CHAPTER 2
Water-Soluble Silicates

Vail's two-volume monograph on soluble silicates (1) after a quarter of a century is still the primary source of technical and industrial information. It is pertinent to review some of the advances made since then in the chemistry of soluble silicates, from which silica colloids and gels are largely derived.

Silicate and polysilicate ions are still not well understood. The main distinction between polysilicate ions and very small negatively charged colloidal silica particles is probably one of terminology. In the past, solutions of alkali metal silicates obtained by dissolving sodium or potassium silicate glasses in water seemed to be clearly distinct from sols of colloidal silica stabilized with a minor amount of alkali. Silicate solutions were made by dissolving glasses with SiO₂:Na₂O ratios less than 4:1. Since these glasses with more silica and less alkali do not dissolve, silicate solutions of higher ratios were not available.

On the other hand, when it was learned how to make silica particles of different sizes it was found that smaller particles could be stabilized as sols by adding more alkali. Thus 5 mm particles were stabilized with a ratio of 25:1. However, attempts to obtain concentrated solutions with still smaller particles and lower ratios of 25:1 to 4:1 led to gelled mixtures when sodium hydroxide was used as the alkali. Then it was found that such solutions could be made using other alkalis so that solutions containing particles smaller than 5 nm, on down to molecular dimensions, were obtained.

Solutions in this range are referred to here as "polysilicates," with the understanding that these polyanions may at the same time be treated as very small charged particles.

Further study of this question was simplified when it was recognized that the sodium ion was unusual in its influence on the gelling behavior of the system. Solutions in this intermediate ratio range made with a potassium, lithium, or tetramethylammonium base proved to be more stable in regard to thickening and gelling. Other stabilizing cations were guanidinium and ethylenediamine copper.

Over the past 50 years there have been major changes in theories of the nature of the silica in the conventional alkali silicate solutions with SiO₂:Na₂O ratios from 2:1 to 4:1. The physical similarity of viscous, "stringy" solutions of soluble silicates to solutions of linear organic polymers led in some cases to the supposition that vis-
cous silicate solutions must contain high molecular weight linear polymers. (This was in spite of the obvious fact that concentrated solutions or syrups of low molecular weight sugars are also very viscous.) Likewise, the rapid gelling of a silicate solution upon adding acid appeared to support the idea that the gelling mechanism involved cross-linking of preexisting linear polymers, by analogy to organic polymer systems. Thus developments in the theory of organic polymers, improperly applied to soluble silicates, may have delayed a correct interpretation of this inorganic system. Polymeric silicate species certainly occur in solution, but they are not highly linear in form and the polymerization mechanism is entirely different from that of any organic system.

SODIUM AND POTASSIUM SILICATES

Manufacture

It has been known since the seventeenth century that sand and sodium or potassium carbonate react at red heat to form a water-soluble glass called "water glass." As noted by Vail (1), Johann Nepomuk von Fuchs was the first to investigate alkali silicates systematically and even before 1850 proposed their uses as adhesives, cements, and fireproof paints. By 1855 water glass was being made commercially, both in Europe and America.

Manufacture has generally been carried out in large open-hearth furnaces above 1300°C by the following reactions:

\[
3 \text{SiO}_2 + \text{Na}_2\text{SO}_4 + \frac{1}{2} \text{C} = \frac{1}{2} \text{CO}_2 + \text{SO}_2 + 3 \text{SiO}_2 \cdot \text{Na}_2\text{O}
\]

\[
3 \text{SiO}_2 + \text{Na}_2\text{CO}_3 = \text{CO}_2 + 3 \text{SiO}_2 \cdot \text{Na}_2\text{O}
\]

Except under unusual circumstances, the latter reaction using "soda ash" is always employed.

The manufacture of soluble silicates was reviewed by Williams (2). Improvements in reaction furnaces have been proposed. Burke (3) discloses coating sand particles with a mixture of sodium silicate and NaOH to give a SiO_2:Na_2O ratio of 2.5:1 to 4:1 and heating the particles in suspension in a flame to more than 3500°F, at which temperature uniform particles of soluble glass are formed. Other proposals are a cyclone type furnace (4), a vertical column furnace in which reactants pass downward into a heated reactor and the product moves upward around the column as a heat exchanger (5), and a submerged combustion furnace in which a 70% reduction in fuel cost and 80% reduction in size can be realized (6). Quantitative data on the rate of dissolution of sand (quartz) in molten Na_2CO_3 or SiO_2-Na_2O glass have become available. Terai, Sugae, and Hayami (7) found that at atmospheric pressure the reaction product at the SiO_2-molten Na_2CO_3 boundary is metasilicate, whereas under vacuum the reaction rate is slower and metasilicate is not detected. Diffusion
of oxygen ions through the silicate boundary layers control the reaction rate, which is not limited by the diffusion of sodium ions. Truhlarova and Veprek (8) found the rate of dissolution of fused silica in molten SiO$_2$–Na$_2$O had an activation energy of 29.8 kcal mole$^{-1}$ at 1050–1250°C. At 1200°C, the rate depended on the diffusion constant, which increased from 1.86 to 64.5 x 10$^{-8}$ cm$^2$ sec$^{-1}$ as Na$_2$O content increased from 22.5 to 50.8 wt. %. Kreider and Cooper (9) measured the rate at which 1 mm quartz spheres dissolved in sodium silicate glass at 950°C and concluded it was diffusion controlled and the coefficient was 4.4 x 10$^{-8}$ cm$^2$ sec$^{-1}$ when the Na$_2$O content was 40%. Similar results were reported by Hlavac and Nadelmyska (10).

Minor improvements in the clarity and purity of solutions continue to be made. For example, Tauch found that if sodium silicate glass of 3.25 ratio is dissolved in water in an autoclave to too high a concentration, the resulting solution becomes turbid. By stopping at a concentration corresponding to 38°Be and then vacuum concentrating to 41°Be, a clear concentrated product is obtained (11). To obtain a clearer solution of sodium silicate, Rathmell disclosed adding TiO$_2$ to the glass-batch to give a concentration in the melt of 400-3000 ppm (12). Apparently the presence of 4 moles of TiO$_2$ per gram-atom of calcium prevents the later formation of insoluble calcium silicates.

The use of sodium salts other than carbonate is still of limited interest. In 1941, Iller and Tauch (13) studied the equilibrium

$$\text{SiO}_2(s) + 2 \text{NaCl}(g) + \text{H}_2\text{O}(g) = 2 \text{HCl}(g) + \text{Na}_2\text{SiO}_3(l)$$

and found $K = [\text{HCl}][\text{NaCl}]^{-2}[\text{H}_2\text{O}]^{-1} = +2.9$ at 1000°C.

Calculations showed the impossibility of producing HCl at a practical concentration while obtaining a reasonable conversion based on NaCl. The equilibrium is more favorable under 1000°C, but the reaction rate is very low. In 1972, Hanf and Sole (14) reexamined the reaction at lower temperatures down to 700°C, and concluded that the equilibrium constant was favorable to using the reaction for processing certain copper ores containing silica.

Sodium sulfate reacts with sand even in an oxidizing atmosphere at 1400°C if reactants are spread in a very thin layer (0.5 mm). However, under reducing conditions (presumably CH$_4$) the reaction proceeds at 900°C with production of H$_2$S (15).

Sodium sulfate in a closed system reacts with silica at 700-900°C as follows (16):

$$3 \text{Na}_2\text{SO}_3 + \text{SiO}_2 = 2 \text{Na}_2\text{SO}_4 + \text{Na}_2\text{SiO}_3 + \text{S}$$

When the cost of NaOH relative to Na$_2$CO$_3$ is favorable, silicate solutions with SiO$_2$:Na$_2$O ratios up to 2.0 or 2.5 can be made directly by autoclaving sand with strong NaOH solution. According to Ordiales (17) if hydrated or microcrystalline silicas such as opal, chalcedony, diatomite, or tripolite are available, it is possible to produce a solution with ratio as high as 3.22. The system water–silica–sodium monoxide has been examined by Morey and Hesselgesser (18) at pressures up to 2500 bars and 400°C. The solid phases are Na$_2$SiO$_3$, Na$_2$Si$_2$O$_5$, and quartz.
Commercial Solutions

Properties and uses of soluble silicates have been summarized by Weldes and Lange (19). Typical commercial (American) solutions are listed in Table 2.1. The key variables in silicate solutions are the following:

1. The alkali metal.
2. The ratio of SiO$_2$ to alkali metal oxide expressed by either weight or molar ratio. In the case of sodium silicate the two ratios are nearly identical.
3. The concentration of solids.

Sodium silicates are produced as glasses having SiO$_2$:Na$_2$O molar ratios of 1.6-3.9. These are sold as lump or pulverized form, partly hydrated powders, and concentrated solutions. Potassium silicate glasses have SiO$_2$:K$_2$O molar ratios of 2.83-3.92 and are sold in pulverized, flake or solution form.

For the production of colloidal and finely divided silica powders the 3.25 ratio sodium silicate solution is almost universally used.

The maximum practical silica concentration in commercial sodium silicate solutions is limited by the viscosity which must be low enough for the solutions to be pumped under ordinary conditions. The higher the SiO$_2$:Na$_2$O ratio, the lower the maximum silica concentration in commercial products, as shown in Figure 2.1.

<table>
<thead>
<tr>
<th>Alkali Metal</th>
<th>Wt. Ratio</th>
<th>SiO$_2$ (%)</th>
<th>Na$_2$O (%)</th>
<th>Density (lb/gal)</th>
<th>Viscosity (centipoise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>2.50</td>
<td>20.8</td>
<td>8.3</td>
<td>10.5</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>2.20</td>
<td>19.9</td>
<td>9.05</td>
<td>10.5</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>2.10</td>
<td>26.3</td>
<td>12.5</td>
<td>11.5</td>
<td>1,050</td>
</tr>
<tr>
<td>Potassium</td>
<td>2.50</td>
<td>20.8</td>
<td>8.3</td>
<td>10.5</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>2.20</td>
<td>19.9</td>
<td>9.05</td>
<td>10.5</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>2.10</td>
<td>26.3</td>
<td>12.5</td>
<td>11.5</td>
<td>1,050</td>
</tr>
</tbody>
</table>
Soluble Crystalline Sodium and Potassium Silicates

Sodium metasilicate nonahydrate Na₂SiO₃·9H₂O (m.p. 47°C) is the only form made chemically pure for use as a standard. For industrial uses, both anhydrous Na₂SiO₃ and Na₂SiO₃·5H₂O are produced along with other more highly alkaline grades.

The following anhydrous crystalline forms, obtained from the melt, have a SiO₂:M₂O ratio of 1 or higher:

<table>
<thead>
<tr>
<th>Silicate</th>
<th>M.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SiO₃</td>
<td>1089</td>
</tr>
<tr>
<td>Na₂Si₂O₅</td>
<td>874</td>
</tr>
<tr>
<td>K₂SiO₃</td>
<td>976</td>
</tr>
<tr>
<td>K₂Si₂O₅</td>
<td>1045</td>
</tr>
<tr>
<td>K₂Si₄O₉</td>
<td>770</td>
</tr>
</tbody>
</table>

There are numerous hydrates of meta- and disilicates, as listed by Vail (1), but Na₂SiO₃·5H₂O (m.p. 72.2°C) is the principal commercial product.

Properties of Solution

The properties of sodium silicate solutions at all ratios and concentrations have been described in detail by Vail (1) in 1952. A very convenient summary of data on key properties such as phase diagrams, pH, density, viscosity, and solubility has been
assembled by Weldes and Lange (19). A few further observations are here noted as follows, although a thorough literature search was not made.

The specific gravity of a silicate solution is used to determine concentration, if the ratio is known. Otherwise, analysis for silica or alkali is required. Shtyrenkov et al. (20) propose titrating the normality of the alkali, from which the molar ratio of SiO$_2$:Na$_2$O can be determined as $55.16(d - 1)N - 2.28$ where $d$ is specific gravity and $N$ is alkali normality.

Measurements have been made of certain physical properties of sodium silicate solutions over a wide range of ratios and concentrations. Accurate pH data have been published by Bacon and Wills (21), who used specially designed electrode cells. Densities of the solutions were also reported and an empirical equation given:

$$d = 1 + aA + bA^2 + cA^3$$

where $d =$ specific gravity, 20°C/20°C

$A =$ wt. % Na$_2$O in the solution

and $a, b,$ and $c$ are constants that vary with the molar ratio of SiO$_2$:Na$_2$O which, however, covered only the range from 1.3 to 0.5.

Electrical conductivity was measured by Ukihashi (22) on solutions ranging in SiO$_2$:Na$_2$O ratio from 1.0 to 3.95 and concentrations from $10^{-3} N$ to maximum viscosity.

The viscosity of 3.41 ratio sodium silicate solutions was measured by Grant and Masson (23) over the concentration range of 0.005-0.3253 g ml$^{-1}$ and the intrinsic viscosity (specific viscosity divided by concentration) was found to be independent of the shear rate. At a concentration of 0.325 g ml$^{-1}$ the intrinsic viscosity was 16 ml g$^{-1}$; at 0.02 g ml$^{-1}$ it was 3.2 ml g$^{-1}$, and at zero concentration the extrapolated value was 3.1 ml g$^{-1}$. This demonstrated that the silicate ions were of low molecular weight and lacked chainlike character even in dilute solution.

**Fields of Use**

There are three major types of uses for soluble silicates, particularly sodium silicates:

1. Cleaners and detergents that depend on controlled alkalinity are made generally from silicates with molar SiO$_2$:Na$_2$O ratios less than 2.5, especially metasilicates and orthosilicates.

2. Adhesive, binder, and deflocculant applications, which depend on the presence of polysilicate ions, require silicates generally with ratios from 2.5 to 3.8. For maximum adhesive strength the lower ratio types are used because they can be obtained with a higher concentration of solids. For more water resistant bonds, the higher ratios are needed.
3. For the production of precipitated silicas, sols, and gels, sodium silicate of ratio about 3.3 is usually used rather than lower ratios, since less acid is required for neutralization of alkali per unit of silica, and this ratio is available at low cost because such large volumes are produced. However, the 3.8 ratio may be used to some further advantage if acid consumption is an important factor in cost.

For each particular application, specific grades of carefully selected ratio and concentration (viscosity) are recommended by the manufacturers.

Trends in uses will no doubt change as organic binders and adhesives become more expensive relative to sodium silicate. Over the last 40 years, starch replaced much of the silicate adhesives used in making corrugated boxboard, but the trend may be reversed. Resins used as binders in foundry molds and cores become less economic with increasing raw material costs and the necessity to reduce atmospheric pollution. Replacement by silicate apparently is becoming attractive as new means of rapid set are devised (24). Fast setting by carbon dioxide, used in a limited way for many years, may become universal (25). The use of silicate as a binder in cores has posed problems not encountered with resins, which burn out easily. The addition of amorphous silica along with silicate binder permits the development of a strong cristobalite-rich bond at high temperature, which disintegrates when cooled below 200°C, according to Yates (26).

Sodium silicates used as adhesives have SiO₂: Na₂O ratios in the range 2:1 to 4:1. A ratio of 3.3 is most commonly used on products of paper or asbestos. At ratios of 2 or less, adhesive bonds are weaker and very water sensitive. At ratios above 4.0 (polysilicates) the adhesive strength is less, although water resistance is better. Since at a workable viscosity, the solids content increases with decreasing ratio, silicate of ratio 2 and of high concentration is used in dense products such as grinding wheels, where water is hard to remove and highest bond strength is needed.

As is discussed later, the silicate adhesive solution of ratio 3.3 may be thought of as a solution of ratio 2 consisting of Na⁺ and H₂SiO₄⁻ ions in which the remaining silica is suspended as exceedingly small colloidal particles 1-2 nm in diameter. At higher ratios, there is a decreasing proportion of ionic silica.

It is observed that when silicate solutions of increasing ratios are spread as uniform thin films on glass and dried, the films crack or craze beyond a certain ratio. This assumes uniform film-forming and drying conditions, since film thickness, rapidity of drying, and temperature can all influence the degree of crazing. The greater the degree of crazing or micro-cracking, the less strength the silicate exhibits as an adhesive.

It is probable that crazing occurs when the volume of dried Na₂SiO₃ is insufficient to fill the spaces or pores between the spherical colloidal particles as they become packed together upon drying. If the residual solid ionic silicate does not fill the pores, then the gel-like network of particles shrinks, and cracks develop in the film. Thus the greater the tendency to micro-crack, the lower the strength of the dried film.

It is possible to calculate the relative volumes of Na₂HiO₃ and colloid present in dried silicates of different ratios. It will be assumed that Na₂HiO₃ solution dries to
its indicated composition, in which case its density is about 2.0 g cm$^{-3}$. The silica particles of about 11 Å diameter contain 23% H$_2$O and 77% SiO$_2$ and have a density of 1.72 (Chapter 1). It is assumed that when the silicate is dried, the sodium ions are coordinated with the oxygen atoms and silanol groups in the system and there is no water bonded to the sodium ions. When a suspension of small spheres is dried, the particles are randomly packed with a packing density about 50% by volume.

To meet the above postulated requirement that the pores must be filled to avoid crazing, the final volume of dried NaHSiO$_3$ must equal that of the colloidal particles. This in turn requires, for 100 cm$^3$ of dried adhesive, 85 grams of the colloid (19.5 grams H$_2$O and 64.5 grams SiO$_2$) and 100 grams of NaHSiO$_3$ (31 grams Na$_2$O, 60 grams SiO$_2$, 9 grams H$_2$O). This overall composition has a SiO$_2$:Na$_2$O weight ratio of 4.0:1, or a molar ratio of 4.13. This is in agreement with the observation that sodium or lithium silicate solutions of ratio higher than 4, generally called "polysilicates" in commerce, do not dry to clear, continuous films as do solutions of lower ratio because micro-cracking occurs.

It should be pointed out that such a composition of 50 vol. % solids dried to an extremely brittle state before the last of the water is removed. In considering the behavior of fillers in plastics, for example, more than about 40% by volume gives a hard, relatively brittle mass. Likewise, less than 40% by volume of colloid in silicate should give a less brittle film as the last of the water is removed. In this case, by similar calculations it is found that this corresponds to a SiO$_2$:Na$_2$O ratio of 3.5. Perhaps by coincidence this is near the common ratio used in adhesives.

It seems, therefore, that at least some of the behavior of soluble silicates with ratios greater than 2 is consistent with the theory that the solutions consist of NaHSiO$_3$ in solution along with very small particles of colloidal silica with silanol surfaces.

THE NATURE OF SILICATE SOLUTIONS

The fundamental equilibria involved have in the past been listed as follows:

$$\text{SiO}_2 + 2 \text{H}_2\text{O} = \text{Si(OH)}_4$$  \hspace{1cm} (1)

$$\text{Si(OH)}_4 + \text{OH}^- = \text{HSiO}_3^- + 2 \text{H}_2\text{O}$$  \hspace{1cm} (2)

$$2 \text{HSiO}_3^- = \text{Si}_2\text{O}_5^{2-} + \text{H}_2\text{O}$$  \hspace{1cm} (3)

$$\text{HSiO}_3^- + \text{OH}^- = \text{SiO}_3^{2-} + \text{H}_2\text{O}$$  \hspace{1cm} (4)

For the above equations at 25°C, taking the ionization constant of water as $10^{-14}$:

$$\frac{[\text{H}^+][\text{HSiO}_3^-]}{[\text{Si(OH)}_4]} = 10^{-8.8} \quad \text{or} \quad \frac{[\text{OH}^-][\text{Si(OH)}_4]}{[\text{HSiO}_3^-]} = 10^{-4.2}$$
\[
\frac{[H^+] [SiO_4^{3-}]}{[HSiO_3^-]} = 10^{-12.16} \quad \text{or} \quad \frac{[OH^-] [HSiO_3^-]}{[SiO_4^{3-}]} = 10^{-1.54}
\]

\[
\frac{[H^+] [Si_2O_5^{2-}]}{[HSi_2O_5^-]} = 10^{-9.8} \quad \text{or} \quad \frac{[OH^-] [HSi_2O_5^-]}{[Si_2O_5^{2-}]} = 10^{-4.2}
\]

\[
\frac{[H^+] [HSi_2O_5^-]}{[Si_2O_5^{2-}]} = 10^{-12.8} \quad \text{or} \quad \frac{[OH^-] [Si_2O_5^{2-}]}{[HSi_2O_5^-]} = 10^{-1.20}
\]

\[
\frac{[Si_2O_5^{2-}]}{[HSiO_3^-]^2} = 2200
\]

The above constants were measured by Roller and Ervin (27) in a system involving calcium as the base. There is now some doubt whether disilicate ions are formed in sodium silicate solution in accordance with the above equations. My observations indicate that in the presence of colloidal particles and at very low sodium ion concentration, only HSiO_3^- and SiO_2^{3-} are in equilibrium with Si(OH)_4 and OH^- ions. A 1% sol of very small particles of colloidal silica was made by polymerizing monosilicic acid made from ethyl silicate, for 24 hr at 25°C, at pH 7.8. There was some increase in pH as the specific surface area, determined by the Sears method (28), dropped to 1040 m^2 g^-1 as the silica particles grew to about 2.6 nm in diameter. To portions of this sol NaOH solution was added to adjust pH to various values between 8.5 and 10.5. These sols were then aged at 25°C while small samples were taken repeatedly to measure the rate of color development with molybdic acid reagent. After 2 hr aging, no further changes were noted in the reaction rates in the different samples. The amounts of silica reacted at indicated times are shown in Figure 2.2. After about 5 min, the slopes of all the curves are alike and correspond to the rate of reaction of the colloidal particles with molybdic acid. As a matter of interest, the rate of reaction was about 300 mg SiO_2 hr^-1 per 10^4 mg of total silica in the sample, which had a total surface area of 10,400 m^2. The specific rate was 3 x 10^-5 g m^-2 hr^-1.

By extrapolating the linear portions of curves in Figure 2.2 to zero time, the total concentrations of soluble, that is, monomeric and ionic, silica in the original sol samples were determined:

<table>
<thead>
<tr>
<th>pH of Sol</th>
<th>ppm</th>
<th>mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.5</td>
<td>175</td>
<td>2.9</td>
</tr>
<tr>
<td>9.0</td>
<td>220</td>
<td>3.7</td>
</tr>
<tr>
<td>9.5</td>
<td>260</td>
<td>4.3</td>
</tr>
<tr>
<td>10.0</td>
<td>450</td>
<td>7.5</td>
</tr>
<tr>
<td>10.5</td>
<td>950</td>
<td>15.8</td>
</tr>
</tbody>
</table>
From Figure 1.10b, line B, the equilibrium solubility of 2.6 nm particles at pH 8 is indicated to be about 150 ppm or 2.5 mM; this is reasonably close to the value extrapolated to pH 8 from the above data (see Figure 2.3).

Taking this value of 2.5 mM for the concentration of Si(OH)$_4$, and Roller's and Ervin's equilibrium constants, it is possible to calculate the concentration of the various species at equilibrium.

\[
\begin{align*}
[\text{HSiO}_3^-] &= [\text{Si(OH)}_4][\text{H}^+]^{-1} \times 10^{-9.8} \\
[\text{SiO}_3^{2-}] &= [\text{HSiO}_3^-][\text{H}^+]^{-1} \times 10^{-12.16} \\
[\text{Si}_2\text{O}_5^{2-}] &= 2200[\text{HSiO}_3^-]^2 \\
[\text{HSi}_2\text{O}_5^+] &= [\text{Si}_2\text{O}_5^{2-}][\text{H}^+] \times 10^{-9.8}
\end{align*}
\]

Calculated concentrations of Si(OH)$_4$, HSiO$_3^-$, and SiO$_3^{2-}$ are plotted cumulatively for various pH values in Figure 2.3. Although the curves are somewhat different at
pH 9, it is clear that at pH 10.5, the total concentration of soluble silica can be accounted for by Si(OH)$_4$ and HSiO$_3^-$, with possibly a small amount of SiO$_4^{2-}$. Thus no other ionic species can be present in appreciable amounts.

According to the above equations, the disilicate ions Si$_2$O$_5^{2-}$ and HSi$_2$O$_5^-$ should also be present in much higher concentrations than HSiO$_3^-$. Since it is well known that disilicic acid reacts completely with molybdic acid in less than 5 min, the total silica reacting in 5 min should have been much higher than observed if the equations relating to disilicate ions were applicable to the present system.

It is therefore concluded that Roller's and Ervin's (27) observations regarding the formation of disilicate ions were valid only in the calcium silicate system in which their studies were made. It would not be surprising to find that the divalent calcium ion promotes the formation of complex disilicate ions in which Si-O-Ca linkages are involved.

**Theory**

A concentrated solution of sodium or potassium silicate with SiO$_2$-M$_2$O molar ratios of 1:1 to 1:2 consists mainly of SiO$_4^{2-}$ and HSiO$_-^-$ ions. However, in solutions of higher ratios it is proposed that an increasing proportion of the silica forms extremely small three-dimensional, internally condensed silicate polymer-ions or charged particles. These are generally equiaxed or spheroidal in shape. The silicon
atoms in the interior are linked only to other silicon atoms by oxygen atoms, but each silicon atom on the exterior bears at least one OH group. These particles are in solubility equilibrium with soluble silica monomer, Si(OH)$_4$, which in turn is in equilibrium with monomeric silicate ions. The particles are also negatively charged by partial ionization of the surface OH groups to SiO$_2^-$ anionic sites.

\[
\text{Si(OH)}_4 + \text{OH}^- = (\text{HO})_2\text{SiO}^- + \text{H}_2\text{O}
\]

\[
(\text{HO})_2\text{SiO}^- + \text{OH}^- = (\text{HO})_2\text{SiO}_{2}^- + \text{H}_2\text{O}
\]

\[
n \text{Si(OH)}_4 = \text{Si}_n\text{O}_{4n-nx/2}(\text{OH})_{nx} + \frac{4n - nx}{2} \text{H}_2\text{O}
\]

where \(x\) is the ratio OH:Si that decreases as the degree of polymerization, \(n\), increases. Upon raising the pH, ionization occurs:

\[
\text{Si}_n\text{O}_{4n-nx/2}(\text{OH})_{nx} + z \text{OH}^- = \text{Si}_n\text{O}_{4n-nx/2}(\text{OH})_{nx-z}\text{O}^- + z \text{H}_2\text{O}
\]

where \(z\) is the number of charges on a polymer containing \(n\) silicon atoms.

Although it has long been known that polymeric silicate ions are present in such silicate solutions, it has not previously been suggested that such polymeric species be considered as silica particles in solubility equilibrium with Si(OH)$_4$, in accordance with the Ostwald-Freundlich equation relating diminishing particle size to increasing solubility. It is suggested that the equation may be at least approximately followed even by spherical particles as small as 10-20 Å in diameter, where a large fraction of the silicon atoms are on the surface.

The existence of such small dense charged silica particles would appear improbable were it not for the fact that particles of this type are known to exist as discrete ions containing as few as eight silicon atoms. As discussed later in connection with the structure of certain crystalline silicates, it is definitely possible for silica to form a compact octameric structure \((\text{HOSiO}_3)_8\) in which the silicon atoms are at the eight corners of a cube, each being linked through oxygen atoms to three other silicon atoms and each having one SiOH group which may ionize to give the polyanion \((\text{Si}_8\text{O}_{20})^{-8}\) (Figure 2.6). This unit is the beginning of a colloidal “particle” that is about 1 nm in diameter. However it is only after it is surrounded by further condensation of monomer that it becomes a “silica particle” having a core of SiO$_2$.

From the various cyclic polysilicate ions that exist in small amounts in solution as the SiO$_2$:Na$_2$O ratio exceeds 2:1, similar polycyclic oligomers appear as the first three-dimensional particulate “colloid” species. These then serve as nuclei as still larger colloid-ion species are formed at higher SiO$_2$:Na$_2$O ratios.

In my earlier book (29), I suggested possible structures of polysilicate ions on the assumption that the silicon might have a coordination number of six. Baker, Jue, and Wills had earlier proposed that polysilicate ions might thus be analogous to isopoly- or heteropolyacid anions (30). However, current evidence indicates that silicon still has a coordination number of four toward oxygen in silicate ions, as will be further
discussed. Accordingly, the present theory does not involve 6-coordinated silicon in any way.

The size of the polymeric or colloidal species in sodium silicate solutions can be estimated from various available data according to the foregoing theory, and can also be determined directly by several means including ultrafiltration, rate of reaction, and conversion to stable species which can be isolated.

According to Bacon and Wills (21) accurate pH values were measured on a silicate of \( \text{SiO}_2 \) : \( \text{Na}_2\text{O} \) molar ratio 3.36 and were reported at different concentrations of \( \text{Na}_2\text{O} \) in solution. Since the ratio of \( \text{SiO}_2 \) to \( \text{Na}_2\text{O} \) was constant, the silica concentrations are also known. Using the foregoing theory it is possible to estimate the particle size of the polymeric silica from its solubility, that is, from the concentration of \( \text{Si(OH)}_4 \) present.

Referring to symbols defined in Table 2.2, and assuming that the only silicate ion present is \( \text{HSiO}_3^- \),

\[
A = H + M'
\]
\[
S_t = M + M'
\]
\[
K_1 = \frac{MH}{M'} = 10^{-4.2} \text{ (value listed earlier)}
\]
\[
M = \frac{K_1M'}{H} = K_1 \frac{A - H}{H}
\]

For solutions containing 0.7-0.10% \( \text{Na}_2\text{O} \) the value of \( H/(A - H) \) is relatively constant and averages 0.008. This also indicates that all the silica can be accounted for as \( \text{Si(OH)}_4 \) and \( \text{HSiO}_3^- \) and that no disilicate is present. From this the concentration of \( \text{Si(OH)}_4 \) can be calculated:

\[
M = 10^{-4.2} \frac{M'}{H} = 10^{-4.2} \frac{A - H}{H}
\]

whence \( M \) is \( 10^{-2.1} \) or 0.0079 \( M \), or 474 ppm as \( \text{SiO}_2 \).

This value remains relatively constant over a sevenfold range of concentration. It is assumed that 474 ppm is the equilibrium solubility of the postulated colloidal silica component in silicate of molar ratio 3.36. From the formulas in Chapter 1 relating particle diameter to solubility (Figure 1.10b), the solubility is that of silica particles about 11 Å in diameter. From equations relating size to molecular weight, this corresponds to a molecular weight of \( 1.15 \times 10^{-21} d^3 \times 6 \times 10^{23} \), or 920, or about 15 silicon atoms per particle.

It is known that such polymeric species are present only when the molar ratio exceeds about 2 \( \text{SiO}_2 \) : \( \text{Na}_2\text{O} \). Hence in a solution of ratio 3.3, about \( (3.3 - 2.0)(3.3)^{-1} \), or 39%, of the silica is polymeric, whereas 61% is mostly monomeric. If the degree of polymerization of the higher molecular weight fraction is about 15,
The Nature of Silicate Solutions

Table 2.2. pH of Sodium Silicate Solutions

<table>
<thead>
<tr>
<th>% Na₂O</th>
<th>A</th>
<th>pH</th>
<th>H</th>
<th>M'</th>
<th>A - H</th>
<th>Sᵢ</th>
<th>(molar SiO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>0.226</td>
<td>11.20</td>
<td>0.00158</td>
<td>0.224</td>
<td>0.00705</td>
<td>0.380</td>
<td></td>
</tr>
<tr>
<td>0.35</td>
<td>0.113</td>
<td>11.00</td>
<td>0.00100</td>
<td>0.112</td>
<td>0.00892</td>
<td>0.190</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>0.0806</td>
<td>10.80</td>
<td>0.00063</td>
<td>0.080</td>
<td>0.00788</td>
<td>0.1354</td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>0.0484</td>
<td>10.60</td>
<td>0.00040</td>
<td>0.048</td>
<td>0.00829</td>
<td>0.0813</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>0.0323</td>
<td>10.40</td>
<td>0.00025</td>
<td>0.032</td>
<td>0.00784</td>
<td>0.0543</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.008</td>
</tr>
</tbody>
</table>

Source. Data from Bacon and Wills (21).

*a A = normality of total alkali in the solution; H = normality of OH⁻ = 10⁻¹⁴⁺ₚH; Sᵢ = total silica concentration as moles SiO₂ per liter; R = molar ratio of SiO₂:Na₂O = 3.36; R = 2Sᵢ/A and Sᵢ = 1.68 A; M' = normality of HSiO₃⁻; M = molarity of Si(OH)₄ = K₁ (A - H)/H, where K₁ = 10⁻⁴².

then one can calculate the number-average and weight-average molecular weights, which are 180 and 284. These values are at least of the same order of magnitude as the number-average molecular weight 280 found by Iler (63) by a cryoscopic method, and the weight-average molecular weight 325 found by Debye and Nauman (37) by light scattering. Aveston's (31) value of 900 by equilibrium centrifugation is probably higher because he measured the molecular weight in sodium chloride solutions. Extrapolation of his data at the lowest salt concentration (0.08 M) suggests a molecular weight of about 600 for this SiO₂:Na₂O ratio; in the absence of salt it would be still lower.

The question might be raised why the polysilicate fraction should not consist of a wide range of polyion or particle sizes. However, if this were the case, since the smaller particles are more soluble than the larger, rapid redistribution of silica would occur until all the charged particles were within a relatively uniform size range.

Ultrafiltration is another method by which at least an approximate idea of polymer size can be obtained. In an unpublished preliminary study, Iler used ultrafilter membranes having pores of known diameters.

The silicate solution is somewhat diluted, aged, clarified, and ultrafiltered in a rapidly stirred pressure cell at 50 psi. By following the concentration of SiO₂ and Na₂O in the filtrate one can calculate by difference how much of the silicate is polymerized to a size that will not go through the pores. Also, it can be shown that Si(OH)₄ and HSiO₃⁻ pass freely through the membrane so that the initial concentration of these species in the filtrate is the same as in the initial solution. The commercial sodium silicate solutions were diluted with an equal volume of water, aged about a week, filtered through fine filter paper to remove traces of suspended matter, and then ultrafiltered.
With sodium silicate of 3.75 ratio the following observations were made:

<table>
<thead>
<tr>
<th>Nominal Pore Diameter of Membrane (Å)</th>
<th>% of Silica too Large to Pass</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>38</td>
</tr>
<tr>
<td>24</td>
<td>25</td>
</tr>
<tr>
<td>33</td>
<td>15</td>
</tr>
<tr>
<td>52</td>
<td>0</td>
</tr>
</tbody>
</table>

In another series of tests using a single type of membrane with 18 Å pores, solutions of different ratios were tested:

<table>
<thead>
<tr>
<th>Molar Ratio SiO₂:Na₂O</th>
<th>% of Silica too Large to Pass Pores of 18 Å Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4</td>
<td>7</td>
</tr>
<tr>
<td>3.25</td>
<td>14</td>
</tr>
<tr>
<td>3.75</td>
<td>25</td>
</tr>
<tr>
<td>SiO₂:K₂O</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>25</td>
</tr>
</tbody>
</table>

In a further study by Iler a 3.25 ratio sodium silicate solution was diluted to 6% SiO₂ and diluted suddenly to 3% by addition to an equal volume of acid, giving a pH of 2. Ultrafiltration showed that about half of the silica would not pass a 24 Å filter. Only 7% of the silica remained as monomer.

As will be shown later, esterification of such silicic acid with n-BuOH gave an organosol that from the composition was calculated to consist of particles about 23 Å in diameter. Apparently when the silicate was acidified the monomer added rapidly to the colloidal nuclei already present. Since 14% of the silica had been particles of 11 Å size they would grow by addition of monomer to a calculated size of 11 × (93/14)² or 21 Å diameter, which is in reasonable agreement with the size calculated from the organosol.

The main conclusion is that colloidal species are present in solutions of sodium silicates having SiO₂:Na₂O ratios greater than 2:1 and that at higher ratios a greater proportion of the silica is present as polysilicate ions or particles generally smaller than 30 nm diameter.

These observations are consistent with the foregoing theory that the particles are in solubility equilibrium with Si(OH)₆, which in turn is in equilibrium with HSiO₃⁻.

Physical Studies

It is true that the results of some investigations in the past led to the conclusion that dimeric species were present in sodium silicate solutions. Thus measurements of dif-
fusion rates of silicate ions by Jander and Jahr (32) in 1940 and still earlier by Jander and Heukeshoven (33) indicated $\text{SiO}_2^{2-}$ is the principal ion present above pH 13.6, but between 13.6 and 10.9 the main ion present is disilicate, $\text{Si}_2\text{O}_3^{4-}$; below pH 10.9 polymeric ions are also present, whereas below about 9.0 the silica exists mainly as colloidal particles in equilibrium with $\text{Si(OH)}_4$.

However, it is possible that the lower diffusion rate ascribed to $\text{Si}_2\text{O}_3^{4-}$ might be due to $\text{HSiO}_3^{-}$ hydrogen-bonded to water molecules, or to a loosely hydrogen-bonded $[\text{O}_3\text{Si}^{1+}\text{H}_2 \text{SiO}_3]^{2-}$ complex and not to the formation of an oxygen-bonded dimeric ion. In any case, the exact nature of the dimer ions in silicate solutions, if present, remains to be determined.

Most investigators, especially since 1950, indicate that in aqueous 3.3:1 ratio sodium silicate solutions there are few dimer and trimer ions and the silica is distributed between monomer ions, $\text{HSiO}_3^{-}$ or $\text{SiO}_3^{2-}$, and three-dimensional polymer ions or charged particles. There is some evidence that a minor amount of cyclic tetramer ion may also be present.

Even in 1928, Harman (34) concluded from conductivity, transfer numbers, activity coefficients, hydrolysis, osmotic activity, freezing point data, phase relations, and diffusion experiments that there are only two simple silicates, $\text{Na}_2\text{SiO}_3$ and $\text{NaHSiO}_3$, and that silicates in the $\text{SiO}_2: \text{Na}_2\text{O}$ ratio range of 2:1 to 4:1 become increasingly “colloidal.”

Viscosity studies by Main (35) led to the conclusion that above a ratio of 2 $\text{SiO}_2$: 1 $\text{Na}_2\text{O}$, colloidal aggregates of some type were present, along with simple silicate ions. Hägg (36) reached similar conclusions from potentiometric measurements.

Nauman and Debye (37) carried out light scattering studies on carefully filtered solutions of different $\text{SiO}_2: \text{Na}_2\text{O}$ ratios and measured the following molecular weights (expressed as anhydrous $\text{SiO}_2$). They concluded that at ratios less than 2.0 there are no polymers or particles, but at higher ratios increasing amounts are present.

<table>
<thead>
<tr>
<th>Molar Ratio $\text{SiO}_2: \text{Na}_2\text{O}$</th>
<th>Average Mol. Wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.48</td>
<td>60</td>
</tr>
<tr>
<td>1.01</td>
<td>70</td>
</tr>
<tr>
<td>2.03</td>
<td>150</td>
</tr>
<tr>
<td>3.32</td>
<td>325</td>
</tr>
<tr>
<td>3.9</td>
<td>400</td>
</tr>
</tbody>
</table>

In a potassium silicate solution of 3.8 molar ratio, Brady, Brown, and Huff (38a) found an average molecular weight of 2000.

Using $^{29}\text{Si}$ nmr, Marsman (38b) examined solutions of sodium potassium and tetraethylammonium silicate with molar ratios of base:Si of 4:1 to 0.02:1. The following species were detected: tetrafunctional branching groups, $\text{Si(OSi)}_4$; trifunctional $(\text{HO})_2\text{Si(OSi)}_3$; middle groups, $(\text{HO})_3\text{Si(OSi)}_2$; end groups, $(\text{HO})_4\text{Si(OSi)}$; and orthosilicate, $(\text{HO})_3\text{SiO}^-$ . These are in equilibrium, and equilibrium constants were derived. With lower ratios of base to alkali, tetrafunctional groups predominate, indicating the presence of colloidal particles.
Engelhardt et al. (38c) reviewed similar studies reported up to 1975 and made more detailed measurements by which they identified different cyclic tetramers and double-ring trimer (a prism-like hexamer). Many types of ions are in equilibrium and as the ratio of Na:Si falls below 1.0 (SiO$_2$:Na$_2$O over 2.0), branching and cross-linking groups begin to predominate. This is in agreement with other types of evidence that as the SiO$_2$:Na$_2$O ratio exceeds 2:1, colloidal species begin to be present.

Infrared measurements can be used to identify simple silicate ions (absorption band at 950 cm$^{-1}$) and distinguish from polymeric species of molecular weight up to $10^4$ (absorption at 1120 cm$^{-1}$) (39).

In similar studies, Borisov and Ryzhenko (40) observed the absorption and reflection spectra (500-1700 cm$^{-1}$) to vary with the SiO$_2$:Na$_2$O ratio. In concentrated 1.5 ratio solution of (HO)$_2$SiO$_2$$^2-$, and (HO)$_3$(SiO)$_3$O$_4$$^4-$ the cyclic tetramer ion predominated, but disappeared when more alkali was added or when the solution was diluted. No dimer or trimer was mentioned.

Dilution with attendant depolymerization probably explains why Greenberg (41) concluded from a study of the literature and his own emf and conductance measurements that the data do not require postulating polymeric species even in solutions of 3 SiO$_2$:Na$_2$O ratio. However, careful measurements at different concentrations gave valuable information as to the variation of pK$_1$, the first ionization constant of Si(OH)$_4$ to HSiO$_3$$^-$, at different ionic strengths, the value being 9.85 at zero ionic strength.

By chronopotentiometric and thermogravimetric methods, Franks and Mukherjee (42) identified in a 2.5SiO$_2$:Na$_2$O ratio melt the ions SiO$_2$$^-$, Si$_2$O$_6$$^6-$, and Si$_3$O$_{10}$$^{8-}$ by their electroreduction potentials. However, there is no evidence that these ions retain their identity when the glass dissolves in water.

Using a technique developed by Sillén and co-workers, Lägerström (43) studied sodium silicate in 0.5 and 3.0 M solutions of sodium perchlorate to maintain constant ionic strength, measuring the emf values with a hydrogen electrode. For solutions corresponding to molar SiO$_2$:Na$_2$O ratios of 2:1 to 2.8:1 (1-0.7 negative charges per Si atom), the data can be explained by assuming that three monomeric species, Si(OH)$_4$, SiO(OH)$_2$$^-$, SiO$_2$(OH)$_2$$^2-$, and the tetramer Si$_4$O$_{10}$(OH)$_8$$^8-$ were present. In 3 M NaClO$_4$ solution some additional ions, Si$_2$O$_3$(OH)$_2$$^2-$, and Si$_3$O$_4$(OH)$_4$$^4-$, were postulated. Different SiO:Na$_2$O ratios were obtained by starting with various proportions of colloidal silicic acid, NaOH, HClO$_4$, deaerated water, and NaClO$_4$, solution with special precautions to exclude CO$_2$. Equilibrium constants were calculated for all species. As long as clear solutions (free from visible colloid) were involved, equilibria were attained rapidly.

In solutions where there were less than 0.75 negative charges per silicon atom (SiO$_2$:Na$_2$O = 2.67:1), the concentration of Si(OH)$_4$, reached the approximate solubility of colloidal silica (120 ppm at 25°C and 216 at 50°C), and colloidal species were formed. Thus sodium silicates with ratios higher than 2.6 contained not only monomeric ion species and tetramer, but also higher polysilicates or very small colloidal particles bearing negative charges.

Ingri (44a) carried out a similar series of pH titrations in a 0.5 M NaCl solution with similar results, and also gave further support to the existence of the tetramer
Si₄O₆(OH)₄²⁻. The following constants were reported:

\[
\begin{align*}
\log \beta_{1,1} \text{ at } 25^\circ C & \\
\text{Si(OH)}₄ + \text{OH}^- & = \text{SiO(OH)}_2^- + \text{H}_2\text{O} & 4.29 \pm 0.05 \\
\text{Si(OH)}₄ + 2 \text{OH}^- & = \text{SiO}_2(\text{OH})_2^- + 2 \text{H}_2\text{O} & 5.28 \pm 0.15 \\
4 \text{Si(OH)}₄ + 2 \text{OH}^- & = \text{Si}_4\text{O}_6(\text{OH})_4^- + 6 \text{H}_2\text{O} & 15.03 \pm 0.20
\end{align*}
\]

Following Ingri, Busey and Mesmer (44b) extended potentiometric studies to 290°C in 1 m NaCl solutions at silica concentrations of 0.005-0.05 m. The equilibrium quotients for the ionization of Si(OH)_4 to SiO(OH)_2^- and SiO_2(OH)_2^- were determined in 0.1-5 m NaCl up to 300°C. In the more concentrated (0.02 m) solutions at around pH 8-10 some of the silica was present as the polyanion Si_4O_6(OH)_4^³⁻, but the amount of this form decreased at higher temperature.

A more detailed picture emerges from ultracentrifuge studies of sodium silicate in 0.5-2 M NaCl solutions, by Aveston (31). He studied solutions in which each silicon atom carried from 0.5 to 1.0 charges, corresponding to SiO_2:Na_2O ratios of 2:1 to 4:1. The data suggest that although the cyclic tetramer may be an important component, there must exist a series of higher polymers in equilibrium, the average molecular weight increasing first gradually and then more rapidly as the SiO_2:Na_2O ratio is increased from 2:1 to 4:1. Converting the "hydroxyl number" (charges per Si atom) to SiO_2:Na_2O molar ratio, the following approximate average degrees of polymerization, hence average molecular weights, were found in 0.5 m NaCl solution. The molecular weight increased with the strength of the solution:

<table>
<thead>
<tr>
<th>Molar Ratio SiO_2:Na_2O</th>
<th>Degree of Polymerization</th>
<th>Mol. Wt. (as SiO_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>2.5</td>
<td>150</td>
</tr>
<tr>
<td>2.2</td>
<td>3</td>
<td>180</td>
</tr>
<tr>
<td>2.6</td>
<td>7</td>
<td>420</td>
</tr>
<tr>
<td>3.1</td>
<td>15</td>
<td>900</td>
</tr>
<tr>
<td>4.0 (extrapolated)</td>
<td>27</td>
<td>1600</td>
</tr>
</tbody>
</table>

In addition to monomers and tetramer, but no dimer or trimer, the polymers were assumed to consist of units containing q silicon atoms with p charges to which monomer and hydroxyl ions are added stepwise:

\[
B_{p,q} = \frac{[\text{Si}_q(\text{OH})_{q-p}^\text{p-}]}{[\text{Si(OH)}_4]^q[\text{OH}^-]^p}
\]

The authors did not assume any condensation of SiOH groups as polymerization progresses. However, the equation might be rewritten on the assumption that the particles contain anhydrous SiO_2 cores and a surface of Si(OH)_n with a certain portion of the hydroxyl groups ionized. Based on the maximum surface charge on larger
particles, about 40% of the SiOH groups on the surface are probably ionized. In this case, there would be a decreasing fraction of the total silica bearing negative charges, that is, the ratio of $p/q$ would decrease with molecular weight once the degree of polymerization reached about 10–12, above which all silicon atoms cannot be on the surface of roughly spherical particles.

For $p = q = 1$:

$$\log \beta_{1.1} = \frac{[\text{Si(OH)}_5^\text{3-}]}{[\text{Si(OH)}_4] [\text{OH}^-]} = 4.72$$

This value compares with 4.29 from Ingri's data (44a).

Electrical conductivity measurements on potassium silicate of SiO$_2$:K$_2$O molar ratios from 0.39 to 4.78 were made by Ivanov and Gur'eva (45). Anion mobilities were determined and interpreted on the basis of the usual assumption that (HO)$_n$SiO$_2$O is in equilibrium with [(HO)$_n$SiOSi(OH)$_n$]$_2^-$ and (HO)$_n$SiO$^-$. Dissociation constants of the silicate ion in dilute sodium silicate solution from 0 to 250°C were calculated from conductivity measurements by Ryzhenko (46).

The nature of silicate ions in molten Na$_2$SO$_4$, 10H$_2$O (m.p. 32.38°C) was extensively studied by Thilo and associates, who used the lowering of the melting point to establish the number-average molecular weight of the silicate ions (47–49). The degree of hydrolysis depended on the SiO$_2$:Na$_2$O ratio and not on concentration. At extreme dilutions the species Si(OH)$_n$, (HO)$_n$SiO$_2$O, and (HO)$_n$SiO$^-$ are present. At higher concentrations equilibria set in between these monomers and higher molecular weight anions or particles.

At equilibrium, the average molecular weight of the silica varied inversely with Na$_2$O content (50).

Higher degrees of polymerization were visualized as occurring stepwise. This could, of course, also be interpreted as a change in particle size:

$$(\text{H}_n\text{Si}_n\text{O}_{3n+1})^{n-} + (\text{HO})_n\text{SiO}^- = (\text{H}_n\text{Si}_{n+1}\text{O}_{3n+4})^{n+1-} + \text{H}_2\text{O}$$

A general equation was developed and an equilibrium constant calculated for SiO$_2$:Na$_2$O ratios from 2.0 to 3.34. However, the relation between these observations in molten Glauber's salt to the molecular weight distribution in water is not known.

Another approach by Thilo and associates (51) was to precipitate silicates from solution as the silver salts. Starting with SiO$_2$:Na$_2$O ratios of 1 and 2, the degree of polymerization of silica in the silver salt varied inversely with the silica concentration and content of neutral salt. It was suggested that the silver salt, containing one silver atom per silicon atom, was a linear polymer, although no viscosity or molecular weight measurements were made.

**Effects of Diluting Silicate Solutions**

Since the concentration of hydroxyl ions and pH are reduced when concentrated alkali metal silicate solutions are greatly diluted, it is not surprising that hydrolysis
of silicate ions occurs and a large part of the silica is converted to higher polymeric species or colloid along with a residual silicate of lower SiO$_2$:Na$_2$O ratio.

The electron microscope was used by McGarry and Hazel (52) to characterize the colloidal particles in 3.45 SiO$_2$:1 K$_2$O potassium silicate solutions which had been diluted out from 10 to 0.03% SiO$_2$ in various ways. The samples were further diluted to 0.015% SiO$_2$ just before being examined. When diluted directly to 0.03%, 89% of the particles were from 1 to 5 nm in diameter. When diluted to 0.3% silica and aged for an hour and then diluted to 0.03%, the number-average diameter was 8 nm.

The results indicate that when the solution is aged at a concentration of 0.3% the 1-2 nm colloidal particles that were in the original 10% silicate act as nuclei upon which the monomeric silica, liberated by hydrolysis of silicate ions, is deposited. On the other hand, when the 10% solution is diluted directly to 0.03% SiO$_2$ or 5 x $10^{-3}$ molar, the pH is 10.26 and all the silica passes into solution as Si(OH)$_4$ and H$_2$SiO$_4^-$ ions, and even the original 1-2 nm polysilicate ions or particles slowly dissolve. As seen in Chapter I, at pH 10.26 the total solubility of silica including Si(OH)$_4$ and H$_2$SiO$_4^-$ is around 0.05%. The authors used pincyanol chloride to detect the presence of colloid species. The dye micelles formed on the colloid by absorption shifted the color from blue to red (600 to 500 nm).

The further polymerization of the colloidal species owing to the lower pH when a 3.3 SiO$_2$:Na$_2$O silicate solution is diluted was also studied by Lehrman and Shuldener (53). They measured the amount of molybdate-reactive silica in solution over a period of days and found that at a concentration of about 0.14% SiO$_2$, the amount of reactive silica, presumably monomeric species, decreased over a period of 2 days, although some further drop was noted over 1 week. The same occurred at 0.07% silica but not at 0.03%, where complete depolymerization occurred and all the silica was molybdate-reactive within a few hours.

When 3.25 ratio sodium silicate solution is diluted to around 2% SiO$_2$ and heated for 1 hr, there is disproportionation whereby colloidal particles grow in size, while the SiO$_2$:Na$_2$O ratio of the so-called crystalloidal or dialyzable soluble silicate approaches 2.6:1 or 2.0:1, depending on dilution. It is my experience that during this time the solution is supersaturated with respect to amorphous silica so that any clean surface of glass or metal oxide becomes coated with a film of silica to a thickness of a few nanometers.

**Effect of Alkali Metal Salts and Other Coagulants**

The addition of a salt of a polyvalent metal to a solution of a soluble silicate results in formation of a precipitate of a metal silicate. In this precipitate, silicate ions are presumably linked together by the metal ions to form an insoluble network. On the other hand, the addition of a salt of a monovalent metal, for example, sodium chloride, to a solution of sodium silicate yields a precipitate that will redissolve if the system is diluted with water.

The alkali metal silicate is salted out especially easily when the ratio of SiO$_2$:Na$_2$O is greater than 2:1. The fact that the precipitate can be dissolved in water suggests that it may consist of polysilicate ions linked together by coordina-
tion through sodium ions; such linkages would persist only in the presence of a large excess of sodium ions.

Further details of the effects of a sodium salt such as the chloride or sulfate on a solution of sodium silicate have been summarized by Vail (1). Thus sodium chloride causes separation of a precipitate of sodium silicate which is more siliceous than the original solution. In smaller amounts, sodium chloride and also the sulfate and carbonate increase the viscosity of sodium silicate solutions. It appears that the added sodium salt coagulates the colloidal or high molecular weight polysilicate ions but has less effect on the metasilicate ions.

The effect of salts on the equilibria in a silicate solution was studied by Pevzner et al. (54) up to a NaCl concentration of 5 M, with silicon concentrations of 0.001–0.3 g-ion l⁻¹ in the pH range 10.2–14.0. Equilibrium was approached from lower and higher pH. The dissociation constants (pK) for water at 25°C in 0.5, 3, and 5 M salt solutions are 13.7, 14.1, and 15.2, respectively. The tetrameric silicate ion was detected, as had also been reported by others (44). It is noteworthy that no dimer or trimer was mentioned. The data are summarized in Tables 2.3 and 2.4.

The effect of salt on the degree of polymerization of the polysilicate ions in aqueous potassium silicate was examined by Brady, Brown, and Huff (55), using the light-scattering method. The molar ratio of SiO₂:Na₂O was 3.8:1 and in freshly diluted solutions the weight-average molecular weight of the SiO₂ was about 2000. When neutral salts were added, the apparent molecular weight increased in proportion to the fourth power of the salt concentration and in inverse proportion to the square root of silica concentration. In alkaline solution, the molecular weight varied with the temperature. The salt-induced polymerization at high pH was reversible upon dilution, but the acid-induced polymerization at neutral or lower pH was irreversible.

It seems likely that at high salt concentrations the cations act as cross-links between polyions through coordination with polysilicate oxygen atoms which replace coordinated water on the cations. This would be reversed when water is added. On the other hand, acid-induced polymerization leads to formation of siloxane (Si-O-Si) bridges between the polysilicate ions which are not broken upon dilution.

| Table 2.3. Composition and Stability of Silicate Ions at 25°C in 0.5, 3.0, and 5.0 M Aqueous Sodium Chloride Solution |
|-----------------------------------------------------|---------------------|---------------------|---------------------|
| Equilibrium                                         | Logarithm of the Equilibrium Constants in Solution with Ionic Strengths |
|                                                     | 0.5                | 2.0                | 5.0                |
| Si(OH)₄ + OH⁻ = Si(OH)₃⁻ + H₂O                   | 4.3 ± 0.1          | 4.6 ± 0.1          | 5.6 ± 0.2          |
| Si(OH)₄ + 2 OH⁻ = SiO₂(OH)₄²⁻ + 2 H₂O             | 5.3 ± 0.2          | 6.0 ± 0.2          | 7.1 ± 0.2          |
| 4Si(OH)₄ + 2 OH⁻ = SiO₄(OH)₄⁴⁺ + 6 H₂O            | 15.1 ± 0.3         | 11.0 ± 1.0         | 12.0 ± 1.0         |
| 4Si(OH)₄ + 4 OH⁻ = SiO₄(OH)₄⁴⁺ + 8 H₂O            | ~25                | ~27                | ~27                |

Source. Data by Pevzner et al. (54).
The Nature of Silicate Solutions

Table 2.4. Changes in Free Energy, Enthalpy, and Entropy for the Formation of Silicate ions in 5.0 M Aqueous Sodium Chloride Solutions at 25°C

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>$\Delta G$ (kcal g-ion$^{-1}$)</th>
<th>$\Delta H$ (kcal g-ion$^{-1}$)</th>
<th>$\Delta S$ (eu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.6 ± 0.3</td>
<td>1.0 ± 0.5</td>
<td>22 ± 3</td>
</tr>
<tr>
<td>2</td>
<td>9.7 ± 0.3</td>
<td>1.5 ± 0.5</td>
<td>28 ± 3</td>
</tr>
<tr>
<td>3</td>
<td>16.4 ± 1.5</td>
<td>3 ± 1</td>
<td>45 ± 8</td>
</tr>
</tbody>
</table>

Source. Data by Pevzner et al. (54).

* The types of equilibria are indicated by the numbers given in Table 2.3.

According to Prikhid'ko and Molchanov (56), the addition of alcohol or acetone to a solution of sodium metasilicate causes the formation of two liquid layers, the silicate accumulating in the lower layer. It seems probable that this is a simple dehydration of the silicate solution, the organic solvent removing water from the silicate solution and being immiscible because of the "salting-out" effect of the ions in the lower layer. Ordway (57) studied silicate of other ratios and concluded that organic solvents always precipitate a liquid or a solid phase containing a higher ratio of $\text{SiO}_2: \text{Na}_2\text{O}$ than the original aqueous solution of silicate. This indicates that, whereas the silicate separates from a fluid layer rich in organic solvent, the sodium hydroxide is soluble in this organic layer and thus leaves a silica-rich aqueous phase.

Ammonium hydroxide is similar to alcohol in its effect. Sodium hydroxide is soluble in strong ammonium hydroxide or liquid ammonia, but sodium silicate is not; a process of purification of sodium hydroxide from small amounts of sodium silicate has been patented by Muskat and Ayres (58a) in which, at certain high concentrations of ammonia and water, the ammonia-rich layer dissolves the sodium hydroxide, while the sodium silicate in the system accumulates in an immiscible lower layer.

Effects of this type are apparently involved in a process for depositing silica coatings on glass from a solution of sodium silicate containing a critical amount of a "clustering" or "coacervating" agent such as $\text{NH}_4\text{OH}$, $\text{Na}_2\text{SO}_4$, or $\text{CH}_3\text{OH}$ at ordinary temperature (58b).

Conversion to Silicic Acids

The nature of the silica in silicate ions in any alkaline solution cannot be determined by a chemical measurement that involves any change in the concentration of silica or alkali, electrolyte content, or temperature because these all shift the equilibrium between monomeric and various polymeric ion species. However, if a sample is simultaneously and instantaneously diluted and acidified to $\text{pH} 2$ at less than 30°C, the resulting silicic acid is sufficiently stable to permit characterization. The problem is to ensure that acidification is so sudden that the various silica species do not have time to polymerize or depolymerize as the $\text{pH}$ is dropped from the usual region of
Water-Soluble Silicates

11–13 to 1.5–2.0. At the same time the silica must be diluted to a concentration of 1% or less to minimize polymerization even at this pH where the rate is at a minimum. Also the temperature should be preferably at 0–5°C if the sample is to be stored for more than a few minutes.

As will be discussed in detail in Chapter 3, this technique has been shown by Alexander and others to allow the formation of Si(OH)$_4$ from Na$_2$SiO$_3$.9H$_2$O. Salt-free solutions can be obtained by ion-exchange techniques. Since conditions have been found for converting monomeric silicate ions to monosilicic acid, which is extremely prone to polymerize, it is evident that higher polysilicates can likewise be converted to the more stable polysilicic acids with even less difficulty.

By this means solutions of sodium metasilicate, Na$_2$SiO$_3$.9H$_2$O, especially when previously mixed with excess alkali, are shown by molecular weight measurements to contain monomeric ions, since only Si(OH)$_4$ is obtained by sudden acidification (59–61). Alexander (62) and Iler (63) described making a 0.1 M solution of monosilicic acid, Si(OH)$_4$, by stirring finely crystalline Na$_2$SiO$_3$.9H$_2$O into a suspension of a sulfonic acid type of ion-exchange resin in the hydrogen ion form at 0°C while maintaining the pH at about 3.0 with 10$^{-3}$ N HCl. The degree of polymerization was 1.1 by the freezing point method. Finely powdered Na$_2$SiO$_3$ was also successfully used.

Similarly, Iler (64) found that a 3.3:1.0 ratio solution of sodium silicate containing 12% SiO$_2$ could be added to the acid resin slurry to obtain silicic acid with a number-average molecular weight of 200, as SiO$_2$. A more dilute solution containing 2% silica gave product with molecular weight of 180 (63). This value compares with 325 found by Nauman and Debye (37) in a more dilute solution of sodium silicate where the lower pH permits some further polymerization of the polysilicic ions.

Reaction with Molybdic Acid

The history and use of the silicomolybdate method for analyzing for soluble silica has been discussed in Chapter 1. It is sufficient here to point out that molybdic acid reacts only with monomeric silica to form the yellow silicomolybdate acid. It is fortunate that the reaction with molybdic acid occurs at pH 1–2, where silicic acid polymerizes least rapidly. Thus polymeric silica must first depolymerize before it can react; hence the higher the degree of polymerization, the longer the time required for depolymerization and color development. This is reviewed in detail in Chapter 3.

This method of characterization of soluble silicates is complicated by the fact that a given type of silicate can give different results if not allowed to age under fixed conditions of concentration and temperature until equilibrium has been established. For example, samples of 3.25 ratio sodium silicate were diluted by Iler from a silica concentration of 400 gl$^{-1}$ to 200 and 100 gl$^{-1}$, and each was divided into two parts: (a) aged at 30°C for 6 hr, and (b) held at 100°C for 6 hr, then cooled and aged at 30°C for 6 hr.

A 50 µl sample of each relatively concentrated silicate solution was injected suddenly from the tip of a microsyringe reaching to within a few millimeters of a high
speed stirrer in 50 ml of the molybdcic acid solution. Ionic species react in less than 10 min, whereas most of the colloidal or polysilicate species require more than 20 min.

Owing to depolymerization upon dilution, the proportion of colloid or polysilicate decreased from about 70% at a silica concentration of 400 g l\(^{-1}\) to 45% at 100 g l\(^{-1}\). However, heating a solution at a given concentration and then cooling had little or no permanent effect at these high concentrations, since equilibrium was reestablished at 30°C in a few hours. This conclusion was also reached by O’Connor (65), who carried out similar experiments on concentrated silicates of different ratios. He found that solutions with SiO\(_2\) : Na\(_2\)O ratios of 0.5–2.4 contain only a minor proportion of polysilicate ions, but there is a marked increase in polysilicate (or colloid) content as the ratio increases from 2.4 to 2.8 and higher ratios. He proposes a rate equation whereby the molybdic acid reaction rate constant can be correlated with molecular weight as determined by light scattering. He showed that the distribution of the ionic species depended mainly on concentration and that equilibrium was reached quickly even when the solution was diluted from 400 g l\(^{-1}\) to 20 g l\(^{-1}\) of SiO\(_2\) and did not change further in 2 weeks at 25°C.

Reaction rates of specific polysilicic acids with molybdic acid have also been measured by Wieker and Hoebbel (66), whose data indicated the time required for 95% of the silica to react was about 1.5 min for monosilicic, 2.5 min for disilicic (almost indistinguishable in a mixture), and 9.5 min for the cubic octasilicic acid. The authors later expressed the rates as reaction velocity constants, \(k_{HM}\), for higher molecular weight species. The rate constant was approximately inversely proportional to the molecular weight of the polysilicic acid (67). From their data the average degree of polymerization \(n_i\), the number of silicon atoms per polysilicic acid molecule, can be related to the reaction rate constant:

\[
k_{HM} = 2 n_i^{-\frac{1}{1.1}}
\]

Coudurier, (68b) further investigated these reactions and proved that mono- and disilicic acids both react directly with molybdic acid, the latter only half as rapidly as the former. Higher polymers all must depolymerize to the monomer before reaction can occur. In this way an empirical relation between molecular weight of the polymer and the rate of formation of silicomolybdic acid was worked out (see Chapter 3).

Thilo, Wieker, and Stade (68a) standardized the molybdate reaction with silicate species and calculated the characteristic reaction rate constants:

\[
k = 2.3 (t_2 - t_1) [\log (1 - r_2) - \log (1 - r_1)]
\]

where \(r_1\) is the fraction of silica converted to silicomolybdate in \(t_1\) min and \(r_2\) in \(t_2\) min. Plotting \(-\log(1 - r)\) versus \(t\), usually gives a linear section with a constant slope between times \(t_1\) and \(t_2\) from which the constant can be calculated.

Certain anhydrous crystalline silicates known to contain SiO\(_2\)\(^{2-}\) ions, such as Na\(_2\)H\(_2\)SiO\(_4\) \(\cdot\) 8H\(_2\)O (Na\(_2\)SiO\(_3\) \(\cdot\) 9H\(_2\)O), Ca\(_2\)SiO\(_4\), Li\(_2\)SiO\(_4\), and MgK\(_2\)SiO\(_4\), all gave the
same constant, which was therefore characteristic of monomeric silica. Other
crystals known to contain the disilicate ion such as Ca₂Na₂Si₂O₇ and Na₆Si₂O₇,
served as standards for dimeric silica.

For monomer, $k = 1.7 \text{ min}^{-1}$ and for dimer, $k = 0.90 \text{ min}^{-1}$. The constant for
cyclic tetramer was about half that of the dimer, using (KH)₂Si₄O₁₂ as the standard.

A solution of SiO₂:Na₂O ratio of 2:1 was shown to depolymerize with increasing
dilution. Thus in a solution 1.0 M in SiO₂, the molybdate reaction curve was very
similar to that of cyclic tetramer. However, upon dilution to 0.1 M it acted like
dimer and at 0.01 M it had hydrolyzed to monomer.

Conversion to Esters of Silicic Acids

Some indication of at least the maximum size of the silicate species in a solution of
sodium silicate of 3.3 ratio SiO₂:Na₂O has been obtained from the nature of the cor-
responding silicic acid ester (69). Silicic acid of low molecular weight is so unstable
in aqueous solutions that any attempt to isolate it by evaporation of water, even at
ordinary temperature, results in rapid polymerization to a gel. The direct esterifica-
tion of silicic acid therefore remained impractical until the discovery of Kirk (70) of
a method for transferring silicic acid of low molecular weight from aqueous solution
to solution in an alcohol. This transfer is accomplished by extraction of the acid with
a suitable polar organic solvent, simultaneously saturating the aqueous phase with
sodium chloride in order to salt the silicic acid into the organic phase. An alcohol
such as n-butyl alcohol is then added, and esterification is effected by azeotropic dis-
tillation of water from the alcohol solution (29).

The polysilicic ester, which is a tacky resin after the butanol is removed under
vacuum, typically contained around 25% carbon and 62% SiO₂. The composition
can be expressed in terms of the molar ratios (C₅H₁₂)₂O:SiO₂ = 0.25 and H₂O:SiO₂
= 0.22.

Viscosity studies showed that polymer consisted of units of spherical rather than
elongated shape. From the composition it can be calculated that the ratio of
hydroxyl plus butoxy groups to silicon is 0.95, which would be the OH:Si ratio in
the corresponding silicic acid. Referring to the formula in Chapter 1 relating particle
size to composition of surface-hydroxylated silica particles, OH:Si = 24.6d²/11.5d₄,
the particle diameter is estimated to be 2.3 nm.

The monomeric and low molecular weight species in the original silicate had
polymerized onto the higher molecular weight polysilicate or colloid fraction, which
has been shown to consist of particles about 1.0–1.5 nm in diameter, so that the final
particle diameter in the ester is somewhat larger.

Conversion to Trimethylsilyl Derivatives of Silicic Acids

The various ion species which might be found in sodium silicate solutions can be
found in pure form only in certain crystalline silicates. Lentz (71) first announced in
1963 that the silica in selected minerals in which the ionic structure is known from
X-ray diffraction data can be converted to the corresponding trimethylsilyl deriva-
tives. Thus olivine, \((\text{MgFe})_2\text{SiO}_4\), contains monomeric silica which can be isolated as \([\text{(CH}_3\text{)}_2\text{SiO}]_2\text{Si}\). Hemimorphite, \(\text{ZnSi}_2\text{O}_4(\text{OH})_2\cdot2\text{H}_2\text{O}\), contains dimeric silica, isolated as \([\text{(CH}_3\text{)}\text{SiO}]_2\text{SiOSi}[\text{SiO( CH}_3\text{)}]_2\). Similarly, natrolite, \(\text{Na}_2(\text{AlSi}_3\text{O}_8)\cdot2\text{H}_2\text{O}\), furnishes the linear trimer, and laumontite, \(\text{CaAl}_2\text{Si}_2\text{O}_7\cdot4\text{H}_2\text{O}\), gives cyclic tetramer, which is isolated as \([\text{(CH}_3\text{)}_2\text{SiO}]_2\text{Si}_2\text{O}_5\).

Lentz then obtained the most direct and convincing evidence of the true nature of the silica in sodium silicate solutions (72a) by developing a technique for converting the silicate species to the corresponding organosilyl derivatives and isolating them by distillation and gas chromatography. Conversions and yields were less than perfect and the study was made on 1 M silicate solutions where some hydrolysis and polymerization is known to occur, as compared with the concentrated solutions of commerce. Also, it must be pointed out that since the technique involves the transient formation of silicic acid, some polymerization may occur under the locally acidic conditions to form dimer and trimer that may not be present in the original alkali silicate.

The results showed that there is always less dimer than monomer and less trimer than dimer, but a significant quantity of tetramer in the diluted solution with \(\text{SiO}_2:\text{Na}_2\text{O}\) ratio of 2:1. Colloidal species comprised an increasing fraction of the total silica with increasing \(\text{SiO}_2:\text{Na}_2\text{O}\) ratio. At 2:1 ratio (\(\text{Na}:\text{Si}\) ratio of 1) it amounted to 45% of the silica and at 3.3:1 ratio it was about 70%.

The colloidal species were converted to silyl derivatives having \((\text{CH}_3)_2\text{SiO}_4)\cdot\text{SiO}_2\) molar ratios of 1.32–1.05. Lentz concluded that these were spherical particles, on the basis of which the diameter was deduced to be 10–15 Å.

The fact that the solutions were somewhat dilute, containing only 6% by weight of \(\text{SiO}_2\) (1 M), no doubt permitted some hydrolysis and polymerization to occur. As shown by Thilo, Wieker, and Stade (68a) still further dilution results in depolymerization to dimer and then monomer. In 1 M metasilicate solution (\(\text{SiO}_2:\text{Na}_2\text{O} = 1:1\)), 22% of the silica was colloidal, 10% was cyclic tetramer, 7% linear trimer, 12% disilicate, and only 26% monomer. (Total recovery was 76%.) However, in concentrated metasilicate solution and in \(\text{Na}_2\text{SiO}_3\cdot9\text{H}_2\text{O}\) it has been shown that under carefully regulated conditions, most of the silica is monomeric by reaction with molybdic acid.

Glasser and Sharma (72b) compared different procedures for trimethylsilylation of the silica in sodium metasilicate solution (\(\text{Na}_2\text{O}:\text{SiO}_2 = 1:1\)). The proportion of polysilicate ions in solution decreased with dilution from 1 to 0.001 M, where only monomer was found. Even in 1 M solution only a third of the silicate was monomeric.

Conditions for reacting \((\text{CH}_3)_3\text{SiCl}\) with minerals in various reaction solvents were investigated by Götz and Masson (73), who found that a small amount of water must be present, hexamethyldisiloxane and isopropyl alcohol are beneficial, and conditions must be carefully controlled to minimize degradation or polymerization, to obtain an optimum yield of the trimethylsilyl derivative of the original silicate ion. Subsequently it was found that sodium silicate was especially difficult to react without polymerizing the silica species to some extent (74).

The structure of ions in numerous crystalline silicates has been further elucidated
by converting the individual silicate ions directly to trimethylsilyl derivatives, which were identified after separation by thin-layer chromatography. This is possible if the derivatives are soluble, that is, if the silicate ion exists as isolated units and not as infinite chains or three-dimensional siloxane networks. Thus Wieker and Hoebbel (66) showed that when Li₂H₂SiO₅ solution is concentrated over H₂SO₄, the ions are largely present as cyclic tetrasilicate. Also, crystalline Na₂�₂O·2CaO·3SiO₂ actually contains cyclohexasilicate ions and should be formulated Na₈Ca₄(Si₉O₁₈).

Similarly, these authors (75) converted the following silicates to the corresponding trimethylsilyl (T) derivatives which are used as standards for the identification of individual silicic acids:

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Formula</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂H₃SiO₅·H₂O</td>
<td>T₉SiO₄</td>
<td>Monomer</td>
</tr>
<tr>
<td>CaSiO₄</td>
<td>T₉SiO₄</td>
<td>Monomer</td>
</tr>
<tr>
<td>Na₄(Si₂O₇)</td>
<td>T₉Si₂O₇</td>
<td>Dimer</td>
</tr>
<tr>
<td>Na₄Cd₄(Si₂O₈)</td>
<td>T₉Si₄O₁₀</td>
<td>Linear trimer</td>
</tr>
<tr>
<td>SiO₂Cl₁₀</td>
<td>T₁₀Si₄O₁₃</td>
<td>Linear tetramer</td>
</tr>
<tr>
<td>(CaSiO₅)₁₀</td>
<td>T₉Si₅O₉</td>
<td>Cyclic trimer</td>
</tr>
<tr>
<td>(KHSiO₃)₆</td>
<td>T₉Si₆O₁₂</td>
<td>Cyclic tetramer</td>
</tr>
<tr>
<td>[CH₃N⁺]₁₀Si₄O₁₉·xH₂O</td>
<td>T₁₀Si₅O₁₉</td>
<td>Tricyclic heptamer</td>
</tr>
<tr>
<td>[CH₃N⁺]₅Si₈O₂₀·69H₂O</td>
<td>T₉Si₈O₂₀</td>
<td>Cubic octamer</td>
</tr>
<tr>
<td>[Cu(en)₂]₄SiO₂₀·3H₂O</td>
<td>T₉Si₉O₂₀</td>
<td>Cubic octamer</td>
</tr>
</tbody>
</table>

In this octamer, referred to as a "double-four-ring" structure there are eight silicon atoms at the corners of a cube.

**Silicates with Coordination Numbers Four and Six**

It has been previously theorized that in aqueous silicate solution silicon is coordinated with six oxygen atoms. Such views of Weyl (76) and Treadwell and Wieland (77) were discussed by Iller (78). However, more recent spectroscopic studies of silicate solutions seem to indicate that the silica is 4-coordinated with oxygen and that the Si(OH)₄²⁻ ion, for example, does not exist, at least in solution. Fortnum and Edwards (79) concluded that Si(OH)₄²⁻ was not present in solution because Raman lines analogous to those of SiF₄²⁻, PF₆⁻, and Te(OH)₆ were not found. The four low intensity lines found at 448, 607, 777, and 935 cm⁻¹ suggested that the ion is (HO)₄SiO₄⁻ since it is similar to (HO)₄PO₄⁻, which gives lines at 401, 511, 885, and 1050 cm⁻¹.

Similar conclusions were reached by Early et al. (80), who also noted the similarity of Raman spectra of (HO)₄SiO₄²⁻ and (HO)₄PO₄. Using H₂O and D₂O, Freund (81) examined silicate solutions with Raman-laser spectra and identified (HO)₃SiO₃⁻, (HO)₂SiO₄²⁻, and (HO)₃SiO₅²⁻, the latter only at very high alkali concentrations. Equilibrium was obtained rapidly and completely. There was no evidence for the presence of dimer species.
On the other hand, it is likely that most reactions of silica and silicates in aqueous solutions do involve a temporary expansion of the coordination number from 4 to 5 or 6. Also in certain crystalline silicates, the silicon atom is coordinated with six oxygen atoms, for example, in thaumasite (82). This was also confirmed by Edge and Taylor (83), who worked out the structure of this calcium silicate sulfate carbonate crystal and demonstrated the presence of Si(OH)₆²⁻ ions.

It is in the hydrated metasilicate crystal that one might expect the silicon atom most likely to be surrounded by six hydroxyl ions, but Jamieson and Glasser have shown that this is not the case (84). In Na₂SiO₃·9H₂O they find by X-ray structure analysis that silicon is surrounded by only four oxygen atoms. The sodium ions are surrounded by six oxygen atoms and the more appropriate constitutional formula is Na₂[(HO)₂SiO₄]·8H₂O. By similar procedures, Jost and Hilmer (85) found a similar structure and concluded that isolated SiO₄ tetrahedra are linked through hydrogen bonds into layers, separated by layers of sodium and water. The same formula was arrived at by quite a different method. The nature of Na₄SiO₃·xH₂O, where x is 9, 6, or 5, was investigated by Thilo and Miedreich (86) by hydrolyzing the salt in wet alcohol. From analysis of residue it was concluded that the salt should be formulated as Na₂[(HO)₂SiO₄]·yH₂O, where y is 8, 5, or 4. A hydrated so-called “disilicate,” is formulated as Na₄[(HO)₂SiO₄]·yH₂O, which has the same structure as Li[(HO)₂PO₄] and is actually monomeric.

From infrared spectra, Borisov and Ryzhenko (87) conclude that in solutions of sodium metasilicate (SiO₂:Na₂O ratio of 1:1) there are mainly ions of (HO)₂SiO₄²⁻ with some cyclic tetramer (HO)₆(Si₂O₇)O⁻⁴, which increases in concentration with increasing ratio, and also that silicon is coordinated with four oxygen atoms.

Thus, except in very rare instances, the silicate ions in solution or in crystals appear to contain silicon with a coordination number of four.

**SOLUTIONS OF POLYSILICATES**

For many years it was supposed that alkali silicate solutions with SiO₂:Na₂O ratios higher than 4:1 could not be made. The corresponding glasses are not homogeneously soluble in water. Attempts to dissolve quartz or amorphous silica powders in a minimum of NaOH solution to achieve the desired higher ratios were not successful. Liquid silicates with ratios higher than 4:1 were sought for use in adhesives because the lower alkali content was anticipated to furnish bonds that are more water resistant. Also, in refractory compositions, lower alkali was needed to raise the softening point and improve refractory character.

As discussed at the beginning of this chapter, silicates with SiO₂:Na₂O ratios of 4:1 to about 25:1 are usually referred to as “polysilicates.” They do not have the high content of sodium and silicate ions as do the conventional soluble silicates, which have ratios less than 4:1. However, they contain much more alkali than necessary to stabilize sols of smallest particle size manufactured and sold as colloids.

The borderline between a polysilicate solution and an “alkali-stabilized sol of colloidal silica” can logically be drawn at the particle size of the silica below which the increased solubility of the silica as Si(OH)₄ at ordinary temperature causes the
particles to grow spontaneously unless more alkali is added. However, when particles less than 5 nm in size are stabilized against growth by adjusting the ratio to less than 25:1, an increasing and substantial fraction of the silica is converted to silicate ions. Thus a "polysilicate" solution may be considered to be an equilibrium mixture of ionic and negatively charged particles of colloidal silica of such extremely small size that they can be classed also as polyanions.

Because lithium silicates are so different in behavior from sodium and potassium silicates, lithium polysilicate is discussed separately.

**Sodium Polysilicate**

The advantage of a binder having a SiO$_2$:Na$_2$O ratio of 10:1, for example, is demonstrated by the fact that such mixtures of an alkali metal silicate and a colloidal silica sol are proposed for making waterproof fireproof coating mixtures even though the mixtures have a short shelf-life (88).

During the development of concentrated silica sols stabilized with NaOH around 1950, it was realized that the smaller the particle size, the more alkali and the lower the SiO$_2$:Na$_2$O ratio required for stabilization. However, in the ratio range of about 4:1 to 25:1 the concentrated compositions were generally found to be unstable, and eventually gelled. When a 3.25 ratio sodium silicate solution was added to a concentrated silica sol to reduce the SiO$_2$:Na$_2$O ratio from 100:1 to 5:1, for example, a gel immediately formed. However, Iler (89) found that by aging or warming the mixture, a stable liquid was again obtained. Thus solutions with ratios from 4.2:1 to 6:1 containing 10–30% SiO$_2$ could be prepared from sols originally containing typically 5–25 nm particles. However, longer heating destabilizes the mixture and an insoluble crystalline polysilicate or gel appears. the polysilicate solution is a clear, transparent fluid of low viscosity in which around half of the silica is present as soluble or ionic silicate, as shown by its reactivity with the molybdic acid reagent. Thus much of the silica that was introduced as colloid remains as such, but the particle size is smaller owing to some depolymerization at equilibrium.

The unique nature of the product is shown by the fact that when it is mixed with a silica sol containing an equal weight of 7 nm colloidal silica along with a sol containing an equal weight of colloidal silica as 100 nm particles, there is formed a mixture which, when cast as a film on glass, dries at 150°C to a clear, hard, adherent, water-resistant coating. The spaces between the 100 nm particles are filled by 7 nm particles and the spaces between these by the still smaller colloidal component of the polysilicate and, in turn, the remaining spaces of molecular size by the soluble ionic silicate species. Once dried, the sodium apparently is adsorbed on the extensive silica surface so that no soluble silica remains and the film is impervious.

Instead of starting with a sol of preformed particles, Oken (90) claimed that by starting with a low molecular weight solution of silicic acid, temporarily stable liquids could be obtained with SiO$_2$:Na$_2$O ratios in the range 4:1 to 6:1, as in Iler's composition, and also from 8:1 to 40:1.

More recently, compositions with ratios higher than 4:1 have been prepared by heating an amorphous silica powder with 3.22 ratio sodium silicate to above 100°C