.39
275	9.07	8.51	7.84	7.41	7.17
300	9.22	8.57	7.78	7.24	6.92

[a] Derived from Q_W given in ref 14 and results from this work.

in the reference compartment of the potentiometric cell, the reaction written in the base form as in reaction 1 was directly observed. Because the ΔZ^2 is zero, a small effect of salt concentration on log Q_{11} was anticipated and observed (Figure 2). The reaction proceeds to a lesser extent to the right in a regular fashion as the temperature increases to 300 °C.

The data of Table II along with the results of Ingri[8] in 0.5 *m* NaCl at 25 °C were fitted by the following expression which is generally of a form previously demonstrated to describe such equilibrium quotients

$$\log Q_{11} = (2.34669 \times 10^3/T) + 2.57979 \ln T - 18.4014 + 0.0964146I - (3.02800 \times 10^{-7})IT^2 + 0.529703F(I)I + 0.0157\phi I \tag{9}$$

where $F(I)$ is a function of ionic strength suggested in the formulation of Pitzer[17] to express the effect of ionic strength on the interaction coefficients in the Bronsted–Guggenheim approach for activity coefficients and ϕ is the osmotic coefficient for sodium chloride solutions. This expression is the form based on the assumption that ΔC_p is a constant. Other tests in which ΔC_p was assumed to be proportional to temperature and then to vary linearly with temperature gave no significantly better fits. The agreement factor obtained with errors assigned to the known experimental observables was 1.9.

The activity coefficients for the cations $\gamma_{M'}$ and anions $\gamma_{X'}$ are given in the Bronsted–Guggenheim formulations by

$$\log \gamma_{M'} = -Z_{M'}{}^2(SI^{1/2}/(1 + I^{1/2})) + \sum_{X} B_{M'X}m_X \tag{10}$$

$$\log \gamma_{X'} = -Z_{X'}{}^2(SI^{1/2}/(1 + I^{1/2})) + \sum_{M} B_{MX'}m_M \tag{11}$$

and the ionic strength effect on the interaction coefficients is given by

$$B_{MX} = B_{MX}{}^0 + B_{MX}{}'F(I) \tag{12}$$

with

$$F(I) = [1 - (1 + 2I^{1/2} - 2I)\exp(-2I^{1/2})]/4I \tag{13}$$

In the expression (9) the ΔB_{11} for reaction 1 is assumed to have the form

$$-\Delta B_{11} = p_4 + p_5T^2 + p_6F(I) \tag{14}$$

where $P_4 ... P_6$ are temperature-independent parameters.

The thermodynamic quantities derived with their calculated uncertainties (three times the standard error) are given in Table III for ionic strengths of 0, 0.5, 1.0, 3.0, and 5.0 *m*. There are no other reported values with which these results can be compared. At $I = 0$ the ΔH goes from −7.51 ± 0.33 kcal mol^{-1} at 0 °C to −3.97 ± 0.47 kcal mol^{-1} at 300 °C with ΔC_p = 11.8 ± 2.6 cal mol^{-1} K^{-1}. The minimum uncertainty is obtained near the middle of the range of the data, i.e., at 125 °C ΔH = −6.04 ± 0.09 kcal mol^{-1}. Within the estimated error there is no change in ΔH with salt concentration at the lowest temperature at high salt concentrations and ΔC_p approaches zero at the highest salt concentrations and temperatures.

Since many researchers choose to consider such processes in the hydrogen ion form (ionization equilibria), we have combined these log Q_{11} values with the ionization quotient for water in NaCl media[14] (at the saturation pressure of water) to express quotients $Q_{11}{}^a$ for the reaction

$$Si(OH)_4(aq) \rightleftarrows H^+ + SiO(OH)_3^- \tag{15}$$

The results are given in Table IV for the same conditions. We have compared these results with those of several previous

Table V. Log $Q_{x,y}$ Values for Selected Schemes for Fitting Data

	Species (x,y)						
	1,1[a]	1,2	3,1	4,2	5,2	6,3	$\sigma(\bar{n})$
This work, 60 °C, 1.0 *m* NaCl	3.854 ± 0.009	4.20 ± 0.05	7.98 ± 0.05				2.20
	3.818 ± 0.007	4.25 ± 0.03		13.38 ± 0.06			2.10
	3.819 ± 0.007	4.14 ± 0.05			15.69 ± 0.07		2.27
	3.812 ± 0.007	4.17 ± 0.05				21.15 ± 0.28	2.25
Ingri, 25 °C, 0.5 *m* NaCl	4.378 ± 0.009	4.05 ± 0.16	9.18 ± 0.03				0.0121[c]
	4.282 ± 0.006	4.60 ± 0.03		14.85 ± 0.03			0.0114
	(4.24)[b]	(5.28)		(15.03)			
	4.278 ± 0.006	4.05 ± 0.14			17.32 ± 0.04		0.0111
	4.253 ± 0.008	4.45 ± 0.07				23.12 ± 0.06	0.0155

Species (x,y)	This work, $I = 1.0$ *m*					
	60 °C	100 °C	150 °C	200 °C	250 °C	288 °C
1,1	3.818 ± 0.007	3.323 ± 0.005	2.819 ± 0.005	2.591 ± 0.008	2.370 ± 0.007	2.197 ± 0.008
1,2	4.25 ± 0.03	3.53 ± 0.07	2.56 ± 0.09	2.81 ± 0.12	No est	1.97 ± 0.15
4,2	13.38 ± 0.06	11.51 ± 0.06	9.54 ± 0.08	9.33 ± 0.19	8.95 ± 0.22	7.30 ± 0.27
$\sigma(\bar{n})$	2.10	1.96	2.22	3.23	2.15	

[a] These quantities were allowed to vary. The values based on dilute solutions are given in Table III. [b] Values in parentheses given by Belinski and Ingri (1967). [c] Unit weights were assigned to Ingri's data.

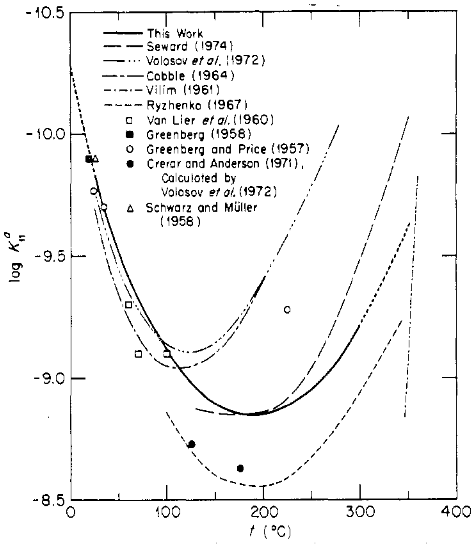

Figure 3. Log $K_{11}{}^{a}$ (ionization equilibrium constant) of silicic acid as a function of temperature obtained in this research (solid line) compared with other determinations and extrapolations (see text). Our data have been extrapolated to 0 and 350 °C.

investigators involving both measurements and extrapolations in Figure 3. The solubility measurements of Seward[1] on quartz in borax solutions are given as a curve with long dashes. These data are in best agreement with our results over the temperature range 130–250 °C as would be expected notwithstanding the uncertainties and approximations in that approach. The early extrapolation from low-temperature data by Cobble[18] and that from the review of Volosov et al.[19] are progressively more in error above about 150 °C. The values from conductance measurements of Ryzhenko[2] and those derived from solubility measurements by Crerar and Anderson[20] appear to be quite uncertain as are the values given by Vilim[21] from the high-temperature solubility studies. Results of earlier measurements[22-25] are also shown in Figure 3.

Extension of our measurements to relatively acidic solutions (pH 3.5) gave no evidence for further ionization as in the production of cationic species. However, at the highest $\bar{n}$ values (1.6 in an experiment in 0.01 *m* silica at 60 °C) estimates of the second ionization quotient were obtained. The accuracy with which it could be determined was limited by the uncertainty in the free hydroxide concentration because of the high hydroxide concentrations at which the process occurs. The results in 1 *m* NaCl are included in Table V which is discussed below (the value given in the table from our analysis of Ingri's data is much more consistent with his data than his value given in parentheses). Written in the hydrogen ion form the second ionization reaction

$$SiO(OH)_3^- \rightleftarrows H^+ + SiO_2(OH)_2^{2-} \tag{16}$$

occurs with log Q of −12.32 at 60 °C in 1 *m* NaCl and −10.2 at 300 °C in 1 *m* NaCl. More negative values for log K (at infinite dilution) would be anticipated which is inconsistent with the results of Ryzhenko[2] from conductance studies on sodium silicate solutions.

We calculate ΔH_{12} for the overall reaction in the hydroxide form to be −8.7 ± 1.5 kcal mol^{-1} over the range 60–200 °C and have not calculated any further thermodynamic quantities because of the large uncertainties in the data at the higher temperatures. Ryzhenko and Khitarov[26] have evidence from conductance measurements of average charges in silica solutions reaching as high as −4 in concentrated and very basic sodium silicate solutions.

Sodium Ion Complexing by Silicates. One question often raised by geochemists concerns the stability of sodium ion (or other cation) complexes by anionic silicates. From the results in this paper it is possible to comment on the possible stability of such complexes. Seward[1] has assigned values of 18–24 for K_{as} for the process

$$Na^+ + SiO(OH)_3^- \rightleftarrows NaSiO(OH)_3(aq) \tag{17}$$

over the temperature range 135–301 °C. In the method used, a number of assumptions are required for derivation of K_{as}. Among the more important assumptions are: (1) γ_{OH^-} and $\gamma_{SiO(OH)_3^-}$ are equal in this medium and are given by $\gamma_\pm$ for NaCl at the same ionic strength; (2) the equilibrium quotients for the borate equilibria in KCl can be used in the NaCl media and reliably extrapolated from 200 to 300 °C; (3) log $K_{11}{}^{a}$ is obtained by extrapolation of log $Q_{11}{}^{a}$ vs. I plots rather than the preferable function $I^{1/2}/(1 + I^{1/2})$ since ΔZ^2 is equal to 2 for the process; (4) there is no interaction between the borate and silicate ions in solution; (5) there is no polymerization of the silicate under the conditions of the equilibrations (at the concentrations occurring at the high temperatures a small amount of polymerization would be expected from our results); and (6) the salting coefficient for $Si(OH)_4(aq)$ is zero.

Figure 2 shows that Q_{11} varies only slightly with ionic strength in going from 0 to 5 *m*. For reaction 1

$$\Delta B_{11} = B_{NaSiO(OH)_3} - B_{NaOH} \tag{18}$$

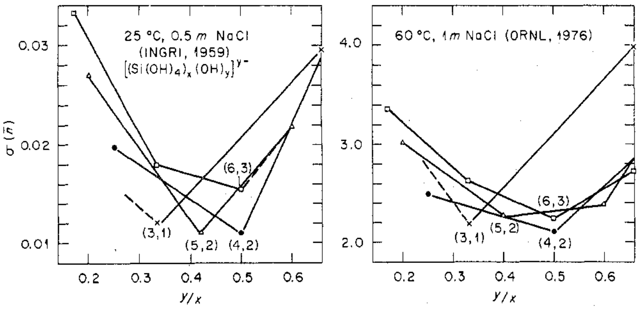

Figure 4. Agreement factors (eq 8) for four-species hydrolysis schemes in the array $Si(OH)_4(aq)$, $SiO(OH)_3^-$, $SiO_2(OH)_2^{2-}$, and $Si_x(OH)_{4x+y}^{y-}$ calculated from Ingri's data at 25 °C and from this research at 60 °C. The (x,y) values are indicated at the minimum of each "curve". The lines join sets of points with the same x.

and assuming the salting coefficient for $Si(OH)_4(aq)$ is zero, ΔB_{11} has a value of -0.12 at 50 °C and -0.03 at 300 °C at 5 m.

The observed quantity ΔB_{11} includes any sodium ion complexing present. A quantity $\Delta B_{11}'$ can be defined by subtracting the contribution of sodium complexing from ΔB_{11} as shown by

$$\Delta B_{11} = [\Delta B_{11}'I - \log(1 + Q_{as}[Na^+])]/I \qquad (19)$$

where Q_{as} is the association quotient (reaction 17) in the medium. With the assumption that $\Delta B_{11}'$ is zero and that no association of hydroxide occurs, then Q_{as} does not exceed 0.6 in 5 m NaCl at any temperature. With our inability to predict $\Delta B_{11}'$ with the accuracy needed for such purposes, Q_{as} could equally well have the value of zero.

We prefer to conclude that the magnitude of the interactions of sodium ion with the silicate anion cannot be unambiguously assigned from evidence such as either the solubility studies or our potentiometric results. It is more reasonable to consider such small salt effects in terms of stoichiometric activity coefficients. In estimating the part of the salt effect to be attributable to complexing one must consider that the hydroxide ion would also exhibit weak complexing.

Polynuclear Silicates. The existence of polynuclear silicates in basic solutions was demonstrated in the potentiometric studies of Lagerström[27] and Ingri[8] in 1959. The $\bar{n}$ vs. pH curves shift to higher pH with increasing silica concentration in the region $\bar{n} \geq 0.7$. We have found that extension of measurements to higher temperatures does not increase the composition region accessible to study. Slowly drifting potentials, probably related to polymerization of $Si(OH)_4(aq)$ or precipitation of amorphous silica, are observed as the concentrations of monomeric $Si(OH)_4(aq)$ exceed the saturation level for amorphous silica which occurs at an $\bar{n}$ near 0.7.

The analysis of potentiometric data by Ingri in terms of $Si(OH)_4(aq)$, $SiO(OH)_3^-$, $SiO_2(OH)_2^{2-}$, and $Si_4(OH)_{18}^{2-}$ (or $Si_4O_6(OH)_4^{2-}$) was reexamined by applying the method of least squares in computer-assisted calculations for assumed equilibrium models. We have assumed the mononuclear equilibria plus the presence of one polynuclear species with the general formula $Si_x(OH)_{4x+y}^{y-}$ (where the water content is undefined) allowing x to increase to 6 with y varying until a minimum agreement factor was obtained for a given x (polynuclearity). The results of these calculations (with unit weights) are summarized in Figure 4. Agreement factors for the models with the same value of x are joined by lines in the figure and the (x,y) values are shown in parentheses for the species giving the lowest agreement factor. We have made the same analysis for data from our work at 60 °C in 1 m NaCl where the spread of curves with silica concentration is greatest (with actual weights assigned). Similar results were obtained in the two cases. Best fits were obtained individually with the species (4,2) and (5,2) and, in addition for the 60 °C data, the (6,3) species as the preferred polynuclear species among all the possible polynuclear species with up to six silicon atoms. The values for log Q_{11} obtained at both 25 and 60 °C using the (3,1) species are significantly different from those given in Table III and therefore this represents a poorer fit than the above mentioned schemes. There is no statistical basis from the agreement factor or systematic variations in the fits which would allow a choice of one of the other species above as a uniquely preferred one.

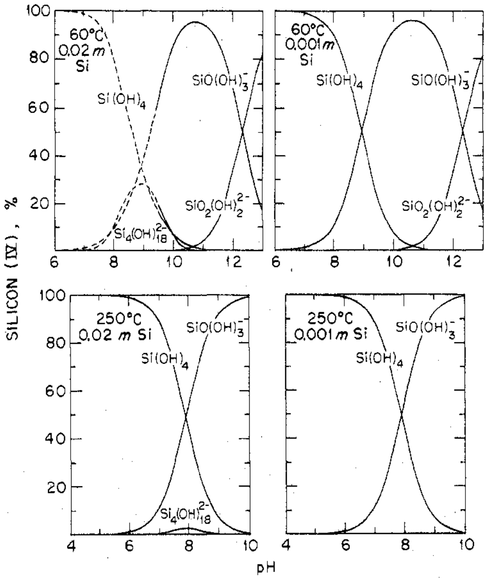

Figure 5. Calculated distribution of species in solutions containing 0.02 and 0.001 m Si(IV) at 60 and 250 °C. Dashed lines represent regions where precipitation or nonequilibrium is encountered.

Table V gives the $Q_{x,y}$ values defined in eq 5. The contribution of polynuclear species is less at high temperatures as evidenced by the reduced spread of the curves in Figure 1. Included in Table V is a listing of results of calculations made assuming the (4,2) species as the polynuclear species. This arbitrary choice, however, enables us to illustrate the reduced tendency for polymerization at higher temperatures in the distribution plots of Figure 5. The distribution of species was calculated for 1 m NaCl at 60 °C and at 250 °C in 0.02 and 0.001 m silica solutions. The region where supersaturation or nonequilibrium is encountered is shown by the dashed curves at 60 °C in 0.02 m silica. At 60 °C the solubility of amorphous silica in water is about 0.004 m which is approximately the point where precipitation was observed in our experiments. At 250 °C only about 3% of the silicon is present as the polynuclear species in an 0.02 m silica solution.

We have chosen not to present detailed calculations of thermodynamic data for the polynuclear species since their composition is not uniquely defined. From the data tabulated in Table V and by assuming a constant change in enthalpy over the interval 60–200 °C, the average heat $\Delta H_{4,2}$ is -18 ± 2 kcal mol^{-1}. This compares with the value of -34 ± 6 given for the analogous borate species at 25 °C.[13]

Several larger species were chosen by Aveston[9] in a rather arbitrary model to fit ultracentrifugation data in somewhat more concentrated solutions of silica. There is, however, agreement with our results in that in this polydisperse system the average polynuclearity approaches unity as $\bar{n}$ of unity is approached. Not much insight is derived from consideration of the preferred structures in solid silicates because (1) many ring systems (4, 6, 8, and 12 silicons) occur and (2) few structures are known for silicates with silanol groups. Likewise, Raman studies of Freund[5] do not succeed in distinguishing the various possible structures in relatively concentrated polysilicate solutions.

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Registry No. $Si(OH)_4$, 10193-36-9; $SiO(OH)_3^-$, 18102-72-2; $SiO_2(OH)_2^{2-}$, 27831-51-2; $Si_4(OH)_{18}^{2-}$, 63588-54-5.

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Sputtered Gold and Silver Atoms Isolated in D_2, Ne, and N_2 Matrices[1]

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The spectra of sputtered gold and silver atoms isolated in D_2, Ne, and N_2 matrices are reported. An inverse relationship between Z_{eff} of the metal atom and α, the polarizability of the matrix, has been extended to include silver atoms in D_2 and N_2 matrices. The correlation breaks down for Ne matrices apparently because the size of a substitutional site and polarizability of neon are such as to cause multiple-site occupation. Evidence for multiple-site occupation of silver in neon is presented. Intense and resolved spectra of silver dimers are also reported, and a correlation with the gas-phase spectra is made.

Introduction

The spectra of matrix-isolated gold[2,3] and silver[3b-9] atoms have been extensively studied and the main spectral features of both species are well characterized. The ground state of both atoms is ^2S giving rise to a relatively simple absorption spectrum in the ultraviolet region, corresponding to the lowest lying P → S transition with the ^2P state split by spin–orbit coupling. The matrix spectra, which generally consist of three absorptions, have been correlated with the spectrum of the gas-phase atomic species by postulating a perturbation of the atomic energy levels by the matrix cage.

Specifically, in the matrix the orbital degeneracy of the $^2P_{3/2}$ level is removed by a crystal field effect, yielding two sublevels, $P_{3/2\pm1/2}$ and $P_{3/2\pm3/2}$. Previous work with matrix-isolated gold atoms[3a] has correlated the variance of the spin–orbit coupling constant, ζ, in Ar, Kr, and Xe matrices with an increase in Z_{eff} of the gold nucleus. The electronic charge density of the 6p electron is increased by compression of the 6p wave function due to the repulsive interaction between the Au atom and the noble gas cage.[3a] The amount of compression depends on site considerations of the isolated gold atoms, the polarizability of the matrix atoms, and the temperature at which the matrix is observed.

When, as is the case for gold atoms isolated in Ar, Kr, and Xe matrices, the substitutional sites have the same symmetry properties, there exists a linear relationship between polarizability α of the matrix and Z_{eff}. ESR studies[10] of gold atoms isolated in Ar, Kr, and Xe matrices are in agreement with optical results indicating a single substitutional site and both the hyperfine and spin–orbit coupling constants increase as the matrix atoms become lighter and less polarizable. However, in neon matrices the ESR studies indicate that gold atoms occupy at least two different sites, and the value of the hyperfine coupling constant, A, in neon is nearly the same as that in Kr. It was of interest, therefore, to see if the spin–orbit coupling constant of Au in Ne undergoes a similar reversal indicative of different site geometries in this matrix.

As a further test of the relationship between the magnitude of the spin–orbit coupling constant and matrix polarizability, it was decided to study silver atoms, whose van der Waals radius and thus matrix behavior should be similar to that of gold. While presently available ESR and optical results for silver atoms isolated in rare gas matrices indicate that the spin–orbit and hyperfine coupling constants show trends similar to gold atoms, there has been up to now no direct evidence for multiple-site occupation.

Thus, to determine the range of applicability of the relationship between matrix polarizability and Z_{eff} and to obtain additional data on multiple-site occupations, the optical spectra of gold and silver atoms in Ne, N_2, and D_2 matrices have been included in our studies.

Throughout this work metal atoms have been produced by sputtering from a metal surface. This method of metal atom production, with the proper experimental conditions, appears to be especially conducive to the formation of metal dimers in the matrix, at least in the case of silver. Dimer formation appears to occur during deposition at the surface or near-surface region of the matrix before the kinetic energy of the sputtered atoms can be dissipated. The energy of sputtered metal atoms is the order of 1–10 eV, which is considerably