

## Equilibrium Studies of Polyanions

### III. Silicate Ions in NaClO<sub>4</sub> Medium

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Equilibria in silicate solutions have been studied in 0.5 m (molal) Na(ClO<sub>4</sub>) medium at 25°C and 50°C, and in 3 m Na(ClO<sub>4</sub>) medium at 25°C, using emf's with a hydrogen electrode, at a series of total Si concentrations,  $B$ . The data are given in the form of curves  $Z(\log h)_B$ , or  $Z(\log [\text{OH}^-])_B$ , where  $Z$  is the average number of OH<sup>-</sup> bound per Si(OH)<sub>4</sub> in the solution, thus the average negative charge per Si. The data for 0.5 m medium,  $Z = 0.70$  to 1.0, could be explained in terms of the species Si(OH)<sub>4</sub>, SiO(OH)<sub>3</sub><sup>-</sup>, SiO<sub>2</sub>(OH)<sub>2</sub><sup>2-</sup>, and Si<sub>2</sub>O<sub>5</sub>(OH)<sub>3</sub><sup>2-</sup>. The data in 3 m medium,  $Z = 0.8$  to 1.6, could be explained assuming equilibria between the three mononuclear species mentioned, and in addition Si<sub>2</sub>O<sub>5</sub>(OH)<sub>3</sub><sup>2-</sup> and Si<sub>4</sub>O<sub>9</sub>(OH)<sub>4</sub><sup>4-</sup>. The equilibrium constants arrived at are given in Table 5; they are not considered as final. Equilibria are rapidly obtained, and the solutions are clear, as long as no part of the solution is allowed to pass, even momentarily, into the "instability range", an area in the ( $B$ ,  $\log h$ ) field, where a colloid precipitates. This may have been one source of error in older work.

Although silicate solutions are being used extensively for various purposes, very little is known with certainty about the formulas of the silicon-containing species. This is borne out by the survey of previous work in the following which, however, is by no means a complete historical review; for such, the reader is referred to monographs by Iler<sup>1</sup> and Vail<sup>2</sup>.

The aim of the present work has been to study equilibria in silicate solutions by experimental and mathematical methods worked out in this laboratory, thus to measure data over as wide a range of concentrations as possible, and to deduce the formulas of the species present and the equilibrium constants involved.

As in the previous work on borate equilibria (Part II<sup>3</sup>), no electrode could be found which responds to the free anion concentration. On the other hand, the concentrations of H<sup>+</sup> (and OH<sup>-</sup>) could be measured accurately using a hydrogen electrode. As previously, they were recalculated to the form  $Z(\log h)_B$ , and these curves (Figs 2, 3, and 4) were the basis of the calculations.

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An initial difficulty was the existence of an "instability range" of the solutions, which was eventually found out and will be discussed below.

The present work, which was, like the following Part IV, generously supported by Columbia-Southern Chemical Corporation, was already completed in 1955, though the publication has been delayed for external reasons.

### SYMBOLS

The symbols are in general the same as in Part II<sup>3</sup>. Thus,  $B$  is the total concentration of Si in the solution,  $b$  the free concentration,  $[\text{Si}(\text{OH})_4]$ ,  $h$  the concentration of free  $\text{H}^+$ ,  $H$  the analytical excess of  $\text{H}^+$  over  $\text{H}_2\text{O}$  and  $\text{Si}(\text{OH})_4$  ( $H$  was negative in most of our experiments), and  $Z$  is the average number of  $\text{OH}^-$  bound per  $\text{Si}(\text{OH})_4$ , thus the average charge per Si.

The silicate species, or complexes, will (in analogy with other work from this laboratory<sup>3,4</sup>) be written as  $A_pB_q$  where A stands for a proton deficiency, ( $-\text{H}^+$ ), or  $\text{OH}^-$ , and B for  $\text{Si}(\text{OH})_4$ . Equilibrium measurements like the present ones cannot distinguish between species with various contents of water, and only indicate the charge,  $p-$ , and the number of Si atoms,  $q$ . For instance,  $A_2B_4$  stands for a complex with 4 Si atoms and the charge  $-2$ . It might have been written as  $\text{Si}_4\text{O}_8^{2-}$ , but this is certainly not correct. In the final formulas of Table 5, it is written as  $\text{Si}_4\text{O}_6(\text{OH})_6^{2-}$  which seems plausible from what is known of the structural chemistry of silicates. However, it is only the charge and the number of Si which can be concluded from the equilibrium data.

To conform with the notations in the IUPAC Tables of Stability constants<sup>5</sup> the formation constants for the complexes will be denoted as  $\beta_{pq}$  when they are formed from  $\text{Si}(\text{OH})_4$  and  $\text{OH}^-$ , and with  $^*\beta_{pq}$  when they are written with  $\text{Si}(\text{OH})_4$  and  $\text{H}^+$  as reactants (see Table 5).

The composition of silicate solutions has often been expressed by  $r$ , the "ratio"  $\text{SiO}_2/\text{Na}_2\text{O}$ , in moles (or grams, which is practically the same). To transform  $r$  to the quantity  $Z$ , which is more practical for equilibrium calculations, we may use the relations

$$\begin{aligned} BZ &= h - H - [\text{OH}^-] = h - H - K_w h^{-1} \\ H &= -2B/r \end{aligned} \quad (1)$$

In solutions with silicate anions,  $h$  is always negligible in comparison with  $BZ$ , and so is  $[\text{OH}^-]$ , at least for  $Z \leq 1$ . Then we have simply  $Z = 2/r$ .

### EXPERIMENTAL

#### Reagents

*Sodium perchlorate*, *perchloric acid*, and *silver perchlorate* were prepared and analysed as described in Part II<sup>3</sup>.

From p.a. *sodium hydroxide*, a 50 % solution was prepared and filtered through a G4 Jena glass filter. Dilute solutions were prepared from this stock solution and deaerated water. The solutions were kept in polythene bottles which had previously been soaked with warm dilute alkali.

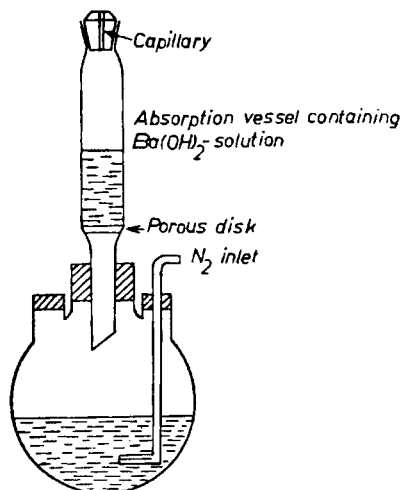


Fig. 1. Apparatus for determining carbonate ions in alkaline solution.<sup>1</sup>

To analyse the 50 % stock solution, a measured quantity of it was transferred to a flask (Fig. 1), filled with nitrogen gas free from  $\text{CO}_2$ . The absorption vessel was filled with 2/3 of its volume of a  $\text{Ba}(\text{OH})_2$  solution. The  $\text{NaOH}$  solution was rapidly acidified with dilute sulfuric acid, and the  $\text{CO}_2$  was driven off by heating and passing a stream of nitrogen. The precipitate of  $\text{BaCO}_3$  was sucked off, washed with 50 % ethanol and dissolved in dilute  $\text{HCl}$ .  $\text{Ba}(\text{IO}_3)_2$  was precipitated, separated, and determined by titration with  $\text{Na}_2\text{S}_2\text{O}_3$  after acidification.

The dilute  $\text{NaOH}$  solutions were analysed as described in Part II<sup>3</sup>. The ratio  $\text{CO}_3^{2-}/\text{OH}^-$  was always less than 0.001.

A silicic acid sol was prepared by recrystallizing "sodium metasilicate",  $\text{Na}_2\text{H}_2\text{SiO}_4 \cdot (\text{H}_2\text{O})_6$  twice from 5 %  $\text{NaOH}$ , dissolving it in water, and passing the solution through a  $\text{H}^+$ -saturated Dowex-50 ion-exchanger. A weighed sample of the sol was evaporated in a Pt crucible, and the residue ignited for 2 h at  $950^\circ\text{C}$ . The crucible was weighed, treated with  $\text{HF}$  in the usual way, and weighed again. The difference gave the concentration of  $\text{SiO}_2$  in the solution. The sol proved to be extremely pure, with no components other than  $\text{SiO}_2$  and water in measurable amounts.

Sodium silicate solutions were not prepared from solid sodium silicate since this product after storage will be contaminated with carbonate, which cannot then be removed. Instead, silicate solutions were prepared from silicic acid sol,  $\text{NaOH}$  solution or perchloric acid, deaerated water, and  $\text{NaClO}_4$  solution.

In the analysis of the stock solutions, the concentrations were obtained in M (mole/liter), since all additions were made from burets. To recalculate the concentrations to the unit m (mole/kg  $\text{H}_2\text{O}$ ), the water content of each solution was calculated from its concentration in M, and its density. All density determinations and mixing operations were carried out in a room thermostated at  $25^\circ\text{C}$ .

## Apparatus

Since it was feared that glassware would be attacked by the alkaline solutions, a considerable effort was made to use polythene vessels. It was not possible to obtain commercially a polythene vessel of the desired size and shape and so attempts were made to coat a suitable glass vessel with polythene. However, the coating was easily scratched, and, once this was done, the alkaline solution crept in between the glass and the coating, which was a nuisance.

Next, attempts were made with all-polythene apparatus. It proved a difficult task to fit an ordinary polythene bottle with extra air-tight necks. Moreover, polythene is water-repellent; a great number of droplets splashed from the rinsing gas stream etc, and kept sitting on the polythene surface. This caused an error in the composition of the solution, which could be overcome by occasional shaking but this was objectionable for other reasons. An additional disadvantage was that polythene is opaque so that the formation of a colloid or a precipitate in the titration vessel could not be observed.

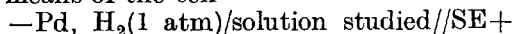
Hence, the use of glass vessels was reconsidered. The dissolution of Si from Jena-Geräte glass was investigated in a series of experiments, in which the conditions (time, volume, stirring, composition of solutions) during the emf titrations was reproduced as carefully as possible. If the Jena-Geräte glass, before the experiment, had been treated first with acid and then with alkali, the maximum concentration of dissolved Si was 0.03 mm ( $3 \times 10^{-5}$  mole/kg  $H_2O$ ). When the glass had first been treated only with alkali, no more than one tenth of this concentration was obtained. For 50°C, the figures are approximately doubled. Considering that the total concentration,  $B$ , of Si added in the experiments is 2.5–80 mm, little objection can be raised to using glass vessels and burets in the study. In order to depress the error in the experiments at 50°C, the buret containing a strongly alkaline solution was kept at 25°C and was only inserted in the vessel very rapidly each time an addition was made.

The titration vessel was made of Jena-Geräte glass, which proved more resistant to alkali than Pyrex. The vessel was of the same type as described in other papers from this institute, and the salt bridge was of the "Wilhelm" type<sup>4</sup>. The hydrogen was purified, the hydrogen and Ag, AgCl electrodes were prepared, and the emf measured as described in Part II<sup>3</sup>.

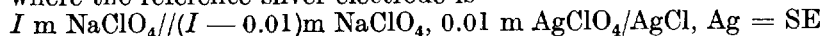
#### TITRATION PROCEDURES

The cell, including the titration vessel, was kept in an oil thermostat at  $25.0 \pm 0.1^\circ C$ , and the whole equipment kept in a room thermostated at 25°C. For the experiments at 50°C, an air thermostat of  $50.0 \pm 0.5^\circ C$  was used.

In the various solutions,  $h$ , or  $(OH^-)$  which is equivalent, was determined by means of the cell



where the reference silver electrode is



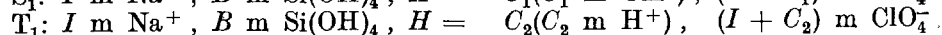
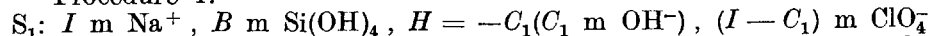
Assuming the activity factors to be constant, the  $E$  may be represented by the equations

$$E = E_{0a} + 59.15 \log [OH^-] + E_j = E_{0a} + 59.15 \log K_w - 59.15 \log h + E_j$$

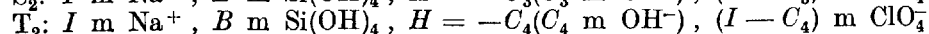
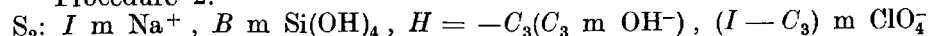
As in Part II<sup>3</sup>, the constant  $E_{0a}$  was determined using solutions of known  $[OH^-]$ ; such measurements also gave the diffusion potential  $E_j = 60[OH^-]$  for  $I = 0.5$ , and  $E_j = 10[OH^-]$  for  $I = 3.0$ . The values obtained for  $K_w$  are given in Table 5.

As ionic medium, 0.5 or 3.0 m  $Na(ClO_4)$  was used ( $I = [Na^+] = 0.5$  or 3.0.) For each titration, two solutions were prepared, S for the titration vessel, and T for the buret, both with the same total silicate concentration,  $B$ . To vary  $Z$  and  $\log h$ , two different procedures were used, both extensively.

Procedure 1:



Procedure 2:



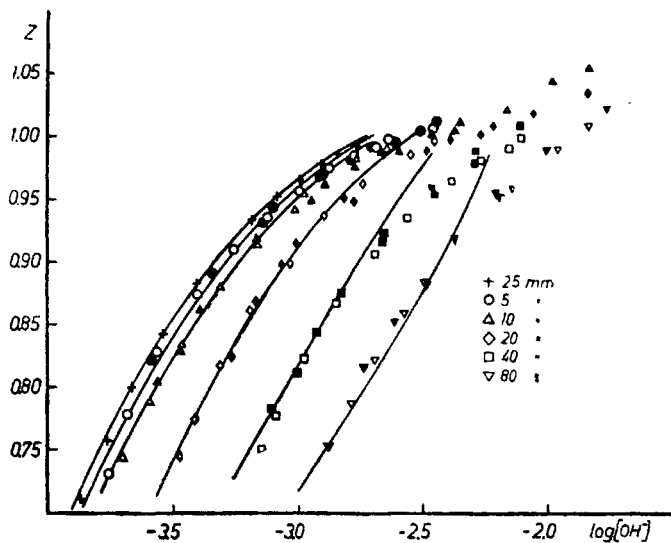


Fig. 2. Silicate equilibria,  $Z(\log [\text{OH}^-])_B$ , 0.5 m  $\text{Na}(\text{ClO}_4)$ , 25°C. Procedure 1, open symbols; procedure 2, filled symbols. Curves calculated with equilibrium constants in Table 3.

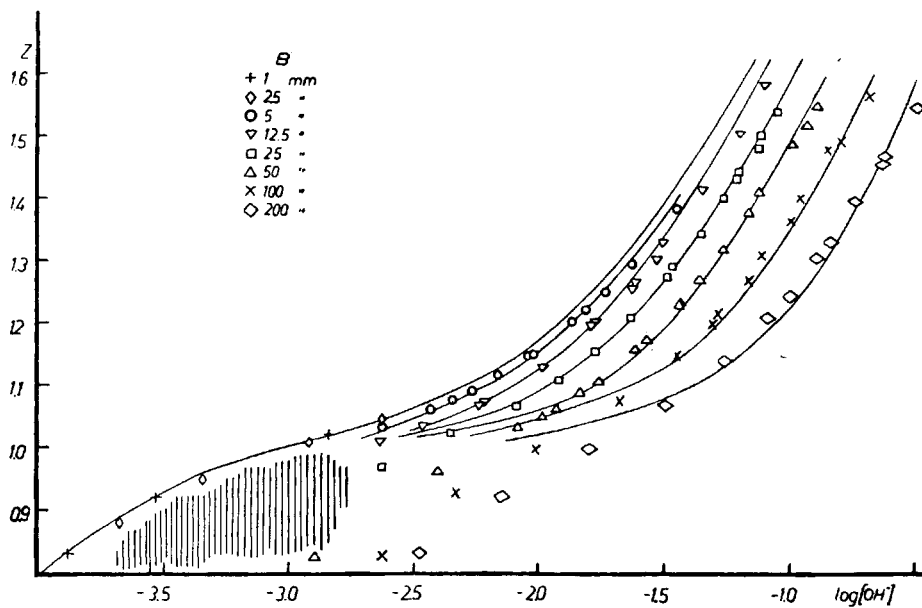


Fig. 3. Silicate equilibria,  $Z(\log [\text{OH}^-])_B$  for 3 m  $\text{Na}(\text{ClO}_4)$ , 25°C. The instability range is shaded. Curves calculated with equilibrium constants in Table 5.

Table 1. Typical titration according to procedure 1.

S: 0.500 m Na<sup>+</sup>, 0.020 m Si(OH)<sub>4</sub>, 0.02595 m OH<sup>-</sup>, 0.474 m ClO<sub>4</sub><sup>-</sup>. Total water content = 59.67 g  
 T (v ml): 0.500 m Na<sup>+</sup>, 0.020 m Si(OH)<sub>4</sub>, 0.01939 m H<sup>+</sup>, 0.500 m ClO<sub>4</sub><sup>-</sup>. 1 ml contains 0.976 g H<sub>2</sub>O

<i>v</i> ml	<i>E</i> mV	log[OH <sup>-</sup> ]	<i>Z</i>
0.00	1 357.00	2.238]	1.008
2.72	1 347.90	2.392]	0.998
5.15	1 337.87	2.5619	0.983
8.11	1 323.40	2.810	0.952
10.43	1 311.63	3.009	0.915
12.76	1 301.61	3.179	0.869
15.14	1 293.73	3.312	0.818
17.54	not stable		

At first, an extensive series of experiments was carried out using procedure 1. They proved to be very time-consuming, since equilibrium was obtained very slowly indeed. At first we thought — like so many previous investigators — that the formation of polysilicate anions is a slow process. It was learned by experience, however, that slow equilibria are only observed when the solution or part of it has been through a region denoted as the "instability range" (shaded in Fig. 3). With procedure 1, for instance, local excess of acid caused a precipitate of colloid, which dissolved only slowly.

With procedure 2, the composition of S<sub>2</sub> is chosen outside of the "instability range", but as close to it as practicable. On addition of an alkaline solution, neither precipitate nor colloid is formed, and equilibrium is established very rapidly. This procedure was preferred in later work. However, with both procedures, true equilibrium states are obtained: in Fig. 2, experiments by procedure 2 (open symbols) and procedure 1 (filled symbols) are seen to give points on the same curves in the  $Z(\log [\text{OH}^-])_B$  diagram, within the experimental error.

Table 1 gives a representative part of a titration with procedure 1. After addition of 15.14 ml of T<sub>1</sub>, the H<sub>2</sub> stream was replaced by N<sub>2</sub>, and the apparatus left over night. Next morning, H<sub>2</sub> was again switched on, and the titration continued. After each addition of acid, *E* (and thus [OH<sup>-</sup>]) decreased, first rapidly, then slowly, and finally reached a constant value. The final *E*-value was obtained more rapidly at the beginning of the titration than in the later part. The direction of the change is expected, if the local excess of acid first forms a precipitate, Si(OH)<sub>4</sub> (with *Z* = 0), or at least one with *Z* less than in the solution, and this then dissolves slowly, consuming OH<sup>-</sup>. Before each new addition, the solution was observed to be clear and free from precipitate.

After addition of 17.54 ml, a new addition of acid caused an initial decrease of *E* (and OH<sup>-</sup>), but then *E* increased again, which would be expected if an increasing amount of precipitate is slowly formed. A visible precipitate remained, and no constant *E* could be obtained.

The titrations at 50°C were very tedious, mainly because of difficulties with thermostating. Only a few series of measurements were made; for a more extensive study, an improved technique would be desirable.

The available range in *B* and *Z* was limited by the instability range, and also by some considerations of experimental accuracy. When the values of *B* or [OH<sup>-</sup>] cease to be negligible in comparison with *I*, variations in the

activity factors may be feared. A closer limit on  $[\text{OH}^-]$  was set by the difficulty of determining  $Z$  accurately at high  $[\text{OH}^-]$ , when  $BZ$  is obtained as the difference between two numbers of comparable magnitude.

The instability range is more pronounced in 3 m  $\text{NaClO}_4$ , which on the other hand permits higher  $Z$  values; thus, the two ionic media allow measurements to be made in different ranges of  $Z$  (cf. Fig. 2—4).

*Some observations in the "instability range".* In Fig. 3, for 3 m  $\text{Na}(\text{ClO}_4)$  medium, the "instability range" is shaded. If a solution corresponding to a point outside this range (say,  $Z = 0.8$ ,  $B = 0.2$ ) was diluted with 3 m  $\text{NaClO}_4$ ,  $Z$  remained practically constant, whereas  $B$  was lowered, and the solution eventually entered the "instability range". The solution might appear absolutely clear for some time but the  $E$  drifted, indicating slow reactions, and no equilibrium could be obtained. On longer standing the solution became turbid, and finally a precipitate formed. The precipitate might appear after a few minutes, or several hours, depending on  $B$  and  $Z$ . The maximum rate seemed to be obtained around  $B = 0.020$  m. If the precipitate was separated from the apparently clear solution, and the latter heated, further precipitation occurred.

The precipitate formed at room temperature was very fluffy and voluminous; on heating it rapidly contracted to a dense, sticky substance, which finally became brittle on boiling.

#### SURVEY OF DATA. CALCULATION OF EQUILIBRIA

The experimental data are given in Tables 2—4, and Figs. 2—4. It is seen that the different ionic media allow different  $Z$ -ranges to be covered. In all cases, the curves  $Z(\log [\text{OH}^-])_B$  are seen to differ for different  $B$  values,

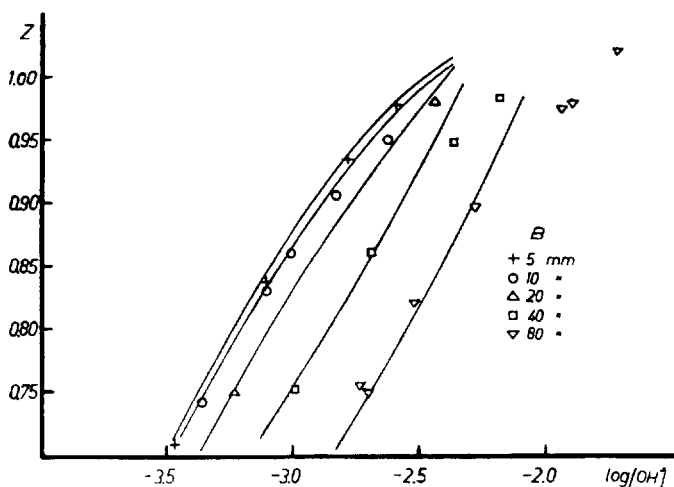


Fig. 4. Silicate equilibria,  $Z(\log [\text{OH}^-])_B$ , 0.5 m  $\text{Na}(\text{ClO}_4)$ , 50°C. Curves calculated with equilibrium constants in Table 5.

Table 2. Experimental data for 25°C and 0.5 m Na(ClO<sub>4</sub>). For each experimental point, Z is given first, and then -log [OH<sup>-</sup>].

$B = 0.0025$  m: Z, -log [OH<sup>-</sup>]; 0.711 3.8719; 0.757 3.7640; 0.800 3.6611; 0.843 3.5406; 0.883 3.4089; 0.910 3.2958; 0.934 3.1832; 0.952 3.0833; 0.966 2.9948; 0.978 2.9074; 0.986 2.8377; 0.992 2.7620 (proc. 2).

$B = 0.005$  m: Z, -log [OH<sup>-</sup>]; 0.822 3.5896; 0.892 3.3470; 0.944 3.1024; 0.968 2.9123; 0.982 2.7764; 0.996 2.6109; 1.006 2.4572 (proc. 1). 0.932 3.1433; 0.970 2.9037; 0.992 2.7061; 1.004 2.5186; 1.012 2.4417 (proc. 1). 0.731 3.7961; 0.779 3.6827; 0.829 3.5632; 0.875 3.4023; 0.910 3.2583; 0.936 3.1246; 0.957 2.9970; 0.973 2.8751; 0.985 2.7733; 0.991 2.6937; 0.998 2.6372 (proc. 2).

$B = 0.010$  m: Z, -log [OH<sup>-</sup>]; 0.743 3.7011; 0.788 3.5952; 0.835 3.4657; 0.881 3.3113; 0.916 3.1646; 0.943 3.0154; 0.962 2.8925; 0.977 2.7733; 0.989 2.6619 (proc. 2). 0.830 3.4735; 0.950 2.9484; 0.988 2.5942; 1.004 2.3700; 1.021 2.1687; 1.044 1.9856; 1.055 1.8420. 0.805 3.5610; 0.863 3.3993; 0.919 3.1748; 0.955 2.9723; 0.982 2.7721; 0.991 2.6425; 1.005 2.4605; 1.011 2.3587 (proc. 1).

$B = 0.020$  m: Z, -log [OH<sup>-</sup>]; 0.746 3.4748; 0.775 3.4173; 0.818 3.3156; 0.862 3.1905; 0.898 3.0668; 0.937 2.8955; 0.962 2.7394; 0.986 2.5460; 0.996 2.4517 (proc. 2). 0.818 3.3124; 0.869 3.1788; 0.915 3.0091; 0.952 2.8095; 0.983 2.5619; 0.998 2.3923; 1.008 2.2375; 0.825 3.2679; 0.899 3.0360; 0.948 2.7691; 0.988 2.4845; 1.001 2.2666; 1.018 2.0517; 1.034 1.8472 (proc. 1).

$B = 0.040$  m: Z, -log [OH<sup>-</sup>]; 0.751 3.1545; 0.777 3.0967; 0.823 2.9784; 0.867 2.8482; 0.906 2.6999; 0.935 2.5671; 0.964 2.3874; 0.980 2.2677; 0.990 2.1537; 0.998 2.1109 (proc. 2). 0.922 2.6608; 0.960 2.4632; 0.988 2.2828; 0.782 3.1115; 0.812 3.0123; 0.843 2.9273; 0.875 2.8274; 0.916 2.6653; 0.956 2.4545; 0.978 2.2909; 1.008 2.1195 (proc. 1).

$B = 0.080$  m: Z, -log [OH<sup>-</sup>]; 0.752 2.8785; 0.787 2.7884; 0.821 2.6919; 0.859 2.5761; 0.883 2.4905; 0.915 2.3666; 0.951 2.1880; 0.958 2.1391; 0.988 1.9630; 1.007 1.8367 (proc. 2). 0.815 2.7361; 0.852 2.6168; 0.887 2.4975; 0.918 2.3705; 0.954 2.2088; 0.988 2.0022; 1.021 1.7667 (proc. 1).

Table 3. Experimental data for 25°C and 3.0 m Na(ClO<sub>4</sub>). For each experimental point, Z is given first, and then -log [OH<sup>-</sup>]. Procedure 2.

$B = 0.005$  m: Z, -log [OH<sup>-</sup>]; 1.061 2.4317; 1.116 2.1550; 1.149 2.0130; 1.220 1.8070; 1.292 1.6200; 1.089 2.2650; 1.145 2.0356; 1.201 1.8690; 1.247 1.7255; 1.380 1.4433.

$B = 0.0125$  m: Z, -log [OH<sup>-</sup>]; 1.073 2.2150; 1.198 1.7814; 1.253 1.6190; 1.329 1.4980; 1.413 1.3367; 1.502 1.1900; 1.578 1.0920; 1.010 2.6307; 1.035 2.4630; 1.072 2.2410; 1.201 1.7703; 1.265 1.6098; 1.306 1.5200.

$B = 0.025$  m: Z, -log [OH<sup>-</sup>]; 1.066 2.0886; 1.107 1.9187; 1.153 1.7720; 1.207 1.6253; 1.290 1.4613; 1.349 1.3408; 1.398 1.2595; 1.440 1.1988; 1.499 1.1075; 1.537 1.0421; 0.968 2.6300; 1.022 2.3517; 1.107 1.9236; 1.274 1.4813; 1.429 1.2020; 1.479 1.1166.

$B = 0.050$  m: Z, -log [OH<sup>-</sup>]; 0.823 2.9007; 0.960 2.4010; 1.060 1.9293; 1.105 1.7551; 1.171 1.5607; 1.225 1.4348; 1.267 1.3518; 1.374 1.1579; 1.532 0.9265; 1.033 2.0803; 1.050 1.9837; 1.088 1.8313; 1.156 1.6085; 1.229 1.4390; 1.317 1.2577; 1.406 1.1155; 1.480 0.9902; 1.546 0.8937.

$B = 0.100$  m: Z, -log [OH<sup>-</sup>]; 0.827 2.6728; 0.927 2.3262; 0.996 2.0107; 1.072 1.6738; 1.144 1.4473; 1.213 1.2823; 1.305 1.1063; 1.397 0.9584; 1.475 0.8502; 1.197 1.3007; 1.265 1.1567; 1.360 0.9907; 1.486 0.7951; 1.560 0.6808.

$B = 0.200$  m: Z, -log [OH<sup>-</sup>]; 1.240 0.9951; 1.328 0.8328; 1.454 0.6273; 1.542 0.4856; 0.832 2.4841; 0.923 2.1481; 0.999 1.7907; 1.068 1.4865; 1.138 1.2546; 1.206 1.0832; 1.303 0.8925; 1.393 0.7384; 1.466 0.6168.

Point interpolated from titrations at constant ratio  $r = 2, 1.82, 1.33, \text{ or } 1.0$ :

$B = 0.001$  m: 0.831 3.8827; 0.921 3.5307; 1.020 2.8400.  $B = 0.0025$  m: 0.882 3.6813; 0.954 3.3491; 1.008 2.9240; 1.045 2.6262.  $B = 0.005$  m: 1.032 2.6310; 1.075 2.3401.  $B = 0.0125$  m: 1.067 2.2370; 1.129 1.9782.



Table 4. Experimental data for 50°C and 0.5 m Na(ClO<sub>4</sub>). For each experimental point, *Z* is given first, and then  $-\log [\text{OH}^-]$ . Titrations always with procedure 2.

*B* = 0.005 m: *Z*,  $-\log [\text{OH}^-]$ ; 0.708 3.4713; 0.837 3.1042; 0.934 2.7731; 0.978 2.5819; 1.004 2.4007. *B* = 0.010 m: 0.746 3.3613; 0.830 3.1029; 0.860 3.0027; 0.906 2.8216; 0.950 2.6193. *B* = 0.020 m: 0.750 3.2330; 0.980 2.3811. *B* = 0.040 m: 0.752 2.9905; 0.860 2.6875; 0.948 2.3590; 0.982 2.1726. *B* = 0.080 m: 0.750 2.7201; 0.756 2.7236; 0.820 2.5183; 0.896 2.2731; 0.974 1.9298; 0.978 1.8875; 1.020 1.7030.

proving that the solutions must contain polynuclear complexes. For low *B*, they are seen to approach a curve, with an inflexion point at *Z* = 1.0. Since the shape of this limiting curve agrees very well with that expected for equilibria between three mononuclear species with *Z* = 0, 1, and 2, there is every reason to conclude that at low *B* the predominant species are Si(OH)<sub>4</sub>, SiO(OH)<sub>3</sub><sup>-</sup>, and SiO<sub>2</sub>(OH)<sub>2</sub><sup>2-</sup>. The mononuclear curve was taken either as the one for the lowest concentration, or from a short extrapolation. The curve was fitted to a normalized curve for two-step equilibria<sup>7</sup>. The results are given in the final Table 5.

For the polynuclear complexes, it would have been desirable to start with an approach free from any assumptions (except possibly the constants for the mononuclear equilibria), as was done with the borate equilibria (Part II<sup>3</sup>). For the borates, the data for each value *B* could be extended to a range with *Z* ~ 0 (B(OH)<sub>3</sub> predominates) and *Z* = 1 (B(OH)<sub>4</sub><sup>-</sup> predominates) which made a double check possible. For the silicates, the curves for the higher *B*'s have no experimental point where the main species of Si is known from the onset, and so the integration method<sup>3</sup> is impossible.

With a limited range of experimental data available, the only approach that could be invented was to start with the simplest possible hypothesis, namely that, in addition to the mononuclear complexes B, AB and A<sub>2</sub>B, a single predominating polynuclear complex A<sub>p</sub>B<sub>q</sub> is formed. Using procedures outlined by Sillén<sup>8</sup> and applied by Biedermann and Sillén<sup>9</sup> and in Part II<sup>3</sup>, sets of normalized curves log *B* (log *a*)<sub>*Z*</sub> were constructed for combinations of

Table 5. Survey of equilibrium constants obtained in the present work. Unit: m (mole/kg H<sub>2</sub>O).

Reaction	<i>I</i> =0.5, 50°C	<i>I</i> =0.5, 25°C	<i>I</i> =3, 25°C
H <sub>2</sub> O ⇌ H <sup>+</sup> + OH <sup>-</sup>	log <i>K<sub>w</sub></i> = -12.97	-13.73	-14.03
A + B ⇌ AB; OH <sup>-</sup> + Si(OH) <sub>4</sub> ⇌ SiO(OH) <sub>3</sub> <sup>-</sup> + H <sub>2</sub> O	log <i>K<sub>1</sub></i> = 3.84	4.27	4.60
A + AB ⇌ A <sub>2</sub> B; OH <sup>-</sup> + SiO(OH) <sub>3</sub> <sup>-</sup> ⇌ SiO <sub>2</sub> (OH) <sub>2</sub> <sup>2-</sup> + H <sub>2</sub> O	log <i>K<sub>2</sub></i> = 1.06	1.17	1.32
2A + B ⇌ A <sub>2</sub> B; 2OH <sup>-</sup> + Si(OH) <sub>4</sub> ⇌ SiO <sub>2</sub> (OH) <sub>2</sub> <sup>2-</sup> + 2H <sub>2</sub> O	log β <sub>2</sub> = 4.90	5.44	5.92
2A + 4B ⇌ A <sub>2</sub> B <sub>4</sub> ; 2OH <sup>-</sup> + 4Si(OH) <sub>4</sub> ⇌ Si <sub>4</sub> O <sub>8</sub> (OH) <sub>8</sub> <sup>4-</sup> + 6H <sub>2</sub> O	log β <sub>24</sub> = 13.38	14.89	—
4A + 4B ⇌ A <sub>4</sub> B <sub>4</sub> ; 4OH <sup>-</sup> + 4Si(OH) <sub>4</sub> ⇌ Si <sub>4</sub> O <sub>8</sub> (OH) <sub>8</sub> <sup>4-</sup> + 8H <sub>2</sub> O	log β <sub>44</sub> = —	—	23.64
2A + 2B ⇌ A <sub>2</sub> B <sub>2</sub> ; 2OH <sup>-</sup> + 2Si(OH) <sub>4</sub> ⇌ Si <sub>2</sub> O <sub>4</sub> (OH) <sub>4</sub> <sup>2-</sup> + 3H <sub>2</sub> O	log β <sub>22</sub> = —	—	9.94
A + B ⇌ AB; Si(OH) <sub>4</sub> ⇌ SiO(OH) <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	log * <i>K<sub>1</sub></i> = -9.13	-9.46	-9.43
A + AB ⇌ A <sub>2</sub> B; SiO(OH) <sub>3</sub> <sup>-</sup> ⇌ SiO <sub>2</sub> (OH) <sub>2</sub> <sup>2-</sup> + H <sup>+</sup>	log * <i>K<sub>2</sub></i> = -11.91	-12.56	-12.71
2A + B ⇌ A <sub>2</sub> B; Si(OH) <sub>4</sub> ⇌ SiO <sub>2</sub> (OH) <sub>2</sub> <sup>2-</sup> + 2H <sup>+</sup>	log *β <sub>2</sub> = -21.04	-22.02	-22.14
2A + 4B ⇌ A <sub>2</sub> B <sub>4</sub> ; 4Si(OH) <sub>4</sub> ⇌ Si <sub>4</sub> O <sub>8</sub> (OH) <sub>8</sub> <sup>4-</sup> + 4H <sub>2</sub> O + 2H <sup>+</sup>	log *β <sub>24</sub> = -12.56	-12.57	—
4A + 4B ⇌ A <sub>4</sub> B <sub>4</sub> ; 4Si(OH) <sub>4</sub> ⇌ Si <sub>4</sub> O <sub>8</sub> (OH) <sub>8</sub> <sup>4-</sup> + 4H <sub>2</sub> O + 4H <sup>+</sup>	log *β <sub>44</sub> = —	—	-32.48
2A + 2B ⇌ A <sub>2</sub> B <sub>2</sub> ; 2Si(OH) <sub>4</sub> ⇌ Si <sub>2</sub> O <sub>4</sub> (OH) <sub>4</sub> <sup>2-</sup> + 2H <sub>2</sub> O + 2H <sup>+</sup>	log *β <sub>22</sub> = —	—	-18.12

$p = 2, 3,$  and  $4$  with  $q = 2, 3,$  and  $4$ . These normalized "projection maps" were then compared with the experimental data  $\log B(\log [\text{OH}^-])_Z$ .

For the data in the range attainable with  $I = 0.5$  m, no acceptable fit could be obtained with any complex other than  $A_2B_4$ . The agreement obtained assuming this complex and the equilibrium constants given in Table 5 is shown in Figs. 2 and 4. It seems quite satisfactory, except for  $Z = 0.9$  at the highest  $B$ . One might probably obtain complete agreement, within experimental error, on assuming that  $A_3B_4$  is also present, and assigning to it a suitable equilibrium constant.

In the experiments at  $I = 3$  m, and higher  $Z$ -values (Fig. 3), fair agreement could be obtained assuming either  $A_3B_4$  or  $A_4B_4$  as the single polynuclear complex; with the other single complexes tested, no acceptable fit could be obtained.

Slight deviations at low values of  $B$  indicate the presence of a complex with  $q$  between 1 and 4. Fig. 3 shows the best agreement obtained assuming the species  $AB, A_2B, A_2B_2,$  and  $A_4B_4$  and the constants in Table 5. The agreement around  $Z = 1.1$  might be improved by introducing the species  $B, A_3B_4,$  and  $A_2B_4$ , which might well be expected to exist in this region.

Deviations at low  $B$  might also be explained assuming complexes with 3 B instead of  $A_2B_2$ . However, one would then have to assume such a high percentage of  $B_3$ -complexes that it is remarkable that they have not showed up in the  $Z$ -range given in Fig. 2.

One might certainly "improve" the agreement between experimental data and calculated values by increasing the number of complexes assumed. However, it is felt that such a procedure would be arbitrary, if there was no other evidence for the formulas of the complexes. As a rule, more than two independent equilibrium constants for the formation of polynuclear ions may be handled simultaneously with confidence only in experimentally very favorable cases — and silicate equilibria is not one of them.

One could certainly set to the task of refining the equilibrium constants for the  $A_pB_q$  species more whole-heartedly, if there were other data available that would confirm the predominance of tetranuclear species, and could indicate which other  $q$  would be important.

To sum up, the data may be explained with reasonable accuracy assuming, apart from the mononuclear species  $B, AB,$  and  $A_2B$ , only tetranuclear species; although only  $A_2B_4$  and  $A_4B_4$  have been assumed in the calculations, it seems reasonable that at least  $A_3B_4$  should also exist.

#### SURVEY OF PREVIOUS SOLUTION DATA

Contrary to common practice, we prefer to give a short survey of previous pertinent work after, rather than before the description of our work. For one thing, the concept of an "instability range" makes it easier to understand many observations by previous workers. Those who want a complete historical review, giving due credit for each step in the development of aqueous silicate chemistry, are referred to the monographs by Iler<sup>1</sup> and Vail<sup>2</sup>. Iler also summarizes the abundant literature on the precipitation of silica gel

and various metal silicates from silicate solutions, a subject which has been left out here completely.

*Reversibility of silicate equilibria.* There is a wide-spread belief — shared, in fact, by ourselves at the beginning of this work — that equilibria in silicate solutions are reached rather slowly. This is only partly true; on the contrary, equilibria are obtained very rapidly so long as clear solutions, free from colloid or precipitate, are studied. When the  $B$  and  $Z$  of the solution are in the "instability range", where a clear solution no longer corresponds to equilibrium, the solution changes its properties over a long period.

In the light of our present knowledge, it is for instance easy to explain the observations of Kohlrausch<sup>10</sup>. When a sodium silicate solution of ratio  $\text{SiO}_2/\text{Na}_2\text{O} = r = 3.4$ , thus  $Z = 0.59$ , was diluted, and then NaOH added after a certain time, the conductance of the resulting solution changed over a period of many hours. The sooner NaOH was added after the dilution, the more rapid was the approach to the final value. This is easy to understand: the concentrated solution is close on the border-line of the "instability range". On dilution, a precipitate is formed (polysilicic acid, perhaps with some adsorbed  $\text{Na}^+$ ), and this then redissolves very slowly, especially if it has had time to grow. With the initial  $r < 2$  ( $Z > 1.0$ ), Kohlrausch found no such timeeffect.

Even if the average composition of a solution is kept within the "clear" area, precipitation of colloid may occur because of local excess of acid. Thus, in commercial silicate solutions, the carbon dioxide of the air has often precipitated a colloid. Titration with acid of a sodium silicate solution (as in procedure 1 above) produces local precipitates, which are not easily redissolved. Such phenomena may explain the divergence of some previous data and the time-effects observed, *e.g.*, by Treadwell and Wieland<sup>11</sup>.

On the other hand, research workers who have taken great trouble to avoid acid impurities, such as Hägg<sup>12</sup>, and Nauman and Debye<sup>13</sup>, seem to agree that in clear solutions equilibria are obtained instantaneously so that the properties of a clear silicate solution depend only on its composition and not on its history.

*Freezing-point data* may be used to calculate the average number of silicate complexes (charged or uncharged) per Si, which will be denoted by  $R$  as in Part II. The inverted value,  $R^{-1}$ , is the average number of Si-atoms per complex. Souchay<sup>14</sup> titrated 0.66 M " $\text{Na}_2\text{SiO}_3$ " with  $\text{H}_2\text{SO}_4$  in a  $\text{Na}_2\text{SO}_4(\text{H}_2\text{O})_{10}$  melt, measuring the freezing-point. He concluded that the " $\text{Na}_2\text{SiO}_3$ " ( $Z = 2$ ) gives mononuclear ions ( $R = 1$ ), whereas at the point corresponding to " $\text{NaHSiO}_3$ " ( $Z = 1$ ), he found  $R^{-1} = 4$ ; for the predominant species Souchay gave the formula  $\text{Si}_4\text{O}_{10}^4$ .

Thilo and Miedreich<sup>15,16</sup> also studied the transition point of  $\text{Na}_2\text{SO}_4(\text{H}_2\text{O})_{10}$ , the melt incidentally providing constant ionic medium. In dilute solutions of  $Z = 1$ , they found  $R = 1$  and concluded that  $\text{H}_3\text{SiO}_4^-$  predominates. With increasing  $B$ ,  $R$  decreases from 1.0 to  $\approx 0.25$ , which might be interpreted by the formation of a tetrasilicate ion; however, Thilo and Miedreich do not commit themselves to giving any formula for it. They also studied solutions of the salts previously denoted as  $\text{Na}_2\text{SiO}_3(\text{H}_2\text{O})_9$  and  $\text{Na}_6\text{Si}_2\text{O}_7(\text{H}_2\text{O})_{11}$ , and concluded that they are really  $\text{Na}_2\text{H}_2\text{SiO}_4(\text{H}_2\text{O})_8$  and  $\text{Na}_3\text{HSiO}_4(\text{H}_2\text{O})_5$ . Since  $[\text{OH}^-]$  was high it was not possible to calculate  $R^{-1}$  accurately.

Miedreich<sup>16</sup> has also recalculated Hägg's<sup>12</sup> and Harman's<sup>17</sup> freezing-point data for ice in sodium silicate solutions. These data are somewhat less accurate, since a correction must be made for  $[\text{Na}^+]$ ; the activity factor correction has been neglected. Nevertheless,  $R$  varies from around 1.0 at low  $B$  to around 0.25 at high  $B$ , as before.

Alexander<sup>18</sup> prepared a solution of  $\text{Si}(\text{OH})_4$ , from crystalline  $\text{Na}_2\text{H}_2\text{SiO}_4 \cdot (\text{H}_2\text{O})_8$  and a slurry of  $\text{H}^+$ -saturated ion exchanger at  $0^\circ\text{C}$ . By freezing-point measurements he proved it to be mononuclear ( $R = 1$ ). Iler<sup>19,20</sup> measured the freezing-point of a polysilicic acid sol, obtained from a sodium silicate solution with  $Z = 0.61$ , adding acid<sup>19</sup>, or  $\text{H}^+$  ion exchanger<sup>20</sup>. In the former case he found  $R^{-1} = 3.25$ , in the latter  $R^{-1} = 4.7$ ; subsequent polymerization was corrected for by extrapolation to zero time.

All this might seem to support the conclusions from the present emf work that the predominant complexes are mononuclear and tetranuclear. However, it is fair to point out that freezing-point measurements for other systems have repeatedly been interpreted in ways that differ from the conclusions obtained by the emf method, which we consider far more accurate, if applied properly.

For instance, freezing-point data have been interpreted<sup>14,21</sup> as a proof that the main hydrolysis product of  $\text{Be}^{2+}$  is  $(\text{BeOH})_4^{4+}$ , whereas the emf data of Kakihana and Sillén<sup>22</sup> in this laboratory give a good fit over a wide concentration range assuming  $(\text{BeOH})_3^{3+}$ , and give no evidence for  $(\text{BeOH})_4^{4+}$ .

*Optical data.* Nauman and Debye<sup>13</sup> studied the light-scattering of carefully filtered sodium silicate solutions. With  $Z \sim 2$  and higher ( $r = 1$  and lower), the calculated molecular weights were around 70, corresponding to monomers, whereas with increasing  $r$  (up to 3.75,  $Z = 0.53$ ) they rose to a few hundreds. There may thus be polynuclear ions with a small number of Si, but certainly no "colloidal" particles in the usual sense. The viscosity of highly concentrated solutions can also be well explained without assuming large particles: the large rise in viscosity occurs, just as with sucrose, only when the molecules come very close together in the solution.

For  $Z = 0.53$ , Nauman and Debye observed an increase in turbidity (and thus molecular weight) with time for  $B = 0.26$  M, whereas the turbidity remained constant with  $B = 0.65$  M. This is another example of the instability of solutions of low  $Z$  (high  $r$ ) on dilution.

Brady, Brown and Huff<sup>23</sup> have found and studied an increase in turbidity with time for potassium silicate solutions of  $r = 3.8$ , which are thus in the "instability range".

*Diffusion data.* Jander and Heukeshoven<sup>24</sup> found that the diffusion coefficient of silicate ions is the same for  $B = 0.167$ , 0.10, and 0.05 M in 3 M  $\text{OH}^-$ . They concluded that a single mononuclear species,  $\text{SiO}_3^{2-}$ , was present. With decreasing pH, the diffusion coefficient at first decreased and then, between pH = 13.5 and 10.9, it kept at a constant value, which was different for different  $B$ 's. In this range they assumed  $\text{Si}_2\text{O}_5^{2-}$  to be the predominant species.

*Emf (pH) data.* Several investigators have measured the pH of silicate solutions, obtained for instance during titrations of silicate with acid, or of silicic acid with alkali, or by mixing or diluting solutions of pure salts like  $\text{NaH}_3\text{SiO}_4$ . The data have in general been interpreted in terms of the dissociation

tion constants of the acid  $H_4SiO_4$  (in older work often called  $H_2SiO_3$ , by analogy with  $H_2CO_3$ ). Some of these workers have noticed deviations which they have ascribed to the formation of polysilicate ions; with the exceptions to be mentioned below, no attempt was made to calculate the constants for their formation.

For the mononuclear constants, the following values have been given: (the figures are  $pK_{a1}$  etc, thus  $-\log *K_1$ , ( $-\log *K_2$ ,  $-\log *K_3$ ,  $-\log *K_4$ ), in our notation) Hägg<sup>12</sup> (20°C) 9.13; Harman<sup>25</sup> (25°C) 9.4 16.3; Hahn and Klockmann<sup>26</sup> (20°C) 10.64; Treadwell and Wieland<sup>11</sup> (20°C) 9.7 12; Flint and Wells<sup>27</sup> 9.66 11.7 12 12; Oka, Kawagaki and Kadoya<sup>28</sup> (25°C) 9.51 11.77; Miedreich<sup>16</sup> (20°C) 9.4 11.4 13.7. Miedreich calculated the constants from his own data, and also from recalculated data of Bogue<sup>29</sup> (30°C), Hägg<sup>12</sup>, and Harman<sup>30</sup>. Alexander, Heston and Iler<sup>31</sup>, from the increase of solubility of "amorphous silica" with increasing pH concluded  $pK_{a1} \sim 9.8$ .

When comparing these data and those of the present work (Table 5) we should notice that the ionic media have been different in different papers. The differences in the constants given may be explained partly by the activity factor correction and partly by the neglect of polynuclear silicate ions by most authors.

Roller and Ervin<sup>32</sup> studied the solubilities of calcium silicates in solutions of various pH and  $[Ca^{2+}]$ . They postulated that  $pK_a$  for  $H_2SiO_3$  and  $H_3Si_2O_6^-$  is 9.8, and for  $H_2Si_2O_6^{2-}$  12.8. On this assumption they calculated for  $pK_{a2} = 12.16 \pm 0.02$ , and moreover  $\log K (2H_3SiO_4 \rightleftharpoons H_2Si_2O_6^{2-} + 2H_2O) = 3.34 \pm 0.03$ .

In a previous communication by the author<sup>33</sup> it was shown that data for a restricted range ( $B, Z$ ) could be explained assuming complexes  $AB_n^-$ , thus with charge  $-1$ . Since this mechanism cannot explain the data for the wider range now available, it will not be upheld.

From emf and freezing point data, Thilo and Krüger<sup>34</sup> deduced the formation of a series of complexes,  $(AB)_n^-$ , in the brief notation, with the equilibrium constant,  $\log K (nAB^- \rightleftharpoons (AB)_n^-) = -1.23(n-1)$ .

*Conductivity* titrations have been reported by Constable and Tegul<sup>35</sup>. From breaks in the conductivity curves they inferred the existence in the solution of "ions from  $Na_4Si_3O_8$ ,  $Na_2Si_2O_5$  and  $NaHSiO_3$ " at 15°C, and " $Na_2O.2SiO_2$  and  $Na_2O.4SiO_2$ " at 100°C. In general, the conductivity method does not seem to be well suited for studying complicated equilibria.

#### SOLUBILITY OF $Si(OH)_4$ , AND INSTABILITY RANGE

According to several authors (Alexander, Heston and Iler<sup>31</sup>; Goto, Okura and Kayama<sup>36</sup>; and Gardner<sup>37</sup>) the solubility of "amorphous silica" in acidic and neutral solutions is around 2 mM =  $10^{-2.7}$  M, probably in the form of  $Si(OH)_4$ . Solutions of a higher concentration may be prepared, but they are unstable and a gel will eventually precipitate.

It is a natural suggestion, that this solubility should determine at least one limit to the range in which stable solutions can be obtained. To test this suggestion, the concentration  $b = [Si(OH)_4]$  has been calculated as a function of  $\log B$  for the constant values  $Z = 0.75$  and 0.80, and  $I = 0.5$ , 25°C, and 50°C, using the equilibrium constants  $K_1$ ,  $\beta_2$ , and  $\beta_{24}$  from Table 5. The results are given in Fig. 5.

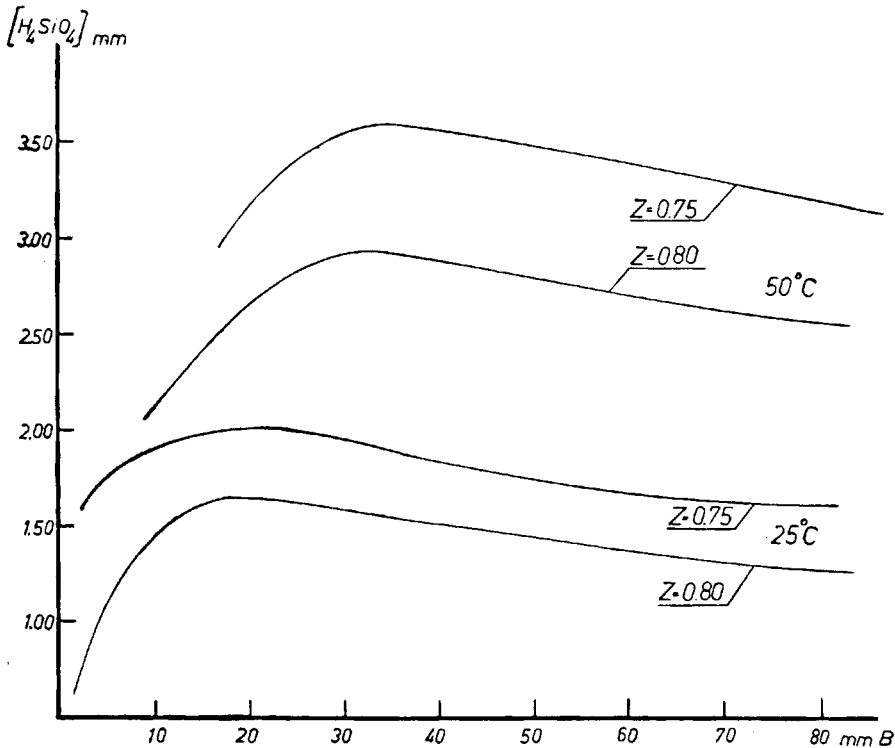


Fig. 5. Equilibrium concentration,  $b$ , of  $Si(OH)_4$  calculated as a function of  $B$ , for constant  $Z = 0.75$  or  $0.80$ ;  $0.5$  m  $Na(ClO_4)$ ,  $25^\circ C$ . Equilibrium constants from Table 5.

Since  $h$  and  $[OH^-]$  are negligible in comparison with  $B$  in (1), the curves will show the behavior of the solution when it is diluted with ionic medium, which keeps  $Z$  constant with good approximation.

It is seen that on dilution,  $b$  passes through a maximum, for  $Z = 0.75$ , and  $25^\circ C$ , of  $b_{max} \sim 2$  mm ( $B = 20$  mm) and for  $50^\circ C$  of  $b_{max} \sim 3.6$  mm (at  $B = 40$  mm). The figures 2 mm and 3.6 mm approximately correspond to the solubility of  $Si(OH)_4$  at these temperatures, and it may be inferred from Fig. 5 that, at lower values for  $Z$ , the solubility will be exceeded.

This agrees with experience: stable solutions have not been obtained for  $Z < 0.75$  except in the very dilute range,  $B < 5$  mm, where the limiting  $Z$ -value decreases with  $B$ , and roughly seems to correspond to a saturated solution of  $Si(OH)_4$ .

For  $I = 3.0$ , the limiting value for  $Z$  was in the range  $0.80$ — $0.95$ , depending on  $B$ . Here, as in the dilute medium, the distinction between stable and unstable solutions was sharp.

The data have not been considered accurate enough to justify a similar calculation for the lower limit at  $I = 3.0$ , nor for the intermediate "instability

range" for  $I=3.0$ . It seems likely that a similar intermediate range should exist for  $I=0.5$  although it has not been met with in the range of  $B$  and  $Z$  studied.

Although the explanation given here is reasonable and agrees fairly well both with present data and with the results of earlier work, it is not considered that the present constants are a final answer to the question. Attempts will be made to study silicate ions in other media, and with other experimental methods, and also to study some related anions.

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