

THE COLLOID SCIENCE OF SILICA AND SILICONES

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ABSTRACT

A detailed explanation of the most important properties of natural and synthetic silica and silica gels is given. Specific reference is made to the differences between the formation of synthetic silica gels and of quartz and cristobalite. The effect exerted by the synthetic products is explained and the importance of their amorphous condition on their reactivity is also referred to. On the basis of ultra- and electron-microscopic studies it is demonstrated that these synthetic products are not crystalline, but amorphous aggregates, and it is also shown how their reactivity can be increased by appropriate dispersion before use.

The colloidal properties of silicone resins are then pointed out and their production explained. Their advantages over purely organic matter and the reasons for this difference are also referred to.

Finally, reasons are given why more attention must be paid to colloid science in any field where silica or silicones are studied or put to use.

INTRODUCTION

In the Preface to his book, "The Colloid Chemistry of the Silicate Minerals" Marshall (1949) stated that duplication of effort in his field had been rare and that the rapid progress which has been made was due in no small measure to the general overriding of traditional subject-matter boundaries. Marshall deserves much credit for having been the first to make a basic general contribution to the colloid chemistry of clay minerals and to admit some of its shortcomings.

Iler (1955), in the preface to his book, "The colloid chemistry of silica and silicates," wrote that although the subject is narrow, since it deals only with certain phases of the chemistry of silica and silicates, it is broad because it traverses diverse fields of technology. He drew references not only in chemistry, but also geology, mineralogy, agronomy, zoology, and many phases of industrial chemistry. In closing he expressed the hope that the material he presented was at least representative of what is available.

My recent book is entitled "Silicic Science" (Hauser, 1955a). Unfortunately, far too many scientists still overlook the fact that we are dealing here with surface phenomena that straightforward chemistry cannot explain. Even in the days when disagreements between physicochemists and men working in the field of colloids were still very strong, some writers had already used other words than "chemistry" in discussing colloidal phenomena. The time has now come when we must realize that the element silicon is at least as important as the element carbon. For this reason I have taken the liberty of classifying the colloidal phenomena connected with the element silicon as a science of its own, and have therefore titled my book "Silicic Science."

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The present paper will discuss only the colloidal problems of natural and synthetic silica and of silicones, since I have discussed the silicates at previous Conferences (Hauser, 1954, 1955).

SILICA

Every colloidal particle carries on its surface an electric charge which must be counterbalanced by ions of opposite sign. The electric charge, or electrokinetic potential, and solvation are predominant in controlling the stability of colloidal sols. The electric forces associated with a given colloidal particle arise from two sources. One set of forces is due either to the ions, predominantly of one sign, which are rigidly adsorbed on the surface of the particle, or to those ions which are located in the surface but are not fully saturated. The other forces are due to the ions of opposite sign which are gathered about the particle in an effort to neutralize the charge which the particle actually carries. However, the total number of ions which gather about the particle are not sufficient to neutralize its charge. One must consider also the solvation or hydration of the adsorbent surface and that of the adsorbed ions. The colloidal particles consist of a charged nucleus which is surrounded by a more or less extended diffuse ionic atmosphere. It is the nucleus and the bound dipoles of the dispersion medium which constitute the colloidal micelle (Fig. 1). Owing to the adsorption of ions from the dispersion medium by the colloidal particle, or to the dissociation of ions from its surface into the dispersion medium, the latter will possess an excess of ions of a charge opposite to that of the particle.

The term "colloidal micelle" was coined by J. Duclaux (1908). According to him it is a colloidal particle composed of its nucleus and all the ions and molecules that have been attracted to it.

"Colloidal silicic acid" refers to fluid mixtures that contain hydrated silica. The term "silicic acid gels" refers to semisolid and partially elastic masses which

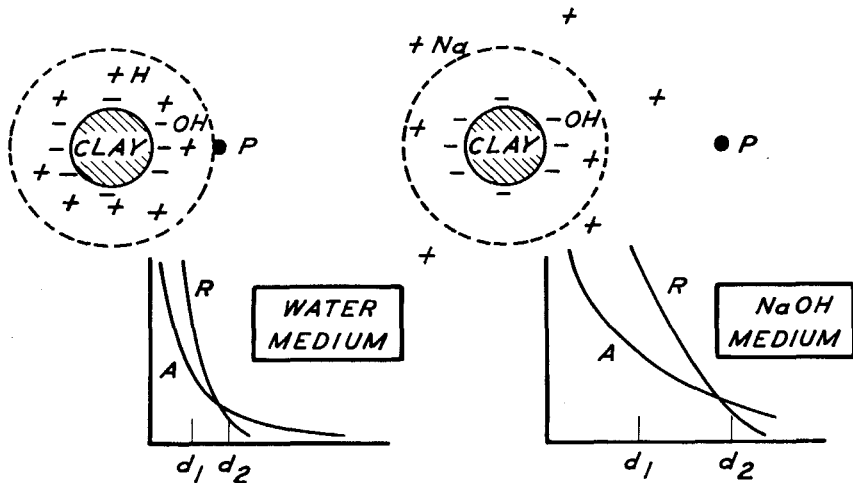


FIGURE 1. — A clay micelle dispersed in pure water (left) and in sodium hydroxide (right).

are due to the setting of the colloidal silicic acid to a gel. In contrast thereto, the term "silica gel" refers to the harder and partially or entirely dehydrated product. Its occurrence has been discussed by Weyl and Hauser (1951) and Hauser (1955a).

One is dealing here with a polymerization process of the $\text{Si}(\text{OH})_4$ molecule which leads to units in which the Si^{4+} ion is octahedrally surrounded by six $(\text{OH})^-$ ions. In the anhydrous silica each Si^{4+} ion is tetrahedrally surrounded by four O^{2-} ions and each of them is shared by two silicon ions. The number of H_2O molecules which can come close to the Si^{4+} ion is restricted by space requirements and by the dipole-dipole repulsion between the oriented H_2O molecules. Because of their lower polarizability, H_2O molecules cannot screen the potential field of the Si^{4+} ion as effectively as the same number of the more polarizable $(\text{OH})^-$ ions. This causes polymerization and leads to the formation of chainlike molecules because the end members have incomplete coordination and their requirements can be met by their reacting with monomer $\text{Si}(\text{OH})_4$ molecules (Fig. 2). The length of the chains or the size of the formed macromolecules depends on such factors as the rate of polymerization, the pH of the solution, its concentration of silica, and on the temperature and the presence of foreign molecules. The formation of such chainlike molecules makes possible a condensation reaction.

When colloidal silicic acid is first formed it consists of comparatively very small molecules but it condenses or polymerizes fairly rapidly. All the molecules aggregate and form larger groups or micelles. The particles of the silicic-acid

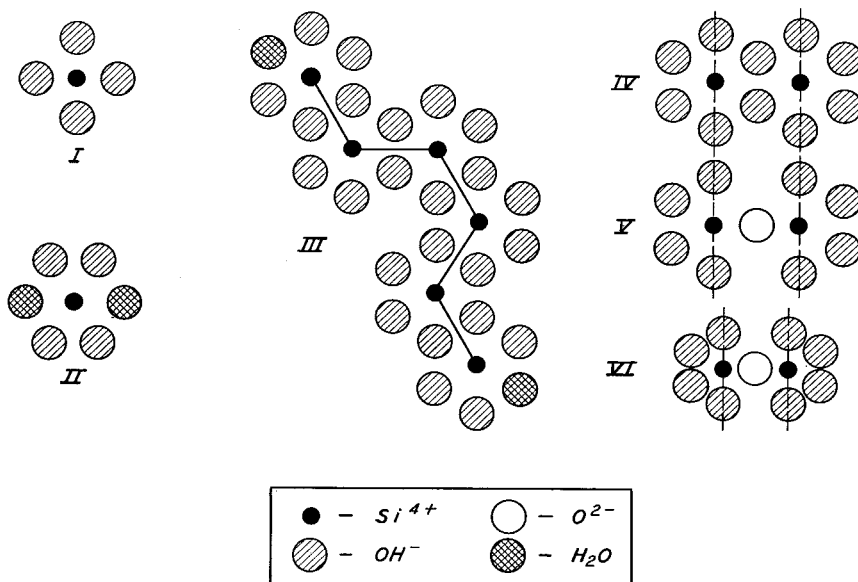


FIGURE 2. — Condensation polymerization of orthosilicic acid molecules. IV-VI explain the phenomenon of condensation and the syneresis of the final particle (W. A. Weyl).

sol carry a net negative charge in alkaline and neutral solutions, and even in weakly acid solutions. In strongly acid solutions, however, the particles exhibit a positive charge. Contrary to previous assumptions, the charge is not due to preferential adsorption of ions, but to the ionization of the silicic acid itself.

Of the four general theories which have been postulated to explain the structure of silicic-acid gels, only the fibrillar or micellar theory offers a truly satisfactory explanation of the phenomena observed; it is also in full agreement with experimental evidence that when silicic acid is first formed it is present as very simple molecules of low molecular weight, but as time goes on it condenses and the molecular weight increases to large values. For this reason the product becomes more and more insoluble as condensation proceeds. The phenomenon of dilatancy (and even elasticity to a considerable extent) in colloidal silicic acid gels also favors the fibrillar theory.

We are indebted to C. B. Hurd (1938) for an important extension of the theory: that condensation polymerization will occur whenever the positive and negative ions that contain the silicon come in close contact. This causes a release of water which, however, remains combined with the structure of silica gel by adsorption.

Figure 3 shows an ultraphotomicrograph of dry SiO_2 , whereas Figure 4 represents the same product after it had been placed in water. These figures clearly demonstrate that we are dealing with aggregated silica particles.

X-ray diffraction patterns of three different types of silica gel reveal that they are all amorphous in structure, and differential thermal analysis of silica gels

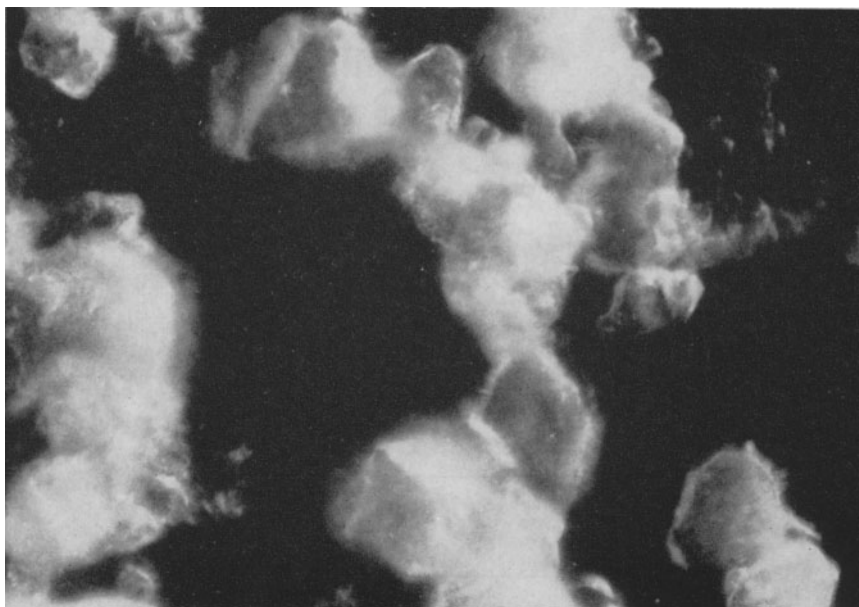


FIGURE 3.—Ultrapak photomicrograph of silica gel. Original magnification 550 \times .

shows a more or less pronounced but in no case drastic endothermic peak between 140° and 175° C, which is absent in the cooling curve. These results clearly indicate that the initial endothermic peak is due to adsorbed water on the surface of the material, but there is no loss of lattice water as in most clay minerals (Fig. 5).

On the basis of all these results we can now offer an explanation for the exceptionally high reactivity of the synthetic silica gels used as catalysts, since even the largest particles are only agglomerates of extremely small particles which form highly porous clusters, and the over-all surface is therefore very great. The fact that all these synthetic compounds are amorphous increases their reactivity because it assures the most reactive surface composition. This also explains the noticeable increase in reactivity of these gels in a humid atmosphere.

All these results offer further proof for the theory that the reactivity of silica gels is based primarily on the ionic structure of their surfaces and that the interior crystal lattice, if existing, is of secondary importance only.

Weyl (1949) deserves special credit for having been the first to point out clearly why more attention must be paid to those properties of glasses which depend specifically on the surface configuration and composition. I quote from his original contribution:

To compare the forces between silicon and oxygen in silica glass with those in cristobalite or quartz, one must assume a broad distribution of binding forces in the random structure of the glass and a well-defined bond strength in the highly symmetrical cristobalite. The lower

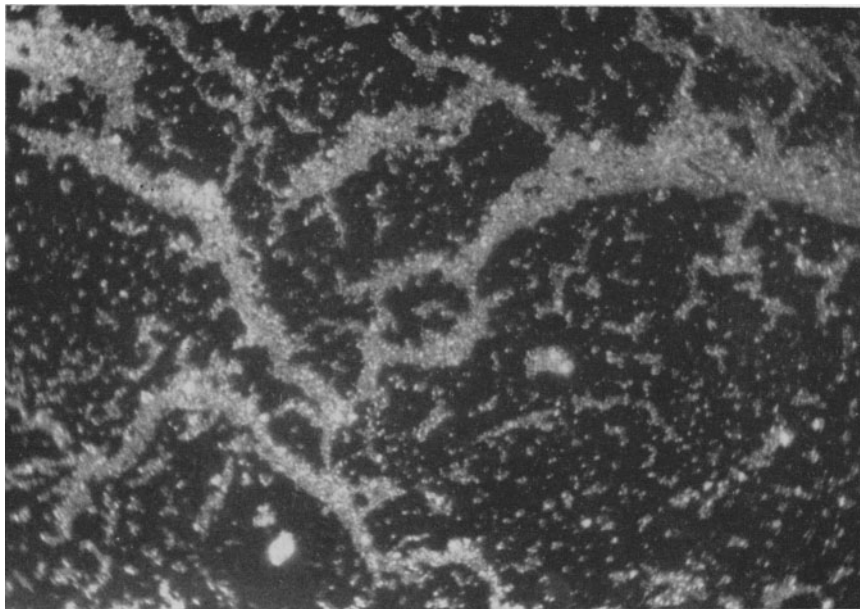


FIGURE 4.—The silica gel of Figure 3 after dispersion in water. Complete dispersion into extremely fine particles is evident. Original magnification $550\times$.

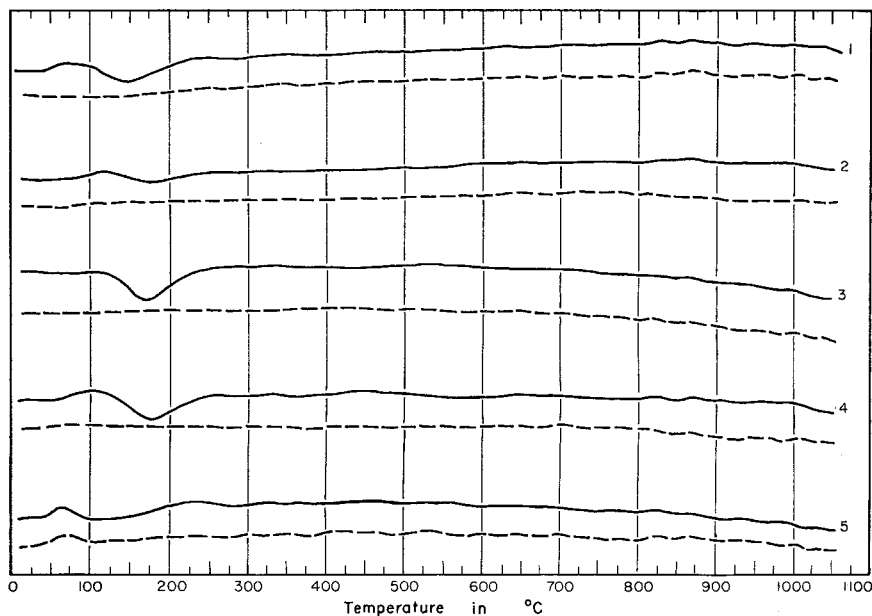


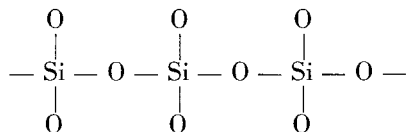
FIGURE 5.—Differential thermal analysis of silica gels. The dotted lines represent the cooling phase. (1) Gel A. (2) Gel A dried at 105° C. (3) Gel B. (4) Gel B dried at 105° C. (5) Gel C.

symmetry of quartz as compared with that of the high-temperature form of cristobalite makes it necessary to consider several attraction and repulsion forces, even at absolute zero. All these forces, even those acting between more distant atoms, must be considered in order to understand the difference in the thermal expansion of quartz, cristobalite, and silica glass.

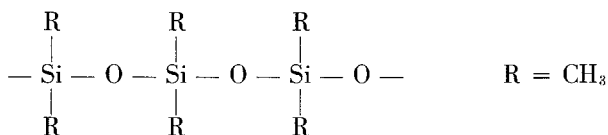
What seemingly has so far been widely overlooked is that large ions which are characterized by an incomplete outer electronic shell are strongly deformed when they are exposed to an electric field. This is always the case when systems characterized by a strong surface development, like glass, are taken into consideration. Since the presence of such asymmetrical ions always has a great influence on the surface properties of the compound, the colloidal range of dimensions must not be overlooked. This also explains why a fresh glass surface is extremely reactive. With time, however, the reactivity drops appreciably, owing to the adsorption of gas ions on the surface, which causes a saturation of its free valencies. This also explains the sorption of water on a glass surface. The ions located in the surface layer of the glass are not so completely saturated as similar ions located in the interior. If one brings into the surface layer, such ions which because of their polarizability are able to extend their forces toward the interior, then the surface will appear "saturated" from the outside, and hygroscopicity of the glass is thereby reduced. For example, the presence of a lead ion in the surface will reduce hygroscopicity because its valence forces are no longer equally distributed in all directions, and an inert surface layer is obtained.

SILICONES

The silicon oxides are composed of networks of alternate silicon and oxygen atoms so arranged that each silicon atom is surrounded by four oxygen atoms and each oxygen is attached to two silicon atoms:

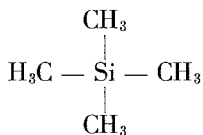


This network could be described as a series of spiral silicon-oxygen chains cross-linked with each other by oxygen bonds. If some of the oxygen atoms are replaced with organic substituents, a linear polymer results:



Considering the stability of structures involving C-Si bonds, we can see that the stability of the basic chain itself is comparable to that of silica and the silicate minerals. If the *R* substituents contain no carbon-to-carbon bonds, as in methyl groups, for example, the combination provides exceptional thermal stability and a pronounced chemical resistance to reagents that is unknown in organic polymers. The size of the molecule and the type of *R* group attached to the silicon atoms therefore control other properties, such as viscosity in organic solvents, elasticity, etc.

It is convenient to describe the structural units that make up different silicone polymers in terms of their functionality. Tetramethylsilane, the first, has no reactive positions and therefore cannot be classified as a siloxane.

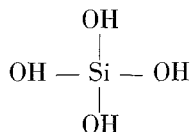


Neither can it be considered as a building unit, or monomer, for the formation of polymers. If one methyl group is substituted with oxygen, however, a trimethylsiloxi group results, and we are now dealing with a monofunctional group which can end a chain but not propagate one.

Methylpolysiloxane, which has a difunctional group, is the most important chain builder, extending linear or cyclic polymers; but it does not act as a chain-terminating or a cross-linking group.

Whenever three oxygen atoms and one methyl group are bonded to silicon, a monomethylsiloxane unit is formed. Since this unit is trifunctional, it not only can extend a chain or enlarge a ring, but also can establish an oxygen bridge or cause cross-linking to other silicon atoms.

The tetrafunctional unit, which occurs in silicon dioxide, is capable of extending two chains or of creating two branches; it has no organic group, but can nevertheless become part of an organosiloxane.



Silica itself is a completely cross-linked rigid network of tetrafunctional groups. Some silicate minerals exhibit a configuration of layers in which metal ions satisfy some of the oxygen bonds and therefore interfere with complete cross-linking of the siloxane chain; this can result in a laminar structure, as in mica, or in a fibrous structure, as in asbestos. Therefore an organosiloxane may be compared with such a silicate mineral since the organic groups in the former perform a function similar to that of the metal ions in the latter.

The difference between them also explains the difference in their properties. The properties of silicate minerals are due primarily to the metallic ions, whereas in organosiloxanes most of the properties are those usually associated with hydrocarbon compounds, such as solubility in specific organic solvents, swelling, and a marked water-repellent character of the surface. These facts are excellent examples to support the statement that colloid science deals with the reactivity of surfaces or interfaces.

When the hydrolysis product of pure dimethyldichlorosilane is treated with agents which are effective in continuing polymerization without causing cross-linking, an elastic substance is obtained. If reagents are used which possess the property of opening up a few silicon-oxygen bonds (thus causing rearrangement of the polymer without involving a condensation reaction) it is possible to build up aggregates composed of several thousand $(\text{CH}_3)_2\text{Si}-\text{O}-$ units without cross-linkage and therefore without forming an insoluble gel.

Silicone rubber can be produced from dimethylsilicones if trifunctional groups are absent. The polymer has a high molecular weight. If some of the methyl groups are replaced by phenyl groups or similar groups, the freezing point of the polymer may be materially reduced, but the product retains its elastic properties over a wide range of temperatures. Its tensile strength lies between 250 and 900 psi and it has a very satisfactory dielectric strength even at temperatures up to 250° C. It is highly water-repellent and has high surface resistivity even under moisture-condensing conditions. Silicone rubbers are also resistant to most bases and weak acids, to salt solutions, and to oils.

A silicone product with especially interesting properties is the one generally known as "bouncing putty." It exhibits dilatancy to a pronounced degree. It is a putty-like material which can be hand-molded but which rebounds when dropped on a hard surface; it exhibits cold flow when left at rest and will form long plastic threads if subjected to slow stretching. If the sample is extended rapidly, however, it will break immediately.

"Bouncing putty" is prepared by mixing about 5 percent of boric oxide with dimethyl silicone and holding it at a temperature between 150° and 250° C for several hours. It disintegrates in water because water breaks the silicon-oxygen-boron bond. This explains in part why the putty appears soft and glossy on the

surface when it stands at rest for a time; when it is tested under high vacuum, no glossy surface is noticeable (Hauser, 1955).

All this information indicates the increasing importance of the colloid science of the element silicon. With better and more comprehensive knowledge of the colloidal phenomena that are encountered every time we deal with the element silicon, we will learn to understand the properties exhibited by siliceous matter better than we have so far. More serious interest should be taken by all chemists, mineralogists, geologists, and members of the pharmaceutical profession, among others, in the increasing importance of silicic science in our lives.

SUMMARY

The colloidal phenomena of silicic acid gels and silica gels are reviewed and attention is drawn to their importance in several fields.

An attempt has also been made to indicate why silicone products are becoming of increasing importance in science and industry.

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