

Equilibrium Studies of Polyanions

IV. Silicate Ions in NaCl Medium

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Equilibria in silicate solutions have been studied in 0.5 m (molal) NaCl at 25°C, using emf's with a hydrogen electrode. The data, which cover total silicate concentrations, B , from 0.0025 to 0.080 m, are given in the form of curves Z ($\log [\text{OH}^-]_B$) as previously. The data indicate, besides the mononuclear $\text{Si}(\text{OH})_4$, $\text{SiO}(\text{OH})_3^-$, and $\text{SiO}_2(\text{OH})_2^{2-}$, the presence of polynuclear species with a fairly low number, three or four, of Si-atoms. Assuming a single predominating polynuclear species in the range studied, the best agreement was obtained with $\text{Si}_4\text{O}_8(\text{OH})_6^{3-}$, as in previous work (Part III¹). The equilibrium constants deduced are given in Table 2, and the agreement obtained with them is shown in Fig. 2.

In Part III¹ of this series, Lagerström investigated equilibria in silicate solutions, using 0.5 m and 3.0 m $\text{Na}(\text{ClO}_4)$ as ionic medium. These data could be explained assuming the mononuclear species $\text{Si}(\text{OH})_4$, $\text{SiO}(\text{OH})_3^-$, $\text{SiO}_2(\text{OH})_2^{2-}$, and one or two tetranuclear complexes. A satisfactory agreement was obtained between calculated and experimental data. Although this was perhaps the most accurate series of equilibrium measurements by modern principles that is as yet available for silicates, it was noted that the range of the data was not as broad as desirable, and that the conclusions thus needed support from other data.

The present work is a direct continuation of Lagerström's work, and the aim has been to find out what difference (if any) it makes if NaCl is substituted for $\text{Na}(\text{ClO}_4)$ as ionic medium. Thus, an investigation very similar to that in Part III has been made using 0.5 m NaCl as ionic medium, and then the data have been treated by mathematical and graphical methods independent of previous knowledge of the results in Part III. It may be considered as satisfactory that, in the end, the conclusions came out much the same.

For many of the experimental details, and for a survey of pertinent previous work on silicate solutions, the reader is referred to Part III¹. In this paper, however, possible structures for the complexes will also be discussed.

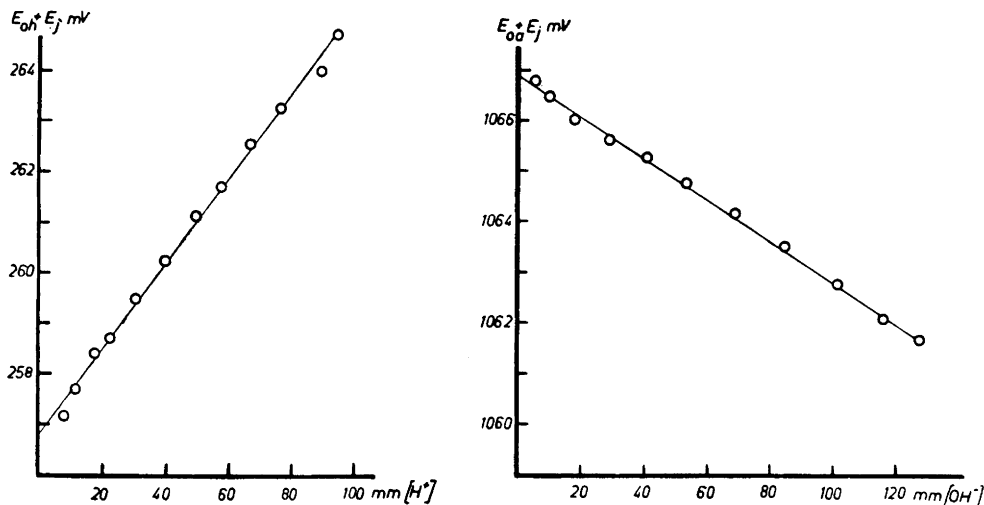


Fig. 1. Diagrams for calculating E_{0a} , E_j and K_w for 0.5 m NaCl medium at 25°C. The values in the two diagrams correspond to the same acid-base titration. The slopes give $E_j h^{-1} = 83$ and $E_j [\text{OH}^-]^{-1} = 41$ and the intercepts E_{0a} and E_{oh} give $-\log K_w = 13.70$. (See Part II.)

SYMBOLS

The symbols are in general the same as in Parts II² and III¹. Frequently it will be convenient to use the symbol $a = [\text{OH}^-]$.

When normalized curves and projection maps have been applied, the normalized quantities B , u and v ; corresponding to B , $a = [\text{OH}^-]$, and b , have been introduced and defined.

The total concentration B is, in some of the treatments, divided into different parts $B_1, B_2 \dots B_q \dots$, each corresponding to complexes $A_p B_q$ with a certain "nuclearity" q . Correspondingly, BZ (the total number of OH^- bound to the $\text{Si}(\text{OH})_4$ per liter, or the total charge on the silicate ions per liter), is also divided into the contributions $B_1 Z_1, B_2 Z_2 \dots B_q Z_p \dots$ for the various "nuclearities" present. The functions $f_1 = (1 + \beta_1 a + \beta_2 a^2)$ and $f_Q = \sum \beta_p a^p$ are defined in eqns (3a) and (4a).

Chemical symbols are in Roman type, concentrations in italics. Concentrations and equilibrium constants are expressed in m or mm (moles or millimoles in 1 000 g water).

EXPERIMENTAL

Reagents and apparatus

Sodium chloride, Merck p. a. was used. No Br^- could be detected using the eosin method³, and the sodium chloride was used after drying at 400°C without further purification.

Hydrochloric acid, Kebo p. a., was standardized against KHCO_3 and standard NaOH .

Sodium hydroxide, silicic acid and alkaline silicate solutions were prepared and analysed as described in Parts II² and III¹, except that solid NaCl was added instead of NaClO₄ solution to obtain the ionic medium desired.

Commercial hydrogen gas was used and purified as described in Part II². The silver-silver chloride electrodes were prepared⁴ by electro-depositing Ag on a Pt foil and afterwards chloridising the silver as anode in dilute HCl.

Following Lagerström's recommendations¹, Jena Geräte glass was used for titration vessels and burets. According to him, during a representative titration, the amount of silica dissolved from the glass-ware will correspond to at most 0.03 mm.

CELL AND PROCEDURE

The same type of *electrode vessel* and *salt bridge* were used as in Part II, except that a different reference electrode was used:

0.5 m NaCl/0.5 m NaCl, saturated with AgCl(s)/AgCl, Ag = SE.

The cell used was thus:

SE/silicate solution/H₂(1 atm), Pt.

The cell including the titration vessel, was kept in an oil thermostat at 25.0 ± 0.1°C, and the whole equipment kept in a thermostated room at 25°C. The emf was measured with a Vernier potentiometer.

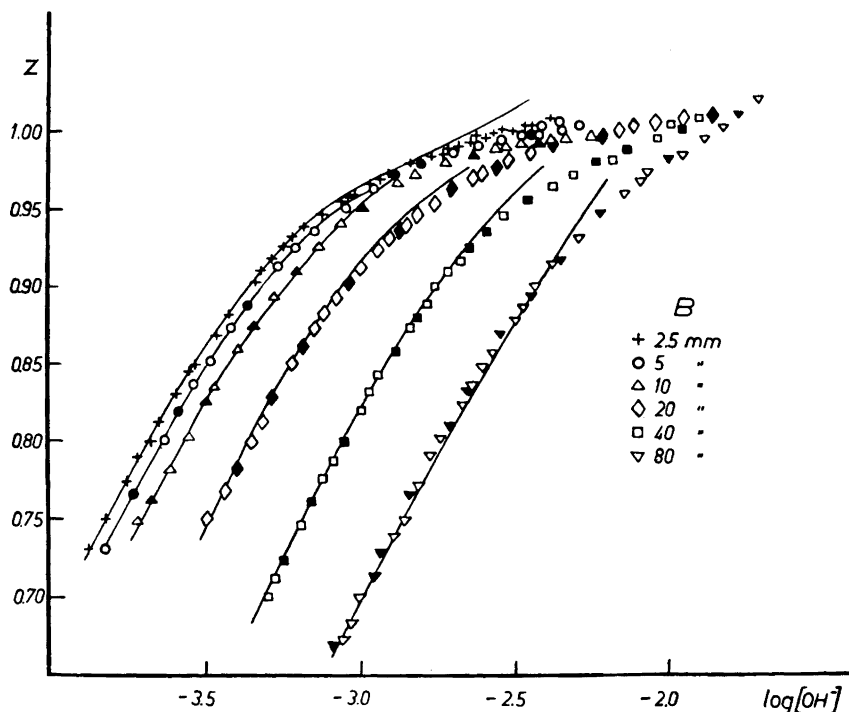


Fig. 2. Experimental data plotted as $Z(\log [\text{OH}^-])_B$. Experimental data: points with different symbols for different total concentration B . (See Table 1.) Titrations according to "procedure 1" have filled symbols, those according to procedure 2 open symbols; mm is millimoles in 1000 g water.

Table 1. Data Z ($\log [\text{OH}^-]$) for silicates at various total concentrations, B , at 25°C , $0.5 \text{ m Na}(\text{Cl})$ ionic medium.

$B = 0.0025 \text{ m}$. Z , $-\log [\text{OH}^-]$: 0.731, 3.877; 0.773, 3.7533; 0.801, 3.6777; 0.831, 3.5953; 0.845, 3.5522; 0.868, 3.4634; 0.882, 3.4246; 0.902, 3.3355; 0.931, 3.2202; 0.968, 2.9344; 1.006, 2.3856; (proc. 2) — 0.750, 3.8252; 0.812, 3.6501; 0.917, 3.2902; 0.954, 3.0608; 0.965, 2.9683; 0.996, 2.6238; 0.998, 2.5652; 1.001, 2.4669; (proc. 2) — 0.910, 3.3203; 0.980, 2.8393; 0.983, 2.7702; 0.989, 2.6819; 1.002, 2.4457; (proc. 2) — 0.789, 3.7142; 0.938, 3.1843; 0.956, 3.0409; 0.962, 3.0162; 0.976, 2.8514; 0.994, 2.6755; 0.998, 2.5086; (proc. 2.) — 0.849, 3.5321; 0.925, 3.2501; 0.958, 3.0157; 0.992, 2.6435; 1.000, 2.5401; (proc. 2) — 0.946, 3.1232; 0.972, 2.9115; 0.984, 2.7168; 0.994, 2.5943.

$B = 0.005 \text{ m}$. Z , $-\log [\text{OH}^-]$: 0.730, 3.8221; 0.837, 3.5385; 0.913, 3.2663; 0.949, 3.0444; 0.962, 2.9563; 0.993, 2.5421; 0.996, 2.4465; 1.004, 2.3623; 1.000, 2.3010; (proc. 2) — 0.766, 3.7314; 0.819, 3.5858; 0.888, 3.3675; 0.971, 2.8864; 0.978, 2.8006; 0.995, 2.4207; (proc. 1) — 0.801, 3.6313; 0.852, 3.4838; 0.873, 3.4167; 0.924, 3.2092; 1.001, 2.4129; (proc. 2) — 0.935, 3.1485; 0.985, 2.7012; 0.996, 2.4778; 1.002, 2.3501.

$B = 0.010 \text{ m}$. Z , $-\log [\text{OH}^-]$: 0.748, 3.7221; 0.803, 3.5608; 0.894, 3.2764; 0.940, 3.6402; 0.972, 2.8233; 0.991, 2.4849; 0.994, 2.3353; (proc. 2) — 0.762, 3.6762; 0.875, 3.3463; 0.983, 2.6367; (proc. 1) — 0.782, 3.6177; 0.835, 3.4703; 0.926, 3.1343; 0.966, 2.8849; 0.997, 2.3645; (proc. 2) — 0.859, 3.4021; 0.979, 2.7504; 0.989, 2.6668; 0.991, 2.4268; (proc. 2) — 0.826, 3.5022; 0.910, 3.2076; 0.951, 2.9958; 0.993, 2.3859; (proc. 1).

$B = 0.020 \text{ m}$. Z , $-\log [\text{OH}^-]$: 0.749, 3.5001; 0.799, 3.3501; 0.839, 3.2513; 0.872, 3.1427; 0.902, 3.0323; 0.923, 2.9428; 0.939, 2.8465; 0.962, 2.7010; 0.979, 2.5202; (proc. 2) — 0.766, 3.4344; 0.861, 3.1842; 0.911, 2.9964; 0.945, 2.8133; 0.976, 2.5583; 0.992, 2.3133; 0.485, 2.2054; 0.990, 2.1549; 1.009, 1.7766; (proc. 2) — 0.781, 3.3962; 0.828, 3.2856; 0.851, 3.2181; 0.892, 3.0721; 0.930, 2.9023; 0.952, 2.7581; 0.972, 2.6004; 0.985, 2.4441; 0.989, 2.3772; 1.009, 1.8681; (proc. 1) — 0.812, 3.3121; 0.882, 3.1109; 0.935, 2.8704; 0.969, 2.6326; 0.996, 2.2554; 1.002, 2.1123; 1.008, 1.9462; (proc. 2).

$B = 0.040 \text{ m}$. Z , $-\log [\text{OH}^-]$: 0.700, 3.3012; 0.711, 3.2818; 0.746, 3.1931; 0.788, 3.0994; 0.819, 3.0010; 0.842, 2.9482; 0.873, 2.8418; 0.900, 2.7643; 0.945, 2.5385; 0.970, 2.3183; 0.980, 2.1821; 0.994, 2.0385; (proc. 2.) — 0.723, 3.2545; 0.761, 3.1603; 0.801, 3.0631; 0.858, 2.8903; 0.880, 2.8169; 0.924, 2.6501; 0.934, 2.5912; 0.955, 2.4581; 0.979, 2.2382; 0.987, 2.1389; 1.000, 1.9534; (proc. 1) — 0.777, 3.1246; 0.832, 2.9701; 0.888, 2.7851; 0.909, 2.7184; 0.916, 2.6752; 0.964, 2.3787; 1.007, 1.9010; (proc. 2).

$B = 0.080 \text{ m}$. Z , $-\log [\text{OH}^-]$: 0.669, 3.0981; 0.713, 2.9601; 0.810, 2.7121; 0.869, 2.5501; 0.917, 2.3553; 0.982, 1.9991; (proc. 1) — 0.672, 3.0593; 0.700, 3.0075; 0.749, 2.8595; 0.791, 2.7763; 0.824, 2.6398; 0.848, 2.6123; 0.886, 2.4756; 0.914, 2.3819; 0.967, 2.0998; 0.984, 1.9545; 1.002, 1.8243; (proc. 2) — 0.728, 2.9404; 0.765, 2.8406; 0.833, 2.6519; 0.894, 2.4501; 0.947, 2.2255; 1.010, 1.7761; (proc. 1) — 0.683, 3.0344; 0.739, 2.8983; 0.772, 2.8152; 0.802, 2.7444; 0.836, 2.6421; 0.857, 2.5742; 0.878, 2.5015; 0.900, 2.4378; (proc. 2) — 0.930, 2.3004; 0.959, 2.1427; 0.974, 2.0683; 0.994, 1.8864; 1.019, 1.7182 (proc. 2).

Assuming the activity factors to be constant, the emf of the cell can be written

$$E = E_{\text{oa}} + 59.15 \log [\text{OH}^-] + E_j = E_{\text{oa}} + 59.15 \log K_w - 59.15 \log h + E_j \quad (1)$$

Using solutions with known $[\text{OH}^-]$, and $[\text{H}^+]$, $K_w = 10^{-13.70 \pm 0.02} \text{ m}^2$ and $E_j = 41 [\text{OH}^-] \text{ mV}$ were obtained. The constant E_{oa} was determined before every titration; for unknown reasons it is slightly different for different hydrogen electrodes. The diagrams in Fig. 1 illustrate this part of the work, which was otherwise quite similar to Part II and Part III.

In the titrations with silicate solutions, the two procedures described by Lagerström as procedure 1 and procedure 2 were used (of course, with Cl^-

instead of ClO_4^-). Thus in each titration, B was kept constant. From the known analytical excess of hydrogen, H , and from the measured $[\text{OH}^-]$, Z was obtained from

$$BZ = h - H - K_w h^{-1} = h - H - [\text{OH}^-] \quad (2)$$

The data obtained are listed in Table 1, and plotted in Fig. 2 in the usual form, $Z(\log [\text{OH}^-])_B$. Within the range shown in Fig. 2, reversible equilibria were obtained, as shown by the fact that points on the same curve were obtained with procedure 1 ($[\text{OH}^-]$ decreasing, black points), and procedure 2 ($[\text{OH}^-]$ increasing, open symbols).

The experimental range ($Z \sim 0.7$ to 1.0) was limited downwards by the "instability range", and upwards by the fact that at high $[\text{OH}^-]$, BZ is obtained as the difference between two large quantities, and thus the accuracy decreases (see eqn. (2)).

The term "instability range", introduced by Lagerström¹, denotes the range where a colloidal precipitate is formed so that stable equilibria, and thus stable emf's cannot be obtained. For $Z < 0.75$, the instability range covers the intermediate total concentrations, B , so that only at low and high values of B , could equilibria be studied.

With titration procedure 1, where, on acidification, part of the solution enters the instability range for a moment, equilibrium was obtained only after some time, whereas with procedure 2 it was obtained practically immediately.

SURVEY OF DATA. CALCULATION OF EQUILIBRIA

In Fig. 2, the data $Z(\log [\text{OH}^-])_B$ are seen to give points on different curves for different values of the total concentration, B . This shows that polynuclear complexes must be present. However, with decreasing B the curves seem to approach a limiting curve and one may reasonably assume that the limiting curve has approximately the same shape as the curve for the low B -values. This curve is easily found to fit into a family of curves calculated for a two-step equilibrium⁵. There is every reason to assume that the limiting curve is the one corresponding to equilibria between the three mononuclear species: $\text{Si}(\text{OH})_4$, $\text{SiO}(\text{OH})_3^-$, $\text{SiO}_2(\text{OH})_2^{2-}$, or, in the shorter notation used in Part II and Part III, B, AB and A_2B .

The calculations may be divided into two parts: firstly, the "mononuclear" equilibrium constants were determined as accurately as possible, and secondly an attempt was made to find the formulas and formation equilibrium constants of the most important polynuclear species.

THE EQUILIBRIA WITH MONONUCLEAR SPECIES

It did not prove practicable to get a better approximation to the "mononuclear" curve by making experiments at lower total concentration, B , than about 0.0025 m. At lower B -values, the experimental uncertainty made the data spread so that Z_1 could not be obtained more accurately.

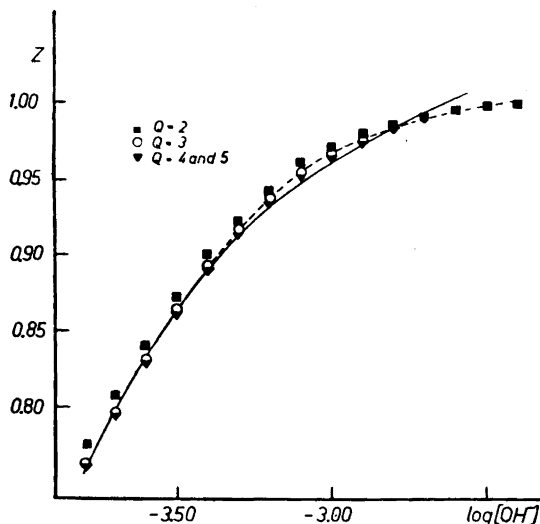


Fig. 3. "Mononuclear curves" $Z_1(\log [\text{OH}^-])$ calculated using equation (7) and different values for Q . A full curve: calculated with equilibrium constants in Table 2; a dotted curve, experimental $Z(\log [\text{OH}^-])$ curve for $B = 0.0025$ m. The full curve calculated with the constants in Table 2 agrees very well with the points for $Q = 4$,

To find the mononuclear curve, $Z_1(\log [\text{OH}^-])$, use was made of a method of extrapolation which will now be outlined: It was assumed that the only species formed are the mononuclear B, AB, and A_2B , and the Q -nuclear A_pB_Q , where Q is constant but p may assume several values.

The law of mass action then gives:

$[\text{AB}] = \beta_1 ab$; $[\text{A}_2\text{B}] = \beta_2 a^2 b$; $[\text{A}_p\text{B}_Q] = \beta_p a^p b^Q$; and introducing the functions

$$f_1 = 1 + \beta_1 a + \beta_2 a^2 \quad (3a) ; \quad f_1 Z_1 = \beta_1 a + 2\beta_2 a^2 \quad (3b) \quad (3)$$

$$f_Q = \sum \beta_p a^p \quad (4a) ; \quad f_Q Z_Q = Q^{-1} \sum p \beta_p a^p \quad (4b) \quad (4)$$

we find for the total concentration of B and the total amount of A bound to B per liter:

$$B = b f_1 + b^Q Q f_Q \quad (5a)$$

$$BZ = b f_1 Z_1 + b^Q Q f_Q Z_Q \quad (5b)$$

We notice that Z_Q is the average number of A bound per B in the Q -nuclear complexes. If these are regarded separately, Z_Q , like Z_1 is a function of a only and independent of B .

We may combine (5a) and (5b) to get

$$Z = Z_1 + b^Q Q f_Q (Z_Q - Z_1) (b f_1 + b^Q Q f_Q)^{-1} \quad (6)$$

If a is constant, f_1 , f_Q , Z_1 and Z_Q are constant; if B is small, $b \sim B f_1^{-1} \sim B$. constant. Thus, for small B 's and constant a we find

$$Z \sim Z_1 + \text{constant } B^{Q-1} \quad (7)$$

Thus one may assume a certain value for Q , and extrapolate a series of plots $Z(B^{Q-1})_a$ to $B = 0$; the intercepts may be used to construct the $Z_1(\log a)$ curve. In Fig 3, the "mononuclear" curve $Z_1(\log a)$ so obtained is plotted for $Q = 2, 3, 4$, and 5. As one extreme, the curve for the lowest B -value used is also given ($B = 0.0025$ m). The equilibrium constants, β_1 and β_2 , may be obtained from these curves by the fitting of normalized curves⁵. The following values were obtained (the limits of error indicate the region which might have given an acceptable fit):

	2.5 mM	$Q = 2$	$Q = 3$	$Q = 4$	$Q = 5$	average value
$\log \beta_1$	4.28	(4.30)	4.29	4.29	4.29	4.29 ± 0.05
$\log \beta_2$	5.22	(5.34)	5.26	5.24	5.23	5.24 ± 0.15
$\log K_2$	0.94	(1.04)	0.97	0.95	0.94	0.95 ± 0.15

As seen from Fig. 3 a better fit is obtained with $Q=4$ than with $Q=2$ or 3.

POLYNUCLEAR SPECIES

Now that the formulas and equilibrium constants of formation for the mononuclear species were settled, it would have been desirable to apply some general method, such as the integration method used for the borates², that would give the average p and q of the polynuclear complexes. Unfortunately, just as in Part III¹, the range of the data is too narrow to allow this method to be applied.

In order to get some information on the formulas of the polynuclear species, an investigation was made to see to what extent the present data could be explained by each of the following three simple assumptions, namely that in addition to the mononuclear species, B, AB, and A_2B , the only species which need be considered are a) a single polynuclear species A_pB_Q , b) a series of complexes A_pB_Q , with p varying but Q constant, and c) a series of uncharged complexes B_q , with q variable.

The assumption c) would mean that all that is formed is a series of polysilicic acids, an idea which has sometimes been suggested; we shall see that it certainly cannot explain the data.

Assumption a) is, of course, a special case of assumption b). The idea that a single value, Q , would predominate is not quite unreasonable, considering that in several hydrolysis systems studied in this Institute (vanadium(V), Rossotti⁶; molybdate, Sasaki⁷; bismuth, Olin⁸) the data quite clearly indicate that in one range the predominating species are a series of complexes with the same number of simple atoms (same Q) but different charges. (In other cases, however, a number of complexes of varying q values have been indicated).

Single polynuclear species, A_pB_Q

Approach with normalized curves. Assuming the species B, AB, A_2B and A_pB_Q , we find from the law of mass action and the definitions of B and BZ :

$$[A_P B_Q] = \beta_{PQ} a^P b^Q \quad (8)$$

$$B = b + \beta_1 ab + \beta_2 a^2 b + Q\beta_{PQ} a^P b^Q \quad (9)$$

$$BZ = \beta_1 ab + 2\beta_2 a^2 b + P\beta_{PQ} a^P b^Q \quad (10)$$

These expressions contain three "unknown" equilibrium constants, two of which (β_1 and β_2) are, however, approximately known. Fixing the ratio

$$l = \beta_2 \beta_1^{-2} = 10^{-3.34}$$

at the best value obtained earlier, the two remaining unknowns may be obtained using normalized projection maps (Sillén⁹) obtained by transforming (9) and (10) to the normalized form

$$B = v + uv + lu^2v + Qu^Pv^Q \quad (11)$$

$$BZ = uv + 2lu^2v + Pu^Pv^Q \quad (12)$$

where the normalized variables are

$$u = \beta_1 a \quad (13a); \quad v = b(\beta_1^P \beta_{PQ}^{-1})^{1/1-Q} \quad (13b); \quad B = B(\beta_1^P \beta_{PQ}^{-1})^{1/1-Q} \quad (13c)$$

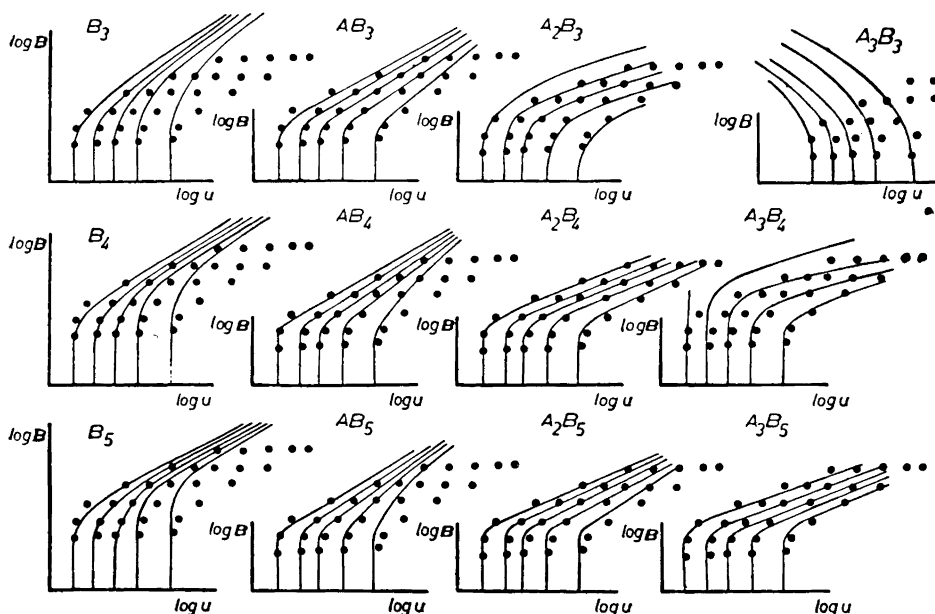


Fig. 4. Projection maps, $B(\log u)z$, calculated assuming the single complex $A_P B_Q$, and various values for P and Q . The experimental data $\log B$ ($\log [\text{OH}^-])z$ are in the position of best fit with the calculated projection maps. The experimental points are given for $B = 0.0025, 0.005, 0.010, 0.020, 0.040$ and 0.080 molal at constant Z . The Z values are from left to right 0.75, 0.80, 0.85, 0.90 and 0.95.

Eliminating v from (11), and (12) we obtain

$$\begin{aligned} (Q-1) \log B &= \log [Z(1 + u + lu^2) - (u + 2lu^2)] + \\ (Q-1) \log [P + (P-Q)u + lu^2(P-2Q)] - P \log u - Q \log (P - QZ) \end{aligned} \quad (14)$$

Using eqn. (14) and the value $l = 10^{-3.34}$ obtained earlier, normalized curves $\log B(\log u)_Z$ have been calculated for a number of sets (P, Q) and moved across the experimental data $\log B(\log [\text{OH}^-])_Z$. Fig. 4 shows the calculated projection maps compared with the experimental data in the position of the best fit, or at least in a position where it is seen that no good fit at all can be obtained. Note that the calculated $\log B(\log u)_Z$ is vertical for $Z = P/Q$, ($Z = 0.75$ for A_3B_4), and bends to the left for $Z < P/Q$ (all curves for A_3B_3).

The best over-all fit is no doubt obtained with A_2B_4 ; small deviations at $Z = 0.90$ and $Z = 0.95$ indicate that other polynuclear species may also occur. With A_2B_3 a reasonable fit is obtained for $Z = 0.90$ and 0.95 , and with A_2B_5 for $Z = 0.75$ and partly, for $Z = 0.80$; however, neither of these complexes alone would give an acceptable fit for the other end of the diagram. Observing how changes in P and Q affect the slope $(\Delta \log B / \Delta \log u)_Z$ and the spacing $(\Delta \log u / \Delta Z)_B$, it is easily seen that no complex outside the range of the (P, Q) sets given in Fig. 4 will be able to give a reasonable agreement with the experimental data.

Our conclusion is thus, just as in Part III¹, that the only single complex which might explain the data in this range is A_2B_4 . Assuming this complex, we obtained from $\log B - \log B$, and $\log u - \log [\text{OH}^-]$ in the position of best fit, using eqns. (13a) and (13c)

$$\log \beta_1 = 4.29 \pm 0.05; \log \beta_{24} = 15.03 \pm 0.20, \log \beta_2 = 5.24 \pm 0.15.$$

The latter comes from the assumed value for l .

Sections at log a = constant. Another approach used the fact that Z_1 and f_1 , defined in (3), are functions of a only, and moreover are known approximately. We may write (9) and (10) in the form

$$B = bf_1 + Q\beta_{PQ}a^Pb^Q; BZ = bf_1Z_1 + P\beta_{PQ}a^Pb^Q \quad (15)$$

which gives by combination

$$B(Z_1 - Z) = Q(Z_1 - PQ^{-1})\beta_{PQ}a^Pb^Q \quad (16)$$

$$b = Bf_1^{-1}(Z - PQ^{-1})(Z_1 - PQ^{-1})^{-1} \quad (17)$$

Eliminating b we find

$$B^{Q-1}(Z - PQ^{-1})^Q(Z_1 - Z)^{-1} = f_1^Q Q^{-1} \beta_{PQ}^{-1} a^{-P}(Z_1 - PQ^{-1})^{Q-1} = \text{function of } a$$

Thus at constant a we would have

$$Q \log (B(Z - PQ^{-1})) = \log [B(Z_1 - Z)] + \text{constant} \quad (18)$$

Plots of $\log (B(Z - PQ^{-1}))$ against $\log [B(Z_1 - Z)]$ were made assuming $PQ^{-1} = 0.00, 0.25, 0.33, 0.50, \text{ and } 0.67$. These plots are given in Fig. 5, except that for $PQ^{-1} = 0.33$.

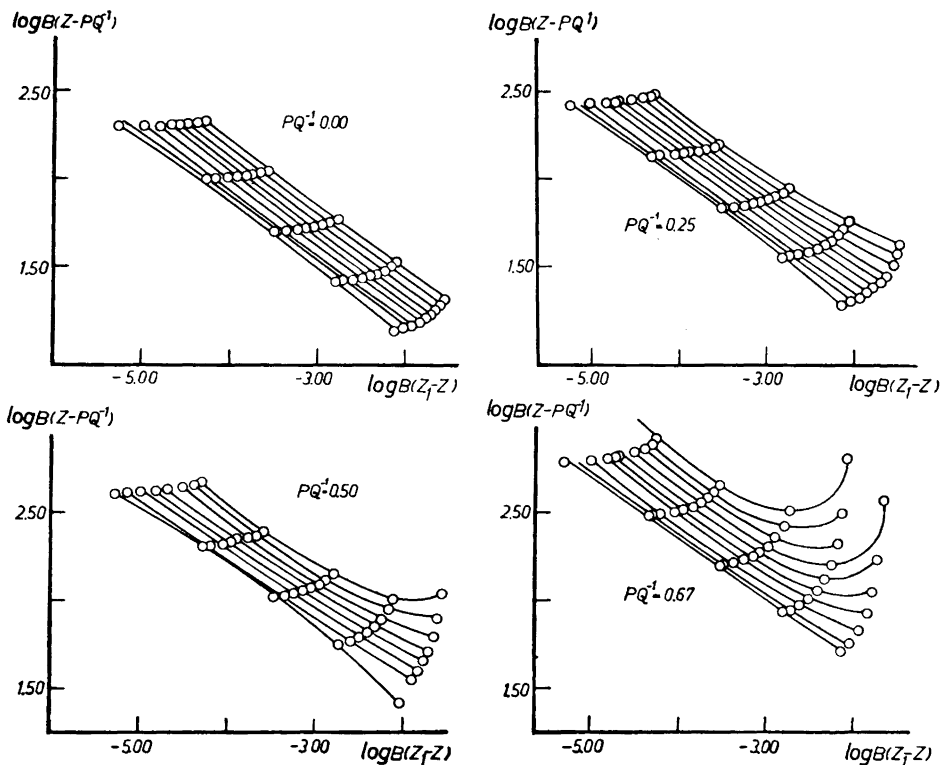


Fig. 5. Plots of $\log(B(Z-PQ^{-1}))$ versus $\log(B(Z_1-Z))$ assuming a single complex with various values of PQ^{-1} (compare eqn (18)). The experimental data are given for $-\log [\text{OH}^-] = 2.40, 2.50, 2.60, 2.70, 2.80, 2.90, 3.00, 3.10$ and 3.20 . For $PQ^{-1} = 0.25$ and 0.67 values for $-\log [\text{OH}^-] = 3.30$ are also given and for $PQ^{-1} = 0.5$, $-\log [\text{OH}^-] = 2.30$. For $PQ^{-1} = 0.50$ the values for $-\log [\text{OH}^-] = 3.10$ and 3.20 have not been calculated.

The complex A_2B_4 would correspond to $PQ^{-1} = 0.50$, and a slope of $Q^{-1} = 0.25$ in the diagrams. As a matter of fact, reasonably straight lines are obtained for all PQ^{-1} lower than 0.67 , and the slope of the lines is somewhere between $1/3$ and $1/4$. This type of plot is less conclusive than the normalized curves, since it pays no attention to the information contained in the distances between the lines. At any rate, it indicates that if any complex predominates, it is a rather small one, with 3 or 4 Si, and with an average charge of less than -1 per Si.

Series of homonuclear complexes A_pB_Q

We have introduced the quantities f_1 , Z_1 , f_Q , and Z_Q , referring to the mono- and Q -nuclear complexes separately, in connection with the extrapolation method (3), (4). They are all functions of a only. Using them, as before, (9) and (10) take the form

$$B = bf_1 + Qb^0f_Q \text{ (19a)}; BZ = Z_1bf_1 + Z_QQb^0f_Q \text{ (19b) which give} \quad (19)$$

$$b = B(Z - Z_Q)(Z_1 - Z_Q)^{-1}f_1^{-1} \quad (20)$$

Using (19b) and (20) to eliminate b we obtain

$$-Q \log(Z - Z_Q) + \log(Z_1 - Z) + (Q - 1) \log(Z_1 - Z_Q) = \log Q + \log f_Q f_1^{-Q} + (Q - 1) \log B \quad (21)$$

We may normalize (21) to the form

$$\log B = (Q - 1)^{-1} \log Z - Q(Q - 1)^{-1} \log(1 - Z) \quad (22)$$

with the normalized variables

$$\log B = \log B + (Q - 1)^{-1} \log Q + (Q - 1)^{-1} \log f_Q f_1^{-Q} \quad (23)$$

$$\log Z = \log(Z_1 - Z) - \log(Z_1 - Z_Q) \quad (24)$$

If a is constant, Z_1 , Z_Q , f_1 and f_Q should keep constant, so that $\log B = \log B + \text{constant}$, $\log Z = \log(Z_1 - Z) + \text{constant}$. For a series of a values experimental curves $\log B(\log(Z_1 - Z))$ were plotted and compared with normalized curves $\log B(\log Z)$, calculated for various values for Q . As shown in Fig. 6, a satisfactory fit could be obtained for $Q = 3$ and 4 (except for $B = 10.00$ mm). For $Q = 2$ and > 4 , the fit was always poor. For $B \leq 0.010$ m, the curves came too close to the mononuclear one, and the spread in $\log(Z_1 - Z)$ made it hard to use (23) and (24). As seen from (23) and (24) the difference $\log B - \log B$, and $\log Z - \log Z$ might be used, for each value of a , to calculate f_Q and Z_Q ; in this special case, the accuracy did not permit this to be used as an independent method for determining the several equilibrium constants β_{pQ} ; in some other systems it might perhaps prove useful. At any rate, these calculations, like the previous ones, indicate a fairly small complex, with 3 or 4 Si atoms.

Series of uncharged complexes, B_q

If the only species present are A, AB, A_2B , and a series B_q , we would have

$$B = f_1b + \Sigma q\beta_{oq}b^q; BZ = f_1Z_1b \quad (25)$$

$$\text{Thus } b = BZf_1^{-1}Z_1^{-1} \quad (26)$$

For each experimental point, BZ , $f_1(a)$, and $Z_1(a)$ are known, so that b can be calculated. A plot $b(B)_a$ was constructed and used for calculating, for a series of round b -values, the function $B - bf_1(a)$.

If the hypothesis were correct, $B - bf_1$ would be $= \Sigma q\beta_{oq}b^q$, and a function of b only. In practice it is found to vary greatly with a , for constant b . Thus it may be concluded that the data cannot be explained assuming the uncharged complexes, B_q , as the only polynuclear complexes.

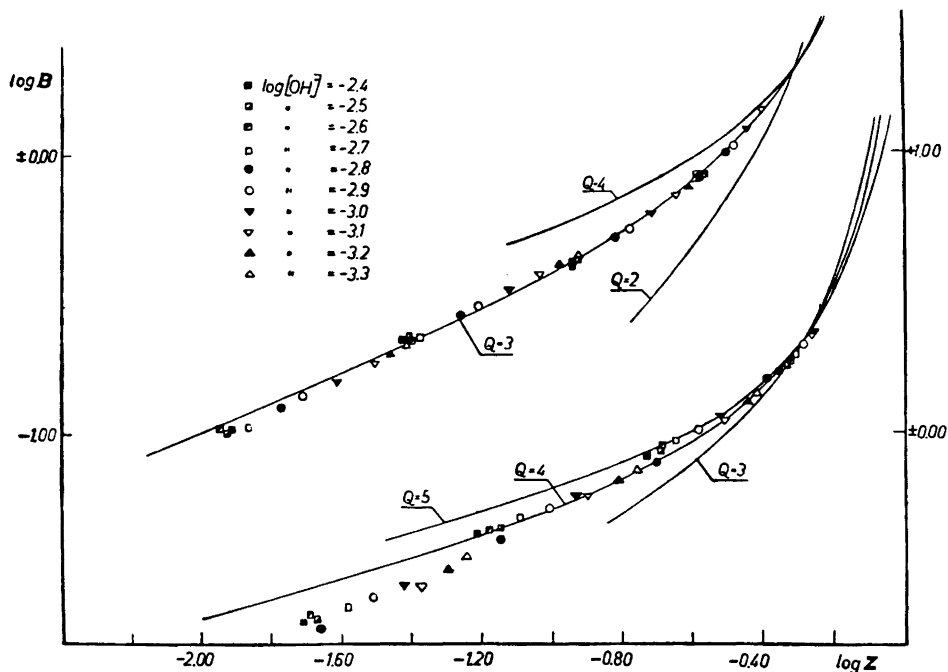


Fig. 6. Series of complexes $A_p B_q$. The experimental data $\log B(\log(Z_1 - Z))_a$ are compared with normalized curves, $\log B(\log Z)_a$, calculated from (22). In the upper left part of the figure the experimental data are compared with the calculated curve for $Q = 3$ and in the lower right part for $Q = 4$. For comparison, calculated curves for $Q = 2$ and 5 are also given.

CONCLUSIONS

Thus the present data for silicate equilibria in 0.5 NaCl medium, for Z between 0.7 and 1.0, have again given evidence for the existence of the three mononuclear species B, AB, and A_2B , and have given equilibrium constants for their formation. For the polynuclear species, no final and complete picture can be drawn. It is concluded, as in Lagerström's work, that the equilibria with polynuclear species are rapidly obtained, as long as all parts of the solution are kept out of the "instability range". It is also concluded that most or all of the polynuclear ions present are fairly small, with only 3 or 4 Si-atoms. The only single complex that can give a satisfactory agreement with the data is A_2B_4 , the same complex as was indicated by Lagerström¹ in NaClO_4 medium.

The equilibrium constants are given in Table 2, and the agreement obtained may be studied in Fig. 2.

It seems reasonable to assume, as a working hypothesis, that A_2B_4 is the most important polynuclear silicate ion in the range studied. The small deviations observed indicate that other polysilicate ions, such as $A_p B_3$ or $A_p B_4$, are present; the data allow no definite conclusion on their formula

Table 2. Equilibrium constants for silicate reactions at 25°C, 0.5 m Na(Cl) medium, deduced from present data. For comparison, Lagerström's data¹ for 25°C and 0.5 m Na(ClO₄) medium are given.

	0.5 m Na(Cl)	0.5 m Na(ClO ₄)
$H_2O \rightleftharpoons H^+ + OH^-$	$\log K_w = -13.70 \pm 0.02$	-13.73
$A + B \rightleftharpoons AB; OH^- + Si(OH)_4 \rightleftharpoons SiO(OH)_3^- + H_2O$	$\log \beta_1 = 4.29 \pm 0.05$	4.27
$2A + B \rightleftharpoons A_2B; 2OH^- + Si(OH)_4 \rightleftharpoons SiO_2(OH)_2^{2-} + 2H_2O$	$\log \beta_2 = 5.28 \pm 0.15$	5.44
$A + AB \rightleftharpoons A_2B; OH^- + SiO(OH)_3^- \rightleftharpoons SiO_2(OH)_2^{2-} + H_2O$	$\log K_2 = 0.99 \pm 0.15$	1.17
$2A + 4B \rightleftharpoons A_2B_4; 2OH^- + 4Si(OH)_4 \rightleftharpoons Si_4O_8(OH)_6^{2-} + 6H_2O$	$\log \beta_{24} = 15.03 \pm 0.20$	14.89
$A + B \rightleftharpoons AB; Si(OH)_4 \rightleftharpoons SiO(OH)_3^- + H^+$	$\log * \beta_1 = -9.51 \pm 0.05$	-9.46
$2A + B \rightleftharpoons A_2B; Si(OH)_4 \rightleftharpoons SiO_2(OH)_2^{2-} + 2H^+$	$\log * \beta_2 = -22.12 \pm 0.15$	-22.02
$A + AB \rightleftharpoons A_2B; SiO(OH)_3^- \rightleftharpoons SiO_2(OH)_2^{2-} + H^+$	$\log * K_2 = -12.74 \pm 0.15$	-12.56
$2A + 4B \rightleftharpoons A_2B_4; 4Si(OH)_4 \rightleftharpoons Si_4O_8(OH)_6^{2-} + 2H^+ + 4H_2O$	$\log * \beta_{24} = -12.37 \pm 0.20$	-12.57

although, of course, an improved agreement probably would be obtained by assuming one or two more complexes, with suitable formation constants.

It seems most desirable to extend the studies of silicate to other media, and also to apply other experimental methods. Work in these directions has been started.

POSSIBLE STRUCTURES FOR SILICATE IONS

Some thought should perhaps be given to the question of what the structures of the silicate ions in solution may be, especially since rather divergent opinions have recently appeared in literature. A short review of the pertinent evidence will be given.

Principles of silicate structures. Beginning with the classical work of the Braggs, the crystal structures have been worked out for a very large number of natural and artificial silicates. They have proved to be built up according to a few simple principles, which are very different from those one might have guessed in the pre-X-ray period of chemistry. This subject has been treated very well in a number of standard text books¹⁰⁻¹².

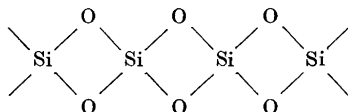
Rule 1: Each Si atom is surrounded by a tetrahedron of 4 O-atoms. The exceptions are very few.

A structure with octahedral coordination Si-6 O has been suggested in SiP₂O₇ (Levi and Peyronel¹³). It is also possible that Si is coordinated to six O's in some organic complexes, such as those with pyrocatechol¹⁴, Si(O₂C₆H₄)₃²⁻, and in a complex with three acetylacetone¹⁵ (CH₃COCH₂COCH₃ = HA) acting like a positive ion, SiA₃⁺, and forming salts like SiA₃AuCl₄, SiA₃FeCl₄, and (SiA₃)₂PtCl₆, soluble in ethanol and acetic acid. A very clear case of 6-coordination around Si is the hexafluorosilicate ion, SiF₆²⁻, which is octahedral¹⁶.

Although carbon is 3-coordinated in a number of compounds (C_2H_4 , CO_3^{2-} , $COCl_2$ etc), no case has been observed with Si coordinated with three O in a crystal structure.

Rule 2: Two SiO_4 -tetrahedra can be joined by sharing an oxygen corner. The tetrahedra do not share edges, neither is an oxygen atom shared between more than two Si-atoms.

The only known case of sharing edges seems to be the fibrous form of SiO_2 described by Weiss and Weiss¹⁷. It seems to have a crystal structure of the same type as SiS_2 (Zintl and Loosen¹⁸), the SiO_4 -tetrahedra forming infinite chains by sharing opposite edges with their neighbors:



We shall disregard these few exceptions and consider instead the overwhelming number of normal structures. In accordance with the two principles given, the SiO_4 -tetrahedra can join to form isolated groups, chains (sometimes double chains), sheets and three-dimensional networks. As to detailed descriptions of the structures and references, the reader is referred to the standard texts (e.g. Wells¹², p. 569—591).

Anhydrous silicates

Separate SiO_4^{4-} groups are found in a number of minerals and artificial silicates, e.g. Mg_2SiO_4 . Separate groups, $Si_2O_7^{6-}$, $O_3SiOSiO_3$, are less common, but are found in a few minerals (thortveitite $Sc_2Si_2O_7$; hemimorphite $Zn_4(OH)_2Si_2O_7$; tilleyite¹⁹). Three-silicon rings, $Si_3O_9^{6-}$, have been reported in the crystal structures of α - and β -wollastonite, $CaSiO_3$, of benitoite, $BaTiSi_3O_9$ and catapleite. Some doubt has been cast upon these rings as Dornberger-Schiff, Liebau and Thilo²⁰ have reinvestigated the structure of β -wollastonite and found it to contain infinite chains, $(SiO_3)_n$, and not separate rings, $(SiO_3)_3$.

Four-silicon rings, $Si_4O_{12}^{8-}$, seem to exist as independent units in the crystal structure of axinite²¹, $Ca_2(Fe, Mn)Al_2(BO_3)(Si_4O_{12})OH$. In the sheet structure of apophyllite, alternate four- and eight-silicon rings occur.

Separate six-silicon rings, $Si_6O_{18}^{12-}$, have been found in beryl, $Be_3Al_2Si_6O_{18}$, and in tourmaline²². In the sheet structures of clays, minerals and micas, six-silicon rings are joined to form infinite sheets.

Silicates containing hydrogen

Although a large number of crystalline hydrated silicates are known (see, e.g., Vail²³, p. 144—150), very few crystal structures have hitherto been determined. The existence of tetrahedral groups, $HSiO_3^{3-}$, in afwillite²⁴, $(Ca_3(SiO_3OH)_2(H_2O)_2)$ and in $Ca_2(SiO_3OH)OH$ (Heller²⁵) seems fairly certain. Thilo and coworkers²⁶ have concluded from reaction studies that some hydra-

ted Ca and Ca-Na silicates contain $\text{H}_2\text{SiO}_4^{2-}$, and HSiO_3^- groups, and that crystalline NaH_3SiO_4 contains H_3SiO_4^- groups²⁷. Also the latter result was corroborated by the great similarity between the X-ray powder photographs of NaH_3SiO_4 and LiH_2PO_4 .

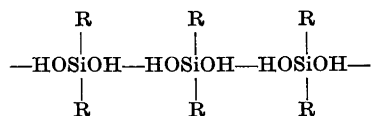
According to a private communication by Machatschki and Preisinger²⁸ the crystal structure for "sodium metasilicate enneahydrate", really $\text{Na}_2(\text{H}_2\text{SiO}_4)(\text{H}_2\text{O})_8$, has been investigated. It contains isolated $\text{H}_2\text{SiO}_4^{2-}$ groups, and no condensed silicate ions, in contrast to anhydrous Na_2SiO_3 which contains chains, $(\text{SiO}_3)_n$, (Grund and Pizy²⁹). According to Heide *et al.*³⁰, diopside, $\text{Cu}_6\text{Si}_6\text{O}_{18}(\text{H}_2\text{O})_8$ contains isolated Si_6O_{18} -rings and H_2O molecules.

Organic Si-O compounds

There are two main series of organic Si compounds, namely silicones and polysilicic acid esters, both of which contain an Si-O skeleton, with R or RO (R = hydrocarbon radical) attached to the remaining corners of the Si tetrahedra.

Silicones are known with straight Si-O chains (2 to 11 Si), with Si-O rings, and also with two rings having one Si atom in common (spiro structures). Rings $(\text{R}_2\text{SiO})_n$ with n between 3 and 8 have been prepared and isolated. The 4- and 5-rings seem to be the most stable (Wells¹², p. 562—566). Ring structures $(\text{SiO})_8$ and $(\text{SiO})_4$ have been proved by X-ray studies^{31,32} on $((\text{CH}_3)_2\text{SiO})_8$ and $((\text{CH}_3)_2\text{SiO})_4$. For *polysilicic acid esters*, no structure determination seems to have been made as yet. The compounds $((\text{RO})_2\text{SiO})_n$ with $n = 3$ or 4 are in all probability ring-shaped (Signer and Gross³³; R = C_6H_{11} , *cyclohexyl*). Iler³⁴ claims to have prepared even larger polysilicate ester rings with up to 8 Si (R = C_4H_9). There are also esters known with a lower proportion of R, say $(\text{ROSiO}_{1.5})_n$, which may contain a dense Si-O core (several condensed rings), surrounded by R groups (Iler³⁵, p. 77—78, n around 10 or 12; Sprung and Guenther³⁶, $n = 6$ and 8).

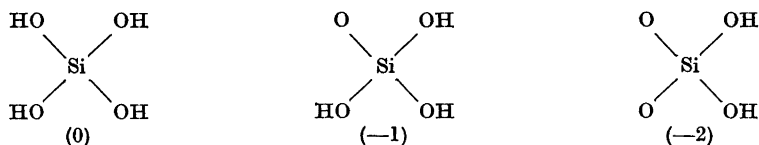
It may be of interest that the methyl and ethyl silanols, R_3SiOH , are, like alcohols, strongly associated in the liquid state and in *cyclohexane* solution (Grubb and Osthoff³⁷). In ROH solutions, R_3SiOH reacts with the ultimate formation of an equilibrium mixture of $\text{R}_3\text{SiOSiR}_3$, R_3SiOR , and H_2O (Grubb³⁸). In crystals, molecules of $\text{R}_2\text{Si}(\text{OH})_2$ form chains by means of hydrogen bonds (Kakudo and Watase³⁹, Kasai and Kakudo⁴⁰).



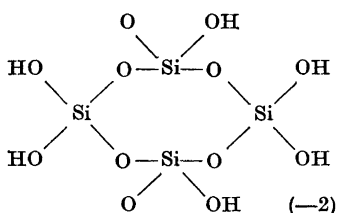
Structures in solutions

It seems plausible that the silicate ions which occur in aqueous solutions are built up on the same principles as have been found in practically all crystalline silicates, namely as SiO_4 -tetrahedra, isolated or sharing O atoms, and with

a certain number of protons attached to the unshared O atoms, forming OH groups. The structures of the mononuclear silicate ions would then be,



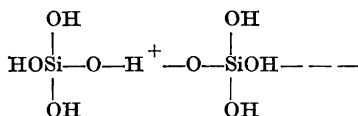
The present data indicate that complexes with a certain number of Si atoms, namely 4, predominate in the solutions. It seems likely that they contain a ring, so that the structure of A_2B_4 would be



If the polysilicate ions had been chain-like, it is hard to understand why, for instance, 4 should be preferred to 2 or 3. One might suggest a still more condensed, tetrahedral structure, $\text{Si}_4\text{O}_{10}\text{H}_2^-$, like P_4O_{10} , however this group has not been found in crystal structures.

Two other hypotheses have been proposed and as far as we can find, are based on insufficient evidence.

Miedreich⁴¹ (p. 14) finds it "very improbable" that Si-O-Si bonds are formed in aqueous solutions, since the equilibria are reached so rapidly in clear solutions. He prefers to think (p. 89) that the polysilicate ions are formed by hydrogen bridging



The argument might seem plausible if one makes a comparison only with the polyphosphates; the P-O-P bonds are certainly hydrolyzed only slowly. On the other hand, the formation of O bonds in aqueous solution is a rapidly reversible process for several neighbors of Si in the periodic table. For instance, the polyborate ions undoubtedly contain B-O-B bonds and still give very rapid equilibria². The same is true with the Be-OH-Be bonds formed in the hydrolysis of Be^{2+} , and with quite a number of other O or OH bonds met with in the hydrolysis of positive ions (Kakihana and Sillén⁴², Sillén⁴³).

With Miedreich's hypothesis it also seems hard to explain the composition of the "X-ray amorphous" precipitates found by Thilo, Wodtke and Funk⁴⁴ on adding Ag^+ to silicate solutions. The general formula, according to them, is $\text{Ag}_{n+2}\text{H}_n\text{Si}_n\text{O}_{3n+1}$, with preference for $n = 1, 2, \text{ or } 4$, whereas Miedreich's

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Received January 13, 1959.