REFERENCES

(1) ANDREAS, J. M., HAUSER, E. A., AND TUCKER, W. B.: J. Phys. Chem. **42**, 1001 (1938).
(2) BRIDGMAN, P.: *The Physics of High Pressure*, p. 58. The Macmillan Company, New York (1931).
(3) BUCKINGHAM, W. D., AND DEIBERT, C. R.: J. Phot. Soc. Am. **12**, 610 (1946).
(4) EILERTS, C. K., *et al.*: Am. Gas Assoc. Monthly **28**, 435 (1946).
(5) KEYES, F. G.: Proc. Am. Acad. Arts Sci. **68**, 529 (1932–33).
(6) MACK, G. L., DAVIS, J. K., AND BARTELL, F. E.: J. Phys. Chem. **45**, 846 (1941).
(7) POULTER, T. C.: Phys. Rev. **35**, 297 (1930).
(8) SMITH, G. W.: J. Phys. Chem. **48**, 168 (1944).
(9) SMITH, G. W., AND SORG, L. V.: J. Phys. Chem. **45**, 671 (1941).

SILICIC CHEMISTRY[1,2]

A NEW BRANCH OF COLLOID SCIENCE

ERNST A. HAUSER

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts

"In science the credit goes to the man who convinces the world, not to the man to whom the idea first occurs." These words were spoken by the British physician Sir William Osler in the last lecture he gave before the Royal Society of Medicine in 1918. One could hardly find a more striking example of their significance than by offering a brief historical review of the colloid chemistry of silicon.

In 1861, Thomas Graham read before the Royal Society in London a paper on "Liquid diffusion applied to analysis." He differentiated therein between matter which would and substances which would not diffuse through a membrane. References to this lecture (3), which must be regarded as the foundation of colloid science, are mostly limited to the following statement: "As gelatine also appears to be of the non-diffusing type, it is proposed to designate substances of the class as COLLOIDS, and to speak of their peculiar form of aggregation as the COLLOIDAL CONDITION OF MATTER."

What has dropped into oblivion, however, is the following sentence:

"The comparatively *fixed* class as regards diffusion, is represented by a different order of chemical substances, marked out by the absence of the power to crystallize. Among the

---

latter are hydrated silicic acid, when it exists in the soluble form. Soluble silicic acid forms a peculiar class of compounds, which are interesting by their analogy to organic substances."

Three years later Thomas Graham wrote another paper (4), from which the following excerpts have been taken:

"We have no degrees of solubility to speak of with respect to silicic acid, like the degrees of solubility of a salt. . . . The ultimate pectization of silicic acid is preceded by a gradual thickening in the liquid itself. The production of the compounds of silicic acid described, indicates the possession of a wider range of affinity by a colloid than could well be anticipated. The organic colloids are no doubt invested with similar wide powers of combination."

Thomas Graham unquestionably deserves credit for having been the first to convince the world that a colloidal condition of matter exists. That siliceous compounds exhibit properties characteristic of this state had already been mentioned eighty-two years prior to Graham's first disclosure, in the dissertation of the Swedish scientist Torbern Bergman, "De Terra Silicea," which a few years later was reprinted in one of his textbooks (1). The following is an excerpt of the most pertinent part therefrom:

"Finally I must still think of those incomplete phenomena, which depend on a seeming solubility. This silicious liquor [alkali silicate solution—E.A.H.] is precipitated by all acids, because the alkali prefers to hang on to them rather than to the gravel. This precipitated gravel has a very expanded and loose texture, is filled with water, so that it is twelve times as heavy when moist, than when dry. However if one first adds more water before adding acid, the solution remains clear, even if more acid is then added as would be needed to neutralyze the alkali. THIS IS A PECULIAR PHENOMENON and the reason for it probably is the following: Through the dilution with water the silicious particles are very much separated from each other, or made finer and better distributed throughout the liquid. Although the particles, being heavier than the liquid, should settle out, they can in this case not overcome the resistance due to friction, because a greater force will be needed to accelerate sedimentation than the one resulting from the difference in specific gravity. The silica particles remain suspended in the liquid and at the same time invisible due to their fineness and transparency."

We colloid chemists must blame ourselves that it took so long, nearly a century, for it to dawn upon us that the colloidal properties of siliceous matter are just as important for the explanation of some phenomena it exhibits as they are with many high-molecular organic compounds. This is the more surprising if one takes into consideration the fact that silicon in combination with oxygen accounts for 76 per cent of the earth's crust. Structural chemistry, largely based on the results of chemical analysis combined with x-ray diffraction studies, has shown that silicon is tetracovalent in its chemical behavior. This is in accord with its position in the fourth group of the Periodic System of elements. Silicon, however, differs from carbon, because its maximum covalency can be 6, as exemplified by SiF_6^{--}. The two elements also differ in their reactivity toward hydration and hydrolysis of their halides and the ease of rupture of silicon-to-silicon bonds by water or hydroxyl ions. The most plausible explanation for these differences is based on the size of the atoms (silicon = 1.172 Å.; carbon = 0.77 Å.) and the

correspondingly greater screening of the nuclear charge of the silicon. It also should be noted that of all the single bonds between tetracovalent silicon and other elements, the Si—O bond with an energy value of 89.3 kg.-cal. per mole is by far the strongest (11).

Another tool for structural research which is becoming more and more important is infrared spectroscopy. Vibrations involving the Si—O bond have shown that the intensity of the bonds is about five times stronger than that of the C—O bonds. As far as the ionic character of silicon bonds is concerned, measurements of relative intensities of absorption in the infrared permitted estimating the ratio of the ionic character of the Si—O bond to that of the C—O bond to be 2.3 (14). This is in line with the relationship between electronegativity difference and per cent ionic character. For the Si—O bond it amounts to 51 per cent, and for the C—O bond to 22 per cent. The ratio 51/22 = 2.3. In the case of Si—F and C—F the ratio, although smaller, is still 1.6 (11).

These facts should suffice to point out how futile it would be to attempt to apply the laws of classical organic chemistry to the chemistry of silicon (12).

There are, however, also many similarities between the elements carbon and silicon and their compounds which are worth recording. To explain them in spite of the difference between the homeo- and hetero-polar bindings of these elements, the colloidal state must be taken more into consideration than has so far been the case. A silicon atom is known to share four electrons with neighboring atoms. But each oxygen atom needs two electrons for saturation. The silicon-oxygen tetrahedron (figure 1) is not saturated. If the oxygen atoms are replaced with hydroxyl groups, the tetrahedron then is saturated because each hydroxyl needs only one electron. Thus, by sharing the right number of electrons, two or more atoms are firmly held together; in this specific case, reference is generally made to a chemical bond or a covalent bond.

If several silicon-oxygen tetrahedra are combined so that two always share one oxygen, a chain-like structure results. In such a chain, two of the oxygen atoms belonging to one silicon atom remain unsaturated. This deficiency may be compensated by attaching a sodium atom to every unsaturated oxygen. A fibrillar aggregate is thus formed, which, if dispersed in water, represents the structure of sodium silicate or water glass (figure 2). The fact that the sodium ion hydrates appreciably and the presence of such long-chain aggregates offer a simple explanation for the solubility of sodium silicate and the high viscosity of its solutions. The entanglement of these fibrillar aggregates on desiccation also explains the formation of coherent sodium silicate films. Their structure is comparable to films obtained from long-chain high-molecular-weight organic compounds such as rubber or cellulose. If sodium silicate is reacted in solution with a solution of an acid, the sodium will exchange for the acid hydrogen, thus forming a silicic acid chain (figure 3). If two or more of these chains come close together or tangle up, condensation between neighboring hydroxyl groups occurs. Water is split off and the chains are now held together by shared oxygen atoms. A loose, unoriented, but nevertheless rigid tridimensional structure results, and a hydrous silica gel has been formed.

Just as it was possible to link two or more silicic acid chains together by condensation, two or more silicon oxygen tetrahedra chains may be joined by having
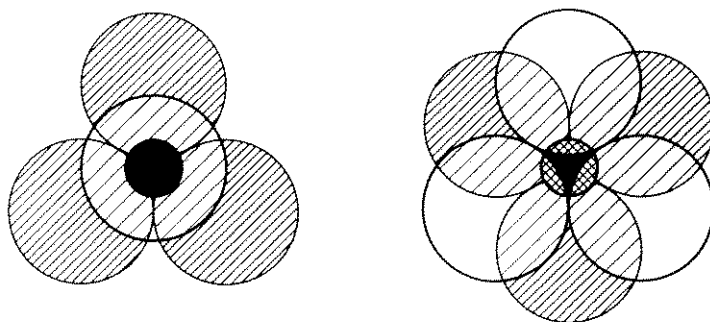

Fig. 1. Left: Silicon-oxygen tetrahedron (schematic), top view. The oxygen atom on top has been drawn transparent to show the location of the silicon atom in the cavity formed by the four oxygen atoms. Right: Aluminum (magnesium) octahedron (schematic).
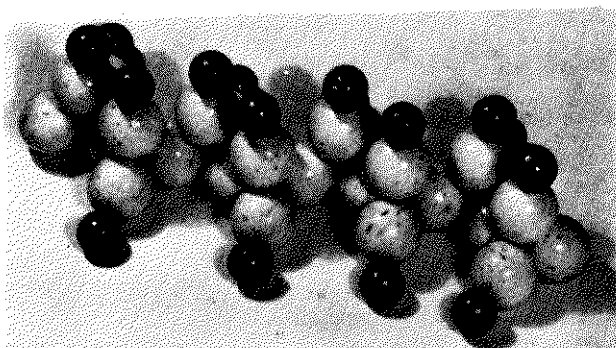

Fig. 2. Model of a sodium silicate chain (theoretical): white balls represent oxygen atoms; smaller black balls, sodium atoms.
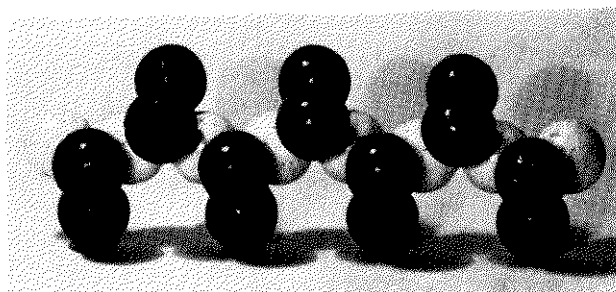

Fig. 3. Model of silicic acid chain (schematic), top view: white balls represent oxygen atoms; black balls, hydroxyl groups.

them share oxygen atoms (figure 4). A hexagonal network or silicon oxygen sheet has been formed. If these hexagons thus formed are symmetrical, a sheet of crystalline structure results; if they are not symmetrically aligned, a silica

glass is obtained. The oxygen in the vertex position of every tetrahedron only remains unsaturated.

Similar sheets may be formed by joining magnesium or aluminum octahedra together (figure 1). If a sheet of aluminum octahedra is superimposed on a hydrated silica sheet, they are held together by secondary valence forces, but they can also condense. This is how the most abundant clay, kaolinite, was formed. When a sheet of aluminum hydroxide octahedra is sandwiched between two silica sheets and condensation follows, the clay mineral pyrophyllite is formed. If the aluminum hydroxide is replaced by magnesium or iron hydroxide, the minerals talc and nontronite, respectively, result by condensation. If some of the silicon is replaced by an ion of lower valency, we have built up the basic structure for mica. If we replace the aluminum with an ion of lower valency, the nucleus for the highly reactive clay mineral bentonite has been formed (5).
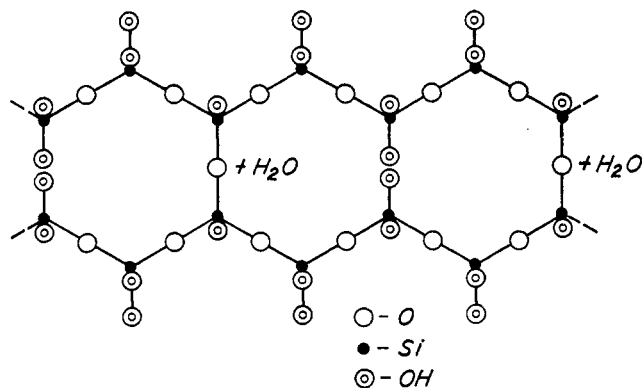

FIG. 4. Condensation of silicic acid chains to form silica sheet

We owe these deductions to the combination of results from chemical analysis and x-ray diffraction studies (2). The first visual proof for the assumed platey shape of these clay particles has only fairly recently been offered by electron-microscopic studies (5).

All this information, however, is still inadequate to offer a satisfactory explanation for many of the properties exhibited by siliceous matter, just as classical organic chemistry alone is unable to account for some properties exhibited by many organic colloids, as for example gelation, the high viscosity of their solutions, and elasticity.

It is here that the importance of colloid science becomes self-evident. It is the bridge which spans the gap in our knowledge of the properties exhibited by matter present in the range of dimensions we may no longer neglect.

To avoid coining new terms for this branch of colloid science, let us see if one cannot adopt some of the terminology already familiar to scientists specializing in the chemistry of high-molecular organic compounds. We shall classify the silicon hydroxide tetrahedra and the octahedra of magnesium, aluminum, and iron hydroxides as monomers (figure 5) comparable to isoprene or styrene. By

condensation of these monomers individually we produce a polymer comparable to natural rubber or to polystyrene (figure 5). If the silicon hydroxide polymer reacts with the aluminum or magnesium hydroxide polymer, or mixtures of these by further condensation, the result is an inorganic copolymer, comparable to the copolymers of butadiene and styrene, or of isobutylene and isoprene (figures 6 and 7). The resulting particle now represents the nucleus of a colloidal micelle. Its properties will depend on the distribution of electrical charges in its surface. The finer the particle, the more surface is exposed and the more pronounced will be the tendency to have its electric charge, caused by the unbalanced electron
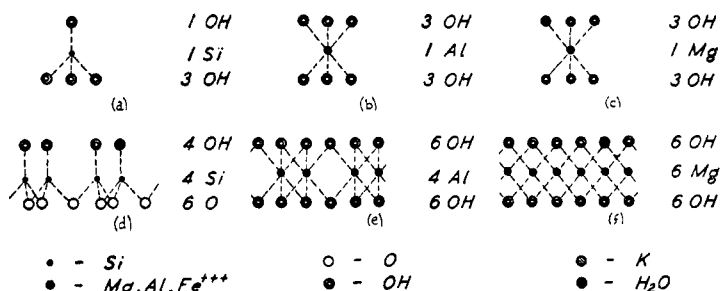

FIG. 5. Monomers: (a) $Si(OH)_4$; (b) $Al(OH)_6$; (c) $Mg(OH)_6$
Polymers: (d) $[Si(OH)_4]_x$; (e) $[Al(OH)_6]_x$; (f) $[Mg(OH)_6]_x$
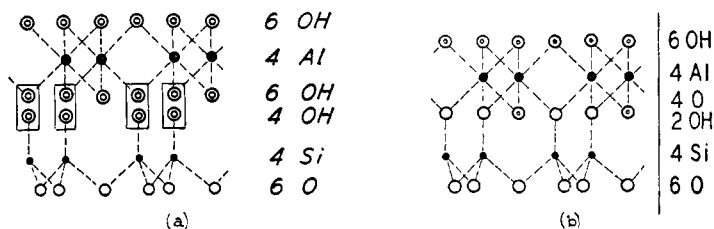

FIG. 6. Copolymers: (a) prior to condensation (halloysite); (b) after condensation (kaolinite).

distribution, neutralized. What this implies can best be explained by offering a few examples.

The question why solutions of alkali silicate polymers have such high viscosities and set to a gel like many high-molecular organic colloids has baffled chemists for a long time. Quite recent work proves that the comparatively high viscosity of water glass solutions and their gelation upon the addition of acids or electrolytes carrying cations of higher valency, or less hydratability, than sodium ion are based solely on the morphology of the alkali silicate particle. Sodium silicate, for example, owes the viscosity of its solutions to the water hulls, or lyospheres, carried by the sodium ions, which must be considered as ionizable counter ions and not as fixed components of the silicate structure. These lyospheres also prevent the colloidal particles from condensing and forming larger particles. Upon the addition of an acid or a multivalent cation, a base-exchange reaction

results, the zeta potential of the micelle drops and its lyosphere is decreased in size (figure 8). This is then followed by condensation and, as previously stated, by the formation of filamentitious polymers. Depending on the type of counter ions involved in this reaction and their concentration, a thixotropic or rheopectic gel with separated particles, or a permanent gel with a three-dimensional structure of interwoven filaments results. This is also the reason why these gels upon desiccation yield extremely porous, highly reactive solids, a result which accounts for their strong adsorbing property. It is nothing but the surface development
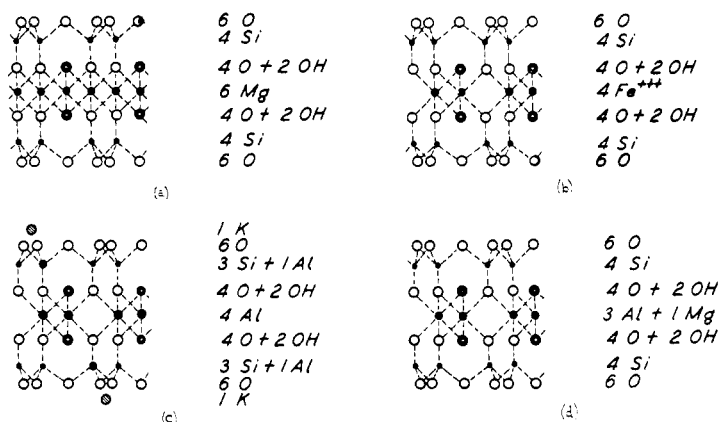

FIG. 7. Copolymers—continued: (a) talc; (b) nontronite. Copolymers (substituted): (c) mica; (d) bentonite.
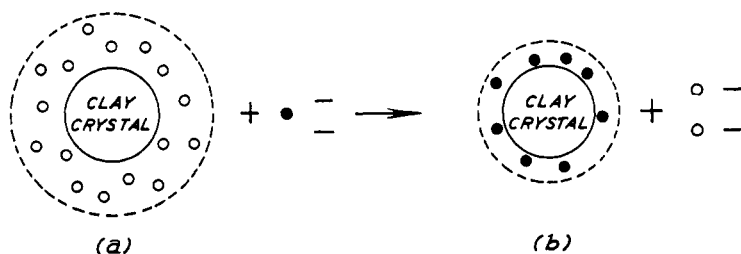

FIG. 8. Effect of ionic valency on dimension of lyosphere. $\bigcirc$, monovalent counter ion; $\bullet$, polyvalent counter ion; $-$, monovalent anion.

and the chemical unsaturation and type of the ions located therein which are responsible for the increasing uses which colloidal silica is finding in such diversified applications as in mouthpiece filters of gas masks, in air- and water-purification units, or as bleaching and decolorizing agents and as catalysts.

Our increasing knowledge of the structure of the condensation copolymers of silicon hydroxide with aluminum or magnesium hydroxide has opened up some entirely new uses for these abundant natural products. When it was discovered that certain colloidal clays exhibit the phenomenon of thixotropy and how it could be controlled, they were put to use in the formulation of oil well drilling muds (10). Since most naturally occurring colloidal clays which give thixotropic gels

are sodium bentonites (5), they will not yield thixotropic gels in contact with a brine solution or oil. On the basis of our knowledge of their composition and their micelle structure, we can now change their reactive surface so that they become reactive even in such environments.

By spreading thixotropic gels of purified sodium bentonite and drying them, the platey particles are aggregated into fibers which interweave and form a coherent self-supporting film (figure 9) (7, 9). By exchanging the sodium ion with a less hydrophilic one, a water-resistant film of high dielectric properties results. If the exchanging ion is potassium, synthetic mica is formed. If the *sodium ion is substituted, with a complex ion carrying an organic radical, the* clay will now expose an organic surface. Such clay exhibits interesting properties as a compounding ingredient for organic matter like rubber and plastics (5, 7). If the organic radicals, like organic ammonium complexes or metal
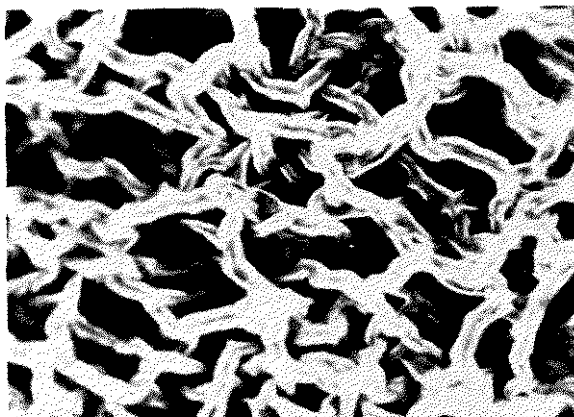

Fig. 9. Filamentitious structure of clay films

acrylates (5, 8), can be polymerized by condensation or addition, the result is a copolymer of organic and inorganic monomers and not just a heterogeneous mixture. This reaction is of course not limited to clay films, but permits the production of plastics for pressure or extrusion molding. Depending on the type of organic radicals involved, thermoplastic or thermosetting compounds can be produced (5, 8, 9).[3]

In recent years the silicon resins have been added to this branch of colloid science. They too are neither entirely organic nor inorganic in composition. They have opened up new vistas for coating, impregnation, lubrication, and even in the field of elastomers (12). In combination with clay films they yield insulating tapes of unsurpassed electrical properties.

[3] The *34th Annual Report of the Mellon Institute*, which came to the author's attention only recently, carries on p. 26 a note under the heading "Clay as a Chemical." Science News Letter (Vol. **51,** p. 333 (1947)) refers thereto in an article "Plastics from common clay." This work, in which the author takes an active part, is carried out under a fellowship sponsored by the National Lead Company and is based on the above-mentioned discoveries.

8

Other fields which would benefit by paying more attention to the colloid chemistry of siliceous matter are geology, petrography, the ceramic and the paper industries, agriculture, highway construction, soil solidification (13), and flood control, to mention only a few. They all depend on the surface composition of clays and the colloidal phenomena based thereupon. In ceramics it is plasticity and shrinkage (5) of the clay slips, in the paper industry dispersion and coating (6), in agriculture the fertility of the soil, in flood control the assurance that sufficient permeability is maintained (13). In geology and petrography it is the phenomenon of rheopexy which deserves special attention. This is particularly so, since it has been shown that its occurrence is most pronounced if colloidal clay is contaminated with colloidal iron oxide (5). This phenomenon is probably responsible for the layer-type deposits of clays and in petrography for the petrifaction of such delicate structures as jellyfish. The Solnhofen slates are famous for these and it has been proven that they are largely composed of colloidal particles of siliceous matter (5).

In closing this survey, I should like to refer to a statement made nearly thirty years ago by a famous Austrian chemist, Dr. Rudolf Wegscheider. He said: "I predict that the day will come when the chemistry of Silicon will be a serious competitor to organic chemistry." It is hoped that colloid chemists who have been active in research with compounds of siliceous compositions will realize that this day has come, and that it therefore is not presumptuous to coin a new name for this branch of colloid science,—namely, "silicic chemistry."

Silicic chemistry has been born and is growing fast, and as with the development of every child, we are in for many surprises!

SUMMARY

The history of the colloid chemistry of silicon is reviewed to prove that this branch of the science of colloids is even older than the term "colloid" itself.

The opinion that certain properties of matter, such as the formation of solutions of high viscosity and the ability to form gels, are limited to organic compounds is disproved. Attention is drawn to the similarity of the reactions responsible for the formation of organic and siliceous colloids and a uniform terminology for these reactions is suggested. Examples of siliceous compounds exhibiting the same properties as organic ones are offered.

Various colloidal phenomena characteristic of silicon compounds and their importance to science and industry are discussed. Attention is drawn to the versatility of this new field, and the suggestion is made to give it the name "silicic chemistry."

Addendum

Only a few days before the author presented this paper, he was visited by Professor Nils Hast of the Royal Technical University and the Nobel Institute for Physics, in Stockholm, Sweden. Professor Hast gave him a detailed description of his new technique for studying the structure of clays and diatomaceous shells with the electron microscope (Nature **159**, 354, 370 (1947)). This new

method of sample preparation has enabled Professor Hast to increase the micro-scope's resolving power far beyond what has been possible so far and to make the changes which the original structure undergoes during hydration and subsequent dehydration actually visible. Besides this, it has enabled him even to make the individual layers of clay particles discernible and also the process by which they are stacked up.

REFERENCES

(1) BERGMAN, T.: *Kleine physische und chemische Werke,* Vol. 3, p. 391. Frankfurt a/Main (1785).
(2) BRAGG, W. H., AND BRAGG, W. L.: *X-Rays and Crystal Structure.* A. Bell and Sons, Ltd., London (1925).
(3) GRAHAM, TH.: Phil. Trans. **1861,** 183; Proc. Roy. Soc. (London) **11,** 243 (1861).
(4) GRAHAM, TH.: Proc. Roy. Soc. (London) **13,** 335 (1864).
(5) HAUSER, E. A.: Chem. Revs. **37,** 287 (1945).
(6) HAUSER, E. A.: Paper Trade J. 8–12–1937; 8–24–1939.
(7) HAUSER, E. A.: U. S. patents 2,266,636; 2,266,637; 2,266,638; 2,317,685.
(8) HAUSER, E. A., AND DANNENBERG, E. M.: U. S. patent 2,401,348.
(9) HAUSER, E. A., AND LE BEAU, D. S.: J. Phys. Chem. **42,** 961, 1038 (1938); **43,** 1037 (1939); **45,** 54 (1941); J. Alexander's *Colloid Chemistry,* Vol. VI, p. 191, Reinhold Publishing Corporation, New York (1946).
(10) LARSEN, D. H.: In J. Alexander's *Colloid Chemistry,* Vol. VI, p. 509. Reinhold Publishing Corporation, New York (1946).
(11) PAULING, L.: *The Nature of the Chemical Bond.* Cornell University Press, Ithaca, New York (1940).
(12) ROCHOW, E. A.: *An Introduction to the Chemistry of the Silicones.* John Wiley and Sons, Inc., New York (1946).
(13) WINTERKORN, H. F.: In J. Alexander's *Colloid Chemistry,* Vol. VI, p. 459. Reinhold Publishing Corporation, New York (1946).
(14) WRIGHT, N., AND HUNTER, M. Y.: J. Am. Chem. Soc. **69,** 803 (1947).