It may be pointed out that because of existing variations in the relative abundances of the isotopes of oxygen there is a slight inexactness in referring to the atomic weight of "natural" oxygen (defined as 16) as the basis of the chemical scale. As yet this does not affect the table of atomic weights because of the limited accuracy with which the values are given. This situation can be remedied, when it is deemed desirable to do so, in either of two ways. One is to agree on a particular kind of oxygen; for example atmospheric oxygen or ocean-water oxygen, as "natural" oxygen. Another and probably better way is to use as the basis a defined mixture of oxygen isotopes, possibly that representing the best knowledge, at the time the decision is made, concerning the average isotopic composition of terrestrial oxygen.

In 1949 the practice was introduced of including in the table, but as bracketed values to distinguish them from true atomic weights, selected mass numbers for "synthetic" elements. This is continued in the new table. Discoveries of isotopes of certain of these elements that have longer half-lives than the previously chosen isotopes, have resulted in four changes in these values. They are as follows: americium, 243[38]; curium, 243[39]; plutonium, 242[40]; and promethium, 145.[41] Two new elements appear for the first time, berkelium (symbol Bk, atomic number 97), and californium (symbol Cf, atomic number 98).

The name wolfram, as the preferred name for the element more commonly known as tungsten in the English-speaking countries, has been dropped from the table because it has failed to gain acceptance in the United States. Both names, tungsten and wolfram, are now recognized by the International Union.

(38) K. Street, Jr., *et al.*, *Phys. Rev.*, **79**, 531 (1950).

(39) S. G. Thompson, *et al.*, *ibid.*, **80**, 781 (1950).

(40) S. G. Thompson, *et al.*, *ibid.*, **80**, 1108 (1950).

(41) F. D. S. Butement, *Nature*, **167**, 400 (1951).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, POLYTECHNIC INSTITUTE OF BROOKLYN]

Cerium(III) Sulfide and Selenide and Some of their Solid Solutions[1]

BY E. BANKS, K. F. STRIPP, H. W. NEWKIRK AND R. WARD[2]

The relationship between the complex and cubic phases of cerium(III) sulfide has been investigated by the use of molten salts to extract the oxide from the complex form. It has been shown that the complex phase is not a mixture containing the cubic phase. Some solid solution of flux constituents in the Ce_2S_3 crystals occurs. Cerium(III) selenide, Ce_2Se_3 and oxyselenide, Ce_2O_2Se have been prepared and shown to be isomorphous with the corresponding sulfides. Cerium(II) selenide has been prepared by the sodium reduction of cerium(III) selenide, and is isomorphous with CeS. Solid solutions of strontium sulfide and selenide in the corresponding cerium(III) compounds have been shown to exist up to complete filling of the defect structure of the cerium compounds (50 mole per cent.) with an increase in lattice constant. In the case of the sulfides, calcium and magnesium sulfides show lower solubility limits, with a contraction of the Ce_2S_3 lattice.

The authors' attention was first focused on rare earth sulfides in an investigation of the state of cerium and samarium ions in alkaline earth sulfide phosphors.[3] In this investigation, preparations of rare earth sesquisulfides were made by standard methods (*e.g.*, heating the oxides or anhydrous salts in an atmosphere of hydrogen sulfide at temperatures in the range 900–1100°. Under these conditions the products are brown to red powders whose X-ray powder patterns are very complex—"linienreich"—in the words of Klemm,[4] who first reported the X-ray investigation of a series of rare earth sulfides prepared in the conventional manner.

Eastman, Brewer, *et al.*,[5] have reported the preparation of cerium(III) sulfide and similar compounds at higher temperatures (*ca.* 1300–1500°) in carbon vessels in a hydrogen sulfide atmosphere. Under these conditions any moisture or oxygen present in the system is converted to carbon monoxide and the resulting sulfide is free of oxide impurity. The cerium(III) sulfide prepared in this way was found by Zachariasen[6] to have a defect structure of the Th_3P_4 type (space group T_D^6; $I\bar{4}3d$) with $10^2/_3$ cerium atoms statistically distributed over 12 equivalent positions in the unit cell. The ideal composition is Ce_3S_4, with all twelve cerium positions filled. Ce_3S_4 is prepared by combining cerium(III) sulfide with cerium(II) sulfide. The latter compound was prepared by Eastman, *et al.*, by allowing cerium(III) sulfide to react with finely divided cerium metal formed by the decomposition of cerium hydride. It has a rock-salt structure with $a_0 = 5.76$ Å. Zachariasen also reports the existence of a continuous homogeneity range between the compositions Ce_2S_3 and Ce_3S_4, having the Th_3P_4 structure.

In the above work, Eastman, *et al.*, state that a very complex X-ray pattern is obtained from cerium(III) sulfide containing very small traces of oxygen, which might be added in the form of the oxysulfide, Ce_2O_2S.[5] Under ordinary conditions our laboratory gases contain enough moisture to convert 5 g. of cerium(III) sulfide to the oxysulfide in about 30 hours at 1000°. Thus, any preparations made without special precautions should yield the complex phase, as observed.

The object of the present work was to determine, if possible, the relation between the cubic cerium (III) sulfide and the complex oxide-containing

---

(1) (a) Supported in part by the Signal Corps; (b) presented at the XII International Congress of Pure and Applied Chemistry, New York, N. Y., September 12, 1951.

(2) The University of Connecticut, Storrs, Connecticut.

(3) (a) E. Banks and R. Ward, *J. Electrochem. Soc.*, **96**, 247 (1949); (b) H. L. Yakel, E. Banks and R. Ward, *ibid.*, **96**, 304 (1949).

(4) W. Klemm, K. Meisel and H. von Vogel, *Z. anorg. allgem. Chem.*, **190**, 123 (1930).

(5) E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles and N. Lofgren, THIS JOURNAL, **72**, 2248 (1950).

(6) W. H. Zachariasen, *Acta Cryst.*, **2**, 57 (1949).

phase; to investigate the solid solubility of divalent sulfides in the defect Ce_2S_3 crystals and to compare the effect of such dissolved cations on the electrical properties of the solid with the effect of cerium(II) sulfide; and to attempt the preparation of the analogous selenium compounds.

Experimental

I. The Preparation of Cubic Ce_2S_3 from the Complex Phase.—In Section II, it is shown that in some cases it is possible to convert the complex form of cerium(III) sulfide to the cubic phase by heating with as little as 0.5 mole per cent. strontium sulfide. It appeared that the strontium sulfide extracted the oxide from the cerium sulfide phase in the form of strontium oxide. If this were so, the complex phase should be converted to the cubic form by extracting the oxide with a molten salt. Previous work in this Laboratory[7] has shown that strontium oxide is much more soluble than strontium sulfide in molten strontium chloride. In general, a molten ionic salt should be a better solvent for an oxide than for a sulfide of the same metal. Lithium fluoride was the "flux" chosen for these experiments.

Samples of the complex cerium(III) sulfide were prepared with the addition of 1, 3, 5 and 10% by weight of lithium fluoride. These samples were heated for two hours at 900° *in vacuo*. X-Ray powder diagrams were taken using a cylindrical camera and filtered copper radiation. The powder photographs show the gradual disappearance of the lines of the complex phase with the lines of the cubic phase appearing concurrently. Figure 1 is a reproduction of X-ray spectrometer traces made over a 3° range of 2 θ. The trace marked A shows a strong doublet in the forward region of the diffraction pattern obtained with the complex material. Traces B, C, D and E show the effect of increasing concentrations of lithium fluoride. The central line shows a steady growth at the expense of the original doublet, which is still present at a low intensity in the sample containing 10% of lithium fluoride. Trace F was obtained from a sample of pure cerium(III) sulfide obtained through the generosity of Professor Leo Brewer of the University of California, Berkeley, California. The single line of the cubic phase is shown quite clearly here. The peak is somewhat shifted to smaller angles, indicating a larger lattice constant. This difference in lattice constant is discussed in Section II.

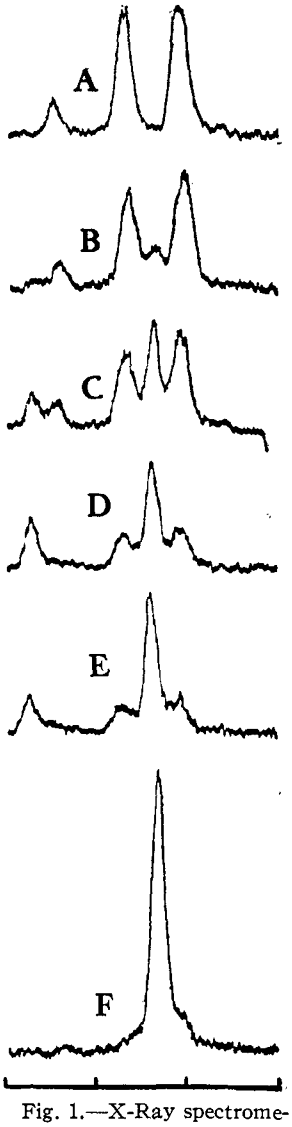

Fig. 1.—X-Ray spectrometer trace (2 θ = 24–27°) showing conversion of complex Ce_2S_3 pattern to cubic pattern by heating with LiF at 900°: A, complex phase; B, 1% LiF; C, 3% LiF; D, 5% LiF; E, 10% LiF; F, pure cubic Ce_2S_3 (Brewer).

These experiments provide strong evidence that the complex phase is not a mixture containing some of the cubic phase, since the lines of the cubic phase distinctly appear in regions where there are no lines in the complex phase. It seems possible that the complex structure of the oxide-bearing phase is a lower symmetry distortion of the cubic structure, caused by the presence of oxide in solid solution.

The lithium fluoride was introduced in these experiments with the idea of providing a solvent to extract the oxide (possibly as Ce_2O_2S) and to facilitate recrystallization of the oxide-free phase. A comparison of the lattice constant of the cubic material prepared with 10% lithium fluoride (a_0 = 8.5957 kX.) with that for the sample provided by Professor Brewer (a_0 = 8.6105 kX.) suggested that some solid solution of the lithium fluoride might be occurring, with a contraction of the lattice. As a check, some of Brewer's material was heated *in vacuo* with 10% lithium fluoride. This material showed a considerably lower value (a_0 = 8.5930 kX.) which is nearly the same as the value obtained with material prepared in this Laboratory.

Sodium chloride was also tried as a flux, in the hope of being able to remove it after conversion of the sulfide. However, this salt proved to be so volatile *in vacuo* that it vaporized completely after one-half hour at 800°, leaving the complex phase. When a flowing nitrogen atmosphere was used, partial conversion to the cubic form was obtained after a one hour run at 1000° with a large excess of NaCl. The lattice constant found was 8.6218 kX., suggesting that sodium ions had entered the crystals with consequent expansion of the lattice. In the latter experiment an additional water insoluble phase was obtained in the form of golden-yellow hexagonal plates, which were mechanically separated and shown by their powder diagram to be the hexagonal cerium oxysulfide,[6] which had previously been obtained here as a dark green powder.

II. Solid Solutions of Divalent Sulfides in Ce_2S_3.—When cerium(II) sulfide enters the Ce_2S_3 structure, a shrinkage of the lattice is observed, from 8.618 kX. in Ce_2S_3 to 8.606 kX. in Ce_3S_4.[5] At the same time the resistivity decreases from 1000 ohm-cm. in Ce_2S_3 to 4×10^{-4} ohm-cm. in Ce_3S_4. In the formation of these solid solutions, a transition to a metallic type of binding seems to be occurring. This has been discussed by Brewer[8] and is consistent with the small lattice constant found for cerium(II) sulfide (5.76 kX.) as compared to that of europium(II) sulfide[9] (5.96 kX.) and strontium sulfide (6.00 kX.). The ionic radius of divalent cerium should be about the same as that for strontium, according to a calculation from Pauling's univalent radii.[10]

Since divalent cerium in cerium(II) sulfide does not appear to form purely ionic bonds, the authors wished to determine whether other divalent cations would enter the Ce_2S_3 defect structure and what effect such solid solution might have on the properties of the crystal. The solid solutions were prepared by grinding together appropriate quantities of alkaline earth sulfides with cerium(III) sulfide and 6% lithium

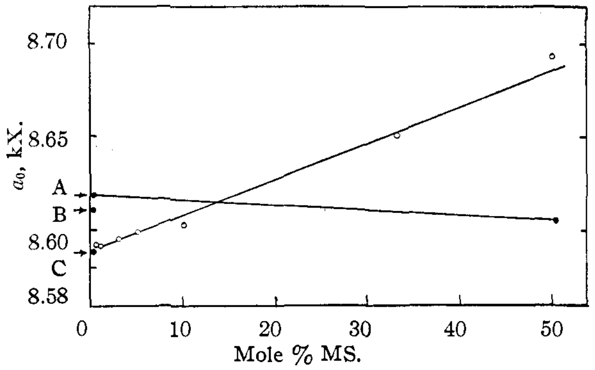

Fig. 2.—Lattice constant *vs.* composition—solid solutions of SrS and CeS in Ce_2S_3: ○, SrS in Ce_2S_3: ●, CeS in Ce_2S_3; A, pure Ce_2S_3 (Zachariasen); B, Brewer's Ce_2S_3 (this report); C, Brewer's Ce_2S_3 heated with 6% LiF.

---

(7) R. W. Mason, C. F. Hiskey and R. Ward, THIS JOURNAL, **71**, 509 (1949).

(8) E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles and W. L. Lofgren, *ibid.*, **72**, 4019 (1950).

(9) W. Nowacki, *Z. Krist.*, **99**, 339 (1938).

(10) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 347.

fluoride (by weight), followed by heating for one hour at 1000° in an atmosphere of hydrogen sulfide.

A series of mixtures was prepared, ranging from 50 mole per cent. of strontium sulfide (corresponding to complete filling of the vacant cation sites) down to about 0.5 mole per cent. The colors of these solid solutions varied from orange-tan at 50 mole per cent. through a brilliant crimson to the characteristic deep purplish red of cerium(III) sulfide at 0.5 mole per cent. strontium sulfide.

All the solid solutions showed the cubic structure of cerium(III) sulfide, with the lattice constant increasing linearly with the strontium sulfide concentration, as shown in Fig. 2. The lattice constant shift between Ce$_2$S$_3$ and Ce$_3$S$_4$ is plotted on the same graph. When the lattice constant of the strontium sulfide series is extrapolated to zero strontium sulfide concentration the value obtained is about 8.59 kX., which is lower than the value reported for pure cerium(III) sulfide by Zachariasen (point A, Fig. 2) by about 3 parts per thousand. However, this lattice constant agrees closely with that of a sample of Brewer's material after heating with lithium fluoride (point C, Fig. 2). As we have shown, this decrease may be caused by the incorporation of some lithium ions into the relatively large interstices of the cerium sulfide structure. We attempted to check this by preparing the solid solutions in the absence of a flux, but otherwise under the same conditions. A 50 mole per cent. mixture had a lattice constant of 8.700 kX., or 0.006 kX. larger than that obtained with lithium fluoride. At zero per cent. strontium sulfide, the shrinkage is about 0.175 kX. The smaller shrinkage found with the "filled" structure is probably due to lower solubility of lithium fluoride in the more closely packed structure.

Attempts to prepare solid solutions of intermediate composition with no flux gave us diffuse X-ray patterns with sharp edges at a lattice constant corresponding to the "filled" structure. Preparations in which mixtures of anhydrous strontium and cerium(III) chlorides were converted to sulfides yielded similar results, indicating inhomogeneity.

A few mixtures of Ce$_2$S$_3$ with calcium and magnesium sulfides were prepared, showing the cubic Ce$_2$S$_3$ X-ray pattern with the lattice constants shown:

Table I

Composition	a (kX.)	
CaS-Ce$_2$S$_3$	8.597	(CaS lines present)
CaS-2Ce$_2$S$_3$	8.602	
MgS-Ce$_2$S$_3$	8.608	MgS lines present in both
MgS-2Ce$_2$S$_3$	8.607	

In the calcium sulfide samples, the appearance of the calcium sulfide lines in the 50 mole % sample suggests a solubility limit slightly below that composition, while the magnesium sulfide preparations indicates a solubility limit below 33$^1/_3$ mole % (probably 5–10%) of magnesium sulfide, with a limiting lattice constant of about 8.607 kX.

Preliminary electrical conductivity measurements on the solid solutions with strontium sulfide indicate high resistances with a positive temperature coefficient of conductivity.

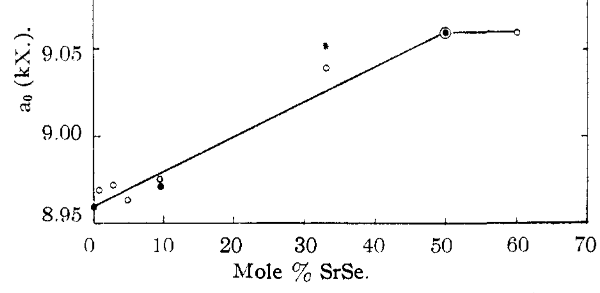

Fig. 3.—Lattice constant *vs.* composition—solid solutions of SrSe in Ce$_2$S$_3$; all samples heated in carbon boats in hydrogen selenide at 100°: ●, after one hour heating; ○, after six hours heating.

The details of this work will be published when more complete data have been obtained.

III. **Cerium Selenides and Oxyselenide.**—Several methods for the preparation of cerium(III) selenide were attempted. Direct combination of the elements led to no reaction at 500° and to an explosive reaction at 600–650°. Passing hydrogen selenide over freshly filed cerium metal in a carbon boat, while its temperature was gradually raised from 600 to 1200° over a five-hour period, yielded a black product which had a complex X-ray pattern like the complex form of cerium(III) sulfide, but with a larger lattice constant. The hydrogen selenide was prepared by passing dry hydrogen through a P$_2$O$_5$ drying tube leading directly into the reaction tube in which a boat containing ultra-pure selenium was maintained in a region whose temperature ranged from 300–450°. Evidently sufficient oxygen was still present to cause the complex type of selenide to be formed.

When we substituted anhydrous cerium(III) chloride for the metal, a dark red material was obtained after a five-hour treatment over the temperature range 500–900°. Weight changes indicated 92.5% conversion, but preliminary runs had indicated that some of the chloride is volatilized in the early stages of the reaction. An X-ray powder photograph gave a cubic pattern which was similar to that of the cubic form of the sulfide except for larger spacings and some intensity differences. The whole pattern was successfully indexed on the basis of the Ce$_2$S$_3$ structure and a precision lattice constant determination using a symmetrical back reflection camera and graphical extrapolation (Bradley and Jay) indicated a lattice constant of 8.9588 + 0.0005 kX. The density calculated from the X-ray data is 6.45 g./cm.^{3} which is comparable with Klemm's measured value[11] of 6.34 g./cm.^{3}.

When cerium(IV) oxide was used as the starting material for the reaction, the product was brown in color with some black material near the rear of the boat. Both the brown and black materials had the same X-ray powder pattern. The pattern was similar to that of cerium(III) oxysulfide except for longer spacings and some intensity differences. The diffraction pattern was indexed in the hexagonal system with the aid of a Hull–Davey chart and the data for the oxysulfide. The product is identified as cerium(III) oxyselenide, Ce$_2$O$_2$Se. The hexagonal unit cell dimensions of this compound are: $a_0 = 4.85$ kX.; $c_0 = 8.47$ kX.

The preparation of the sulfide and selenide of divalent cerium was attempted by reducing the trivalent salt with a slight excess of sodium or calcium. The reactions were carried out in sealed evacuated silica tubes at 600° with sodium and 1000° with calcium. After cooling, the tubes were opened and X-ray powder photographs taken. In the case of the selenide, the product gave a face-centered cubic pattern whose lattice constant was 6.05 ± 0.02 kX. This differs by 0.27 kX. from the lattice constant of cerium(III) sulfide ($a_0 = 5.778$ kX.).[12] The difference in cell dimension between calcium sulfide and selenide, based on Wyckoff's[12] compilation, is 0.23 kX. This corresponds to twice the difference in radius between sulfide and selenide ions. Goldschmidt radii give a difference of 0.22 Å. while Pauling radii give a difference of 0.28 Å. In view of the unusual combination of bond types found in these crystals, the slight departure from additivity is not surprising. On the basis of these considerations, it was concluded that the product was cerium(II) selenide, with the same structure as cerium(II) sulfide, and with essentially the same type of binding, as evidenced by the anomalously low lattice constants. The authors have not found it possible to prepare cerium(II) sulfide in the same manner.

Solid Solutions of Strontium Selenide in Ce$_2$Se$_3$.—Mixtures of strontium and cerium selenides were prepared and heated in hydrogen selenide at 1000° in the same manner as the sulfides. No flux was used, since the starting material had the cubic structure. The colors of the solid solutions ranged from a light tan with 50–60 mole per cent. SrSe through various red and deep purples to almost black as the percentage of strontium selenide decreases. The lattice constant–composition curve is shown in Fig. 3, where the deviation of the intermediate composition points from the

---

(11) W. Klemm and A. Koczy, *Z. anorg. allgem. Chem.*, **233**, 84 (1937).

(12) R. W. G. Wyckoff, "Crystal Structures," Vol. I, Supplement, Interscience Publishers, Inc., New York, N. Y., 1951.

straight line seems to be due to a lack of homogeneity. This is substantiated by the closer approach of the points to the line after additional heating periods. As with the sulfides, the solubility limit is 50 mole per cent. and the lattice constant is increased as the vacancies are filled by strontium ions.

Discussion

The results of the experiments described in Section I, Experimental, indicate that the complex form of cerium(III) sulfide described here is identical with the complex phase described by Eastman, Brewer, *et al.*, when traces of oxide are present. The cubic phase, which has been shown to be a distinct phase from the complex phase, is stabilized in the presence of strontium sulfide in solid solution as well as by the removal of oxide by solution in a molten flux. The stabilizing effect of strontium sulfide on the cubic form in the presence of oxygen, even when a flux is absent, may possibly be due to the separation of strontium oxide as a separate solid phase. The manner in which lithium fluoride and sodium chloride enter the Ce_2S_3 lattice has not been determined, but it is possible that the alkali metal ions enter into certain interstices between the sulfide ions with an equivalent number of halide ions entering in other interstitial positions. Another possibility, of course, is the substitution of three alkali ions for one cerium ion by filling vacancies in the cation lattice. In this case, the displaced cerium ions might form a separate cerium halide phase. In view of the shrinkage of the lattice with lithium fluoride and the expansion with sodium chloride, it may be that the halide ion is entering the sulfide lattice. However, the effect is rather small and a determination of the exact mechanism of solid solution may not be readily feasible.

The solid solutions of strontium sulfide and selenide in the corresponding cerium compounds represent cases of filling of a defect structure by the incorporation of cations of lower charge than those originally present. They differ from the solid solutions of cerium(II) sulfide in cerium(III) sulfide in that the additional metallic binding forces are not present either in the original compound of the divalent metal or in the solid solutions. With the alkaline earth metals, the binding is predominantly ionic and the cerium sulfide or selenide lattice expands when a large cation-like strontium is added, and contracts when a smaller cation-like calcium or magnesium is added. It is noteworthy that divalent europium forms a "normal" sulfide with no metallic binding. It should be of some interest to determine whether other rare earths which would have one or two "d" or "f" electrons in the divalent state, would also form semimetallic sulfides and selenides like CeS and CeSe.

Acknowledgment.—We wish to express our gratitude to Professor I. Fankuchen for his invaluable advice on the interpretation of X-ray diffraction data and to Professor Leo Brewer who so generously provided us with samples of his materials and information in advance of publication.

Brooklyn 2, New York Received November 12, 1951

[Contribution from the Insulation Department, Westinghouse Research Labs.]

A New Highly Silicious Soda–Silica Compound

By Leon McCulloch

A new soda–silica compound, of silica to soda ratio between 9.4 and 13.1 to one, has been made by crystallization of silicious sodium silicate solutions at 100°. The crystals are rectangular plates, single and in groups. Being readily prepared and easily filtered and washed without change, this compound should invite investigation. Incidental mention is made of a sodium tetrasilicate having an X-ray pattern unlike the one found in the literature.

A new soda-silica compound high in silica has been obtained by crystallization of silicious sodium silicate viscous solutions. Analyses of several such products give silica–soda ratios between 9.4:1 and 13.1:1. The most silicious compound heretofore reported has a ratio 4.0 or 4.3:1, the tetrasilicate.

The new silicate is made by the prolonged heating of a silicious solution of the following formula:

Silica gel or silicic acid (Dry but not anhydrous)	15 parts
Sodium hydroxide (pellets)	3.6 parts
Water	30 parts

This ratio of $SiO_2:Na_2O$ is about 5.0:1. Commercial sodium silicate solutions are below 4.0:1 in ratio.

The ingredients were enclosed within Pyrex ampoules (1″ × 6″) or friction-top tin cans (quarter pint) kept at 100° in a laboratory oven. These containers were inverted frequently to cause flow and stirring of the viscous solution. Within a week or two, the mass became clouded. In three or four weeks, precipitation was complete, yielding well-settled sediment and clear, thin liquor. Three such liquors had silica–soda ratios of 3.7, 3.6 and 3.8. Nine of the sediments, washed and dried, had ratios between 9.4 and 13.1. The analyses are collected into Table I, and also in Fig. 1, where Na_2O is plotted against SiO_2. Analyses were made of three of the liquors, also of some suspensions and sediments damp from a centrifuge, and of the sediments

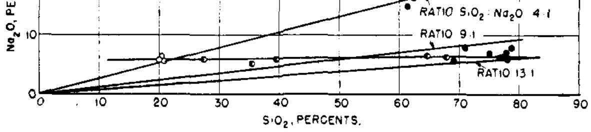

Fig. 1.—Silicious sodium silicates.