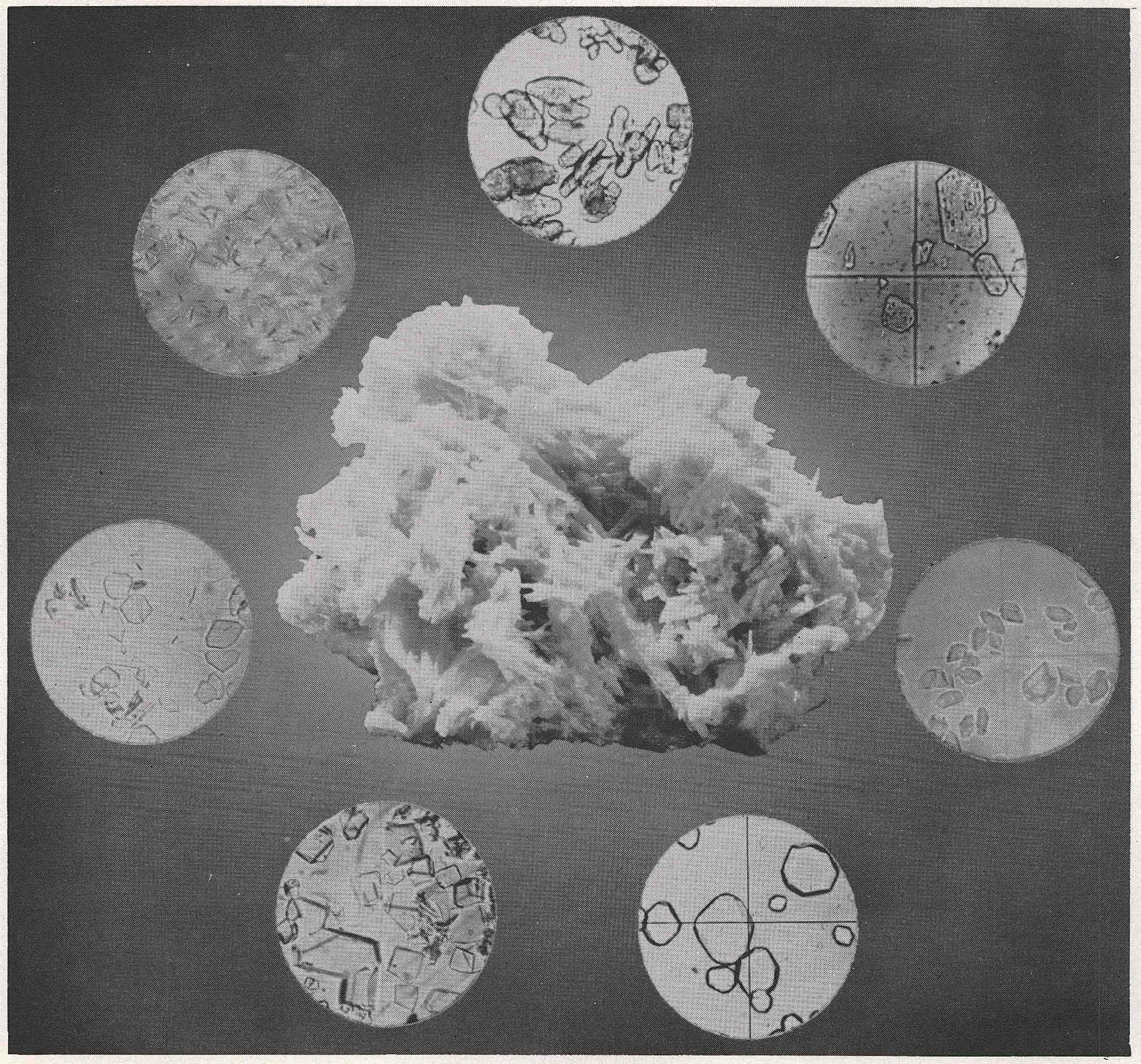
H. T. Hall

CHEMISTRY OF THE SOLUBLE SILICATES

REYNOLD C. MERRILL
Philadelphia Quartz Company

BULLETIN NO. 17–19

[Reprinted from Journal of Chemical Education, Vol. 24, Page 262, June, 1947.]



Photomicrographs of Crystalline Sodium Silicates

Center, anhydrous metasilicate; clockwise, beginning at top, $3Na_2O \cdot 2SiO_2 \cdot 11H_2O$*, a lower hydrate of* $3Na_2O \cdot 2SiO_2$, $Na_2SiO_3 \cdot 5H_2O$, $Na_2SiO_3 \cdot 6H_2O$, $Na_2SiO_3 \cdot 8H_2O$, $Na_2SiO_3 \cdot 9H_2O$, $Na_2O \cdot 4SiO_2 \cdot 7H_2O$ *[the sesquisilicates and metasilicate hexahydrate are from the paper by* S*PRAUER and* P*EARCE, J. Phys. Chem., 44, 909 (1940)].*

CHEMISTRY OF THE SOLUBLE SILICATES

REYNOLD C. MERRILL
Philadelphia Quartz Company, Philadelphia, Pennsylvania

Soluble silicates are systems containing varying proportions of an alkali metal and silica (SiO_2), usually with at least some water. More than 50 products containing these three constituents are commercially available, and at least 15 crystalline alkali metal silicates are known. The alkali metal most frequently encountered is sodium, although potassium silicates have been commercially available for many years. Recently the manufacture of lithium metasilicate, for use in porcelain enamels and glazes, has been announced. No ammonium silicates have apparently yet been isolated, although the properties of a solution of silica in aqueous ammonia indicate that they may exist. Rubidium and caesium silicates have been made but not studied extensively and at present have no industrial importance.

Although alkali and silica may be combined in all proportions, present commercial products do not exceed a silica to alkali ratio of about four by weight because of the very low solubility of fused silicates above this ratio. By combining alkali, silica, and water in varying proportions, a large number of different products with widely varying properties can be obtained. These range from readily and highly soluble crystals to white powders which do not dissolve in boiling water, thin slightly sticky fluids of the consistency of maple sirup, heavy viscous materials which barely flow, soft plastic masses which bounce like rubber, sticky plastics which do not bounce and behave like old-fashioned taffy, and lumps of transparent glass which may have sharp edges.

This variety of properties and forms has led to wide industrial utilization of the soluble silicates. Plants in the United States produced during 1944 an amount of silicate equivalent to around one and a half billion pounds of the 41° Baumé solution (containing about 38 per cent solids.) Sodium silicates are used as detergents, both by themselves and with other detergents such as soaps, as adhesives, and in cements, sizes, coatings, textile operations, water treatment, oil-well drilling, roofing granules, and for many other purposes.

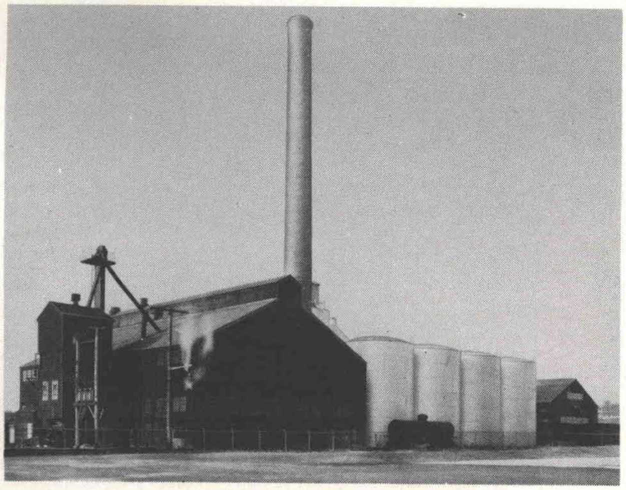


Figure 1. Typical Present Day Silicate Manufacturing Plant

History. The discovery of the soluble silicates has been attributed to a group of Phoenician sailors who used lumps of natural soda ash to support their cooking vessels in a camp fire on a sandy beach. They observed that a glass was formed, although they were probably not aware that it may have been water soluble. As early as A.D. 77 Pliny described the preparation of a "glass" by fusing a mixture of white sand with 3 parts of niter. Porta in 1567 produced a glass by fusion of cream of tartar with rock crystal, and Agricola in 1621 by fusion with ground flint. J. B. van Helmont realized that such a glass can be slowly dissolved in water. He writes, "If stones, gems, sand, flint, etc., be boiled in alkali-lye, they will dissolve, and the liquid when treated by acids will yield a dust (precipitate) equal in weight to that of the original mineral used." J. R. Glauber called the aqueous solution of the fused alkali and sand "oleum silicum" or "liquor silicum," and J. N. Von Fuchs, "wasserglass." Von Fuchs investigated the soluble silicates quite extensively during the 19th century and suggested many of the present uses.

Preparation. At least six methods may be used to prepare the soluble silicates. They are manufactured in the United States at present almost exclusively by the fusion of sand and soda ash in large open hearth furnaces at temperatures around 1300°C., according to the equation

$$Na_2CO_3 + nSiO_2 \rightarrow Na_2O \cdot nSiO_2 + CO_2\uparrow$$

The most common commercial silicates correspond to values of n in the above equation equal to 2.0 and 3.2. Intermediate ratios may be made by mixing, and more alkaline grades by adding caustic soda. The reaction forming the most alkaline silicates can be completed below the fusion temperature of the mixture.

The more alkaline silicates may be made by fusing sand or a higher ratio silicate with sodium hydroxide. This reaction can also be completed below the fusion temperature.

In Europe the soluble silicates are made using sulfate and coal in place of soda ash. The equation may be written

$$2Na_2SO_4 + C + nSiO_2 \rightarrow 2Na_2O \cdot nSiO_2 + 2SO_2\uparrow + CO_2\uparrow$$

The mechanism of this process is not known, although it is common knowledge in the industry that, due to side reactions, more coal is required than indicated by this equation. In order to make sure that no coal remains in the product, an excess of sulfate is generally used. The product of this process is usually less pure than that made by soda ash fusion.

The soluble silicates may also be made by dissolving siliceous materials in concentrated caustic soda solution at elevated temperatures, usually under pressure. The reaction may be written

$$n\mathrm{SiO_2} + 2\mathrm{NaOH} \rightarrow \mathrm{Na_2O}\cdot n\mathrm{SiO_2} + \mathrm{H_2O}$$

Powdered flint, infusorial earth, precipitated silica, or charred rice hulls (which contain about 35 per cent silica) dissolve in 20 per cent sodium hydroxide solution in about three hours with agitation under three to four atmospheres pressure. Quartz takes longer and a higher pressure. It is reported that silica dissolves more rapidly in potassium than sodium silicate solutions and even faster in mixtures of the two.

The amount of silica which dissolves is apparently limited, although silica to alkali ratios as high as 2.7 have been reported in the literature. Ratios as high as 4.2 have been produced by electrolyzing more alkaline silicates in a cell with a mercury cathode.

Silicon and its alloys with iron or manganese react with sodium hydroxide solutions, liberating hydrogen and forming sodium silicates. The reaction may be written

$$\mathrm{Si} + 2\mathrm{NaOH} + \mathrm{H_2O} \rightarrow \mathrm{Na_2O}\cdot\mathrm{SiO_2} + \mathrm{H_2}\uparrow$$

This Jaubert or Silicol process was used in Great Britain for a short time in World War I but does not appear to be economical under present conditions.

A great deal of work has been done on the preparation of silicates directly from salt and sand by the reaction

$$2\mathrm{NaCl} + n\mathrm{SiO_2} + \mathrm{H_2O} \rightarrow \mathrm{Na_2O}\cdot n\mathrm{SiO_2} + 2\mathrm{HCl}$$

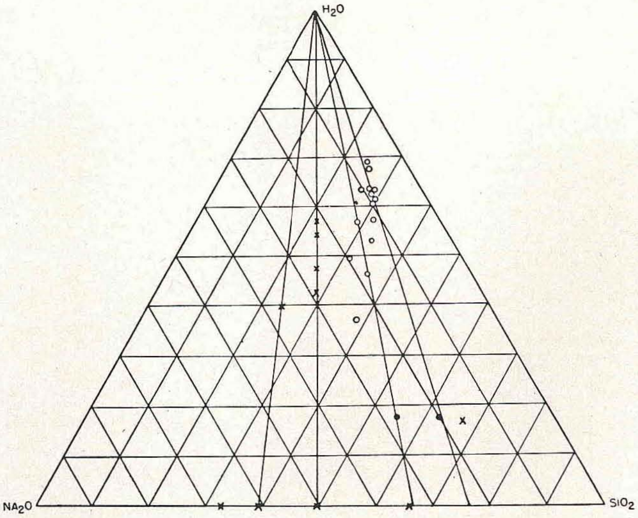
Silicate can be made by this method, but the reaction equilibrium apparently does not favor the production of silicate. For this reason and because of the slow rate and low thermal efficiency involved in carrying out the reaction, it seems unlikely that silicates will be produced extensively on a commercial scale by this method.

Dissolving Silicate Glass. The silicate produced by the soda ash fusion process forms, on cooling the melt, a clear light bluish green glass. The color is due to traces of iron or other impurities. For commercial sodium silicate glasses made in the United States the impurities amount to less than one per cent. Silicate glasses or powders with a silica to alkali ratio of about two by weight dissolve if finely ground. Those with a ratio above 2.5 do not dissolve when brought in contact with either cold or boiling water, although some alkali is leached out. The siliceous silicates must be dissolved by steam under pressure with mixing in the presence of excess solid or concentrated solution.

This dissolving is usually done by the manufacturer and the solution sold as concentrated as convenience permits. The silicate with a silica to alkali ratio by weight of 3.2 can be handled readily only below concentrations of 40 per cent solids, corresponding to a specific gravity of 1.41 or 43° Baumé. The more alkaline silicates can be handled readily at higher concentrations. The 2.0-ratio silicate is frequently sold at a concentration of 54 per cent solids, corresponding to a specific gravity of 1.69 or 60° Baumé.

The compositions of the silicate solutions available commercially are shown in the ternary phase diagram of Figure 2 by open circles. The line nearest the silica apex represents the series of products obtained by adding water to a 3.2-ratio glass. That next to it represents those from a 2.0-ratio glass. The lines on the left correspond to metasilicate and sesquisilicate compositions. The compositions of the commercially available amorphous solids are indicated by solid circles. Those containing around 17 per cent water are spray-dried products.

Crystalline Alkali Metal Silicates. Some properties of those crystalline alkali metal silicates whose existence is adequately established experimentally are summarized in Table 1. Photomicrographs of eight of these are shown in the Frontispiece. The existence of the anhydrous compounds sodium metasilicate ($\mathrm{Na_2SiO_3}$) and sodium disilicate ($\mathrm{Na_2Si_2O_5}$) is well established by phase diagrams and by the optical properties of single crystals, as determined by Morey, Kracek, and collaborators. The phase diagram for the system $\mathrm{Na_2O}$-$\mathrm{SiO_2}$ is given in Figure 3. Recent work has indicated the existence of an anhydrous orthosilicate ($\mathrm{Na_4SiO_4}$) and sodium "sesquisilicate" or "pyrosilicate" ($\mathrm{Na_6Si_2O_7}$).



×, Crystalline silicates
O, Silicate solutions commercially available and
●, Commercially available amorphous solids

Figure 2. Ternary Phase Diagram Showing Crystalline Silicates and Commercially Available Forms

TABLE 1. Crystalline Alkali Metal Silicates

Ratio	*Formula*	*Melting point, °C.*	*Density at 20°C.*	*Refractive indices*	*Crystal system*	*Optical properties*
$2Na_2O\cdot SiO_2$	Na_4SiO_4	1083,* 1120				
$3Na_2O\cdot 2SiO_2$	$Na_6Si_2O_7$	1115	2.96	$\alpha = 1.524$ $\gamma = 1.529$		Opt. negative
$3Na_2O\cdot 2SiO_2\cdot 11H_2O$	$N_3HSiO_4\cdot 5H_2O$	88		$\alpha = 1.502$ $\beta = 1.510$ $\gamma = 1.524$	Rhombic	$2V = 60° \pm 30$ Birefringence = 0.008 Biaxial
$Na_2O\cdot SiO_2$	Na_2SiO_3	1086		$\alpha = 1.513$ $\beta = 1.520$ $\gamma = 1.528$	Orthorhombic Prismatic	$2V$, large Opt. negative Biaxial
$Na_2O\cdot SiO_2\cdot 5H_2O$	$Na_2SiO_3\cdot 5H_2O$	72.20	1.749	$\alpha = 1.443$ $\beta = 1.452$ $\gamma = 1.462$	Triclinic Pinacoidal	$2V$, 70° Opt. positive Slight disp., $v > r$
$Na_2O\cdot SiO_2\cdot 6H_2O$	$Na_2SiO_3\cdot 6H_2O$	62.85	1.807	$\alpha = 1.453$ $\beta = 1.462$ $\gamma = 1.470$	Monoclinic Sphenoidal	$2V$, 75° Opt. negative Dispersion: $r > v$
$Na_2O\cdot SiO_2\cdot 8H_2O$	$Na_2SiO_3\cdot 8H_2O$	48.35	1.672	$\alpha = 1.458$ $\beta = 1.460$ $\gamma = 1.462$	Monoclinic Prismatic	$2V$, 64° Opt. negative Dispersion: $r > v$
$Na_2O\cdot SiO_2\cdot 9H_2O$	$Na_2SiO_3\cdot 9H_2O$	47.85	1.646	$\alpha = 1.451$ $\beta = 1.454$ $\gamma = 1.458$	Rhombic Bipyramidal	$2V = 90°$ Opt. positive Dispersion: $r > v$
$Na_2O\cdot 2SiO_2$	$Na_2Si_2O_5$	874		$\alpha = 1.497$ $\beta = 1.514$ $\gamma = 1.508$	Orthorhombic Pinacoidal	$2V = 50°–55°$ Opt. negative
$Na_2O\cdot 4SiO_2\cdot 7H_2O$	$Na_4Si_9O_9\cdot 7H_2O$			$\alpha = 1.463$ $\beta = 1.483$(?) $\gamma = 1.483$		
$K_2O\cdot SiO_2$	K_2SiO_3	976		$\alpha = 1.520$ $\gamma = 1.528$	Orthorhombic	$2V = 35°$ Opt. positive Biaxial Dispersion: $v > r$
$K_2O\cdot SiO_2\cdot {}^1/_2H_2O$	$K_2SiO_3\cdot {}^1/_2H_2O$					$2V$, large Opt. positive (?)
$K_2O\cdot SiO_2\cdot H_2O$	$K_2SiO_3\cdot H_2O$	370				High birefringence Opt. positive Biaxial
$K_2O\cdot 2SiO_2$	$K_2Si_2O_5$	1045	2.54	$\alpha = 1.503$ $\gamma = 1.513$	Orthorhombic	$2V$, large Opt. negative Biaxial
$K_2O\cdot 2SiO_2\cdot H_2O$	$K_2Si_2O_5\cdot H_2O$	405				$2V$, small Opt. positive Biaxial
$K_2O\cdot 4SiO_2$	$K_2Si_4O_9$	770	2.38	$\alpha = 1.477$ $\gamma = 1.482$	Monoclinic or triclinic	$2V$, large Opt. positive Biaxial
$K_2O\cdot 4SiO_2\ H_2O$	$K_2Si_4O_9\cdot H_2O$	515	2.42	$\alpha = 1.480–1.495$ $\gamma = 1.530–1.535$	Rhombic	$2V = 69.5$ Opt. positive Biaxial
$Na_2O\cdot Li_2O\cdot 4SiO_2$	$NaLiSiO_3$	847		$\alpha = 1.552$ $\beta = 1.557$ $\gamma = 1.571$	Orthorhombic	$2V$, very large
$2Li_2O\cdot SiO_2$	Li_4SiO_4	Decomp.	2.39	$\alpha = 1.602$ $\gamma = 1.610$		
$Li_2O\cdot SiO_2$	Li_2SiO_3	1201		$\omega = 1.591$ $\epsilon = 1.611$		Uniaxial
$3Li_2O\cdot 2SiO_2$	$Li_6Si_2O_7$	1032 (incong.)		$\alpha = 1.614$ $\beta = 1.594$		$2V$, very small Opt. positive Biaxial
$Li_2O\cdot 2SiO_2$	$Li_2Si_2O_5$	1033		$\alpha = 1.547$ $\beta = 1.550$ $\gamma = 1.558$	Orthorhombic	$2V = 50°–60°$

* KRACEK [*J. Phys. Chem.*, **34,** 1583 (1930)] reports an incongruent melting point at 1120°, probably with decomposition. D'ANS AND LOFFLER [*Z. anorg. allgem. Chem.*, **191,** 1 (1930)] give a congruent melting point of 1083° and a transition at 960°.

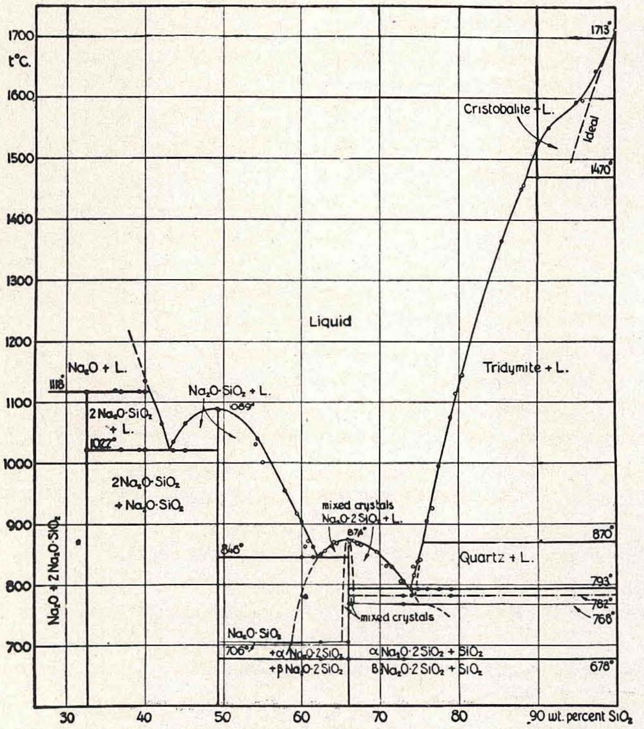


Figure 3. Phase Diagram of Na_2O-SiO_2 System [From Kracek, *J. Phys. Chem.*, 34, 1583 (1930)]

Numerous attempts to produce a definite hydrated sodium orthosilicate have not been successful. Thermodynamic calculations by Dr. N. W. McCready of this Laboratory indicate that sodium orthosilicate would not be stable in contact with water at ordinary temperatures.

A stable crystalline compound of the composition $3Na_2O \cdot 2SiO_2 \cdot 11H_2O$ was isolated about 1930. It is commonly referred to as sodium sesquisilicate. A name more in conformity with present nomenclature is sesquisodium silicate. This compound may also be regarded as a pentahydrate of trisodium orthosilicate, $Na_3HSiO_4 \cdot 5H_2O$. According to the International Union of Chemistry's rules for naming inorganic compounds, it is to be regarded as the eleven hydrate of sodium (3:2) silicate.

Sodium metasilicate was first reported in 1838 by Fritzche who described the six and nine hydrates. Although 12 additional hydrates have been reported since then, the existence of only the five, six, eight, and nine hydrates has been adequately established. A method for successfully producing the pure pentahydrate on an industrial scale was developed for the first time in 1928 by C. L. Baker. Since then it has been commercially available as a white, dry, free-flowing, pure chemical and is used in large quantities as a detergent in laundries, dairies, textile, and metal-cleaning plants. Since it is somewhat hygroscopic the metasilicate pentahydrate should be protected in humid atmospheres. Ordinary packages of wood or metal, asphalt lined or multi walled bags are used for shipment.

The pentahydrate melts in its own water of crystallization at 72.2°. The solution thus formed is so easily supercooled that crystallization does not ordinarily occur under usual conditions.

The various metasilicate hydrates may be prepared by allowing a solution of the proper composition to crystallize or solidify, with or without seed crystals, at a temperature just under the melting point of the desired hydrate.

Crystalline tetrasilicate hydrates of the general formula $Na_2O \cdot 4SiO_2 \cdot 9H_2O$ were patented in 1939 by Wegst and Wills. Their use in enamels, cements, and cleaners is suggested.

Other crystalline forms of the soluble silicates which have been reported in the literature but not thoroughly studied include one difficultly soluble and one readily soluble hydrated lithium metasilicate, a lower hydrate of sodium "sesquisilicate," three polymorphic forms of sodium disilicate, and two crystalline forms of potassium tetrasilicate. More work needs to be done on the phase behavior of the systems R_2O-SiO_2-H_2O where R_2O is an alkali metal oxide.

Potassium Silicates. None of the crystalline potassium silicates listed in Table 1 is commercially available. The available potassium silicate solutions have silica to potassium oxide ratios of 2.5 and 2.1 by weight, corresponding to molecular ratios of 3.9 and 3.3. They are sold at concentrations of 27.3 and 39.4 per cent, respectively. They are more expensive than the sodium silicates, so are used only when some special

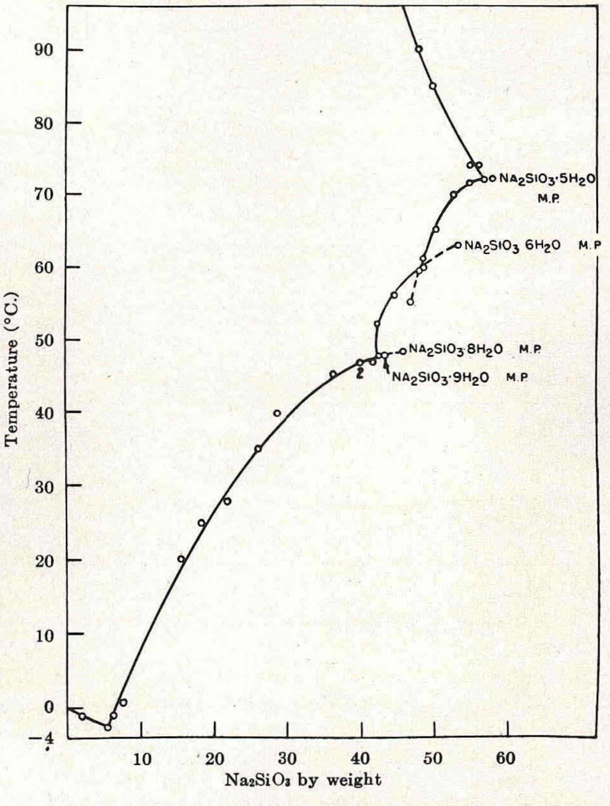


Figure 4. Solubility of Sodium Metasilicate in Water [From Baker and Jue, *J. Phys. Chem.*, 42, 165 (1938)]

property justifies the higher cost. Their comparative freedom from a tendency to effloresce or "bloom" makes them preferred for special paints, coatings, and binders. Their smooth flame and freedom from the yellow glare of sodium vapor causes welding rod coatings made from potassium silicates to be preferred. A high solubility and small tendency to salt out soap, together with a marked detergent action, lead to their use in liquid and rapid sudsing soaps.

Physical Properties. Sodium or potassium silicates vary in their water solubility from the very soluble ortho, sesqui, and metasilicates to those silicates having a silica to alkali ratio greater than four, which are essentially insoluble. Even these can apparently be obtained as stable aqueous colloidal dispersions of limited concentration. The solubility of sodium metasilicate is shown in Figure 4. In general the solubility of the silicates decreases with increasing silica content. The commercially available hydrated sesquisilicate and metasilicate pentahydrate dissolve freely and completely in water just as readily as sodium chloride. The former has a slight positive heat of solution whereas that of the latter is somewhat negative. Silicates of silica to alkali ratios greater than about 2.5 appear to be essentially insoluble even in boiling water, although as mentioned previously, aqueous dispersions are prepared by special dissolving techniques. The isolation of a tetrasilicate may indicate that some of the more concentrated siliceous silicate solutions of commerce might be supersaturated although they rarely, if ever, crystallize under ordinary conditions.

The specific gravity of silicate solutions increases regularly with concentration. For a given concentration of solids the solution of the more alkaline silicate has the higher specific gravity. The specific gravity of silicate solutions decreases regularly with temperature. The more concentrated the solution, the smaller is its coefficient of expansion.

The soluble silicates may be regarded as salts of orthosilicic (H_4SiO_4), pyrosilicic ($H_6Si_2O_7$), metasilicic (H_2SiO_3), disilicic ($H_2Si_2O_5$), and other silicic acids. Despite many attempts none of these acids has been isolated. The absorption of water by silica is more or less continuous. No definite break or flats in the vapor pressure vs. moisture content curve, indicating a definite hydrate or compound, have been obtained.

Since all these silicic acids are weak, their alkali-metal salts hydrolyze in solution, although not to the extent formerly believed. Even the most alkaline silicates in dilute solution are not more than 30 to 40 per cent hydrolyzed into colloidal silica and sodium hydroxide. For ratios more siliceous than one to one and concentrations above molar, the per cent hydrolysis is less than six per cent.

The pH of sodium silicate solutions of composition corresponding to the "orthosilicate," metasilicate, sesquisilicate, disilicate, and "trisilicate" as a function of concentrations from 0.001 to 5 N are shown in Figure 5. The effect of soluble silica in reducing the pH and change of pH with concentration is indicated. Electrometric titrations with acids show that the high pH's of silicate solutions are maintained until almost completely neutralized and that soluble silica increases their buffer capacity. The regular decrease with temperature and soluble silica content up to the metasilicate is shown in Figure 6. Sodium metasilicate is more alkaline than trisodium phosphate, sodium carbonate, or tetrasodium pyrophosphate. Solutions of the more siliceous silicates have pH's less than soda ash, although still somewhat higher than those of tetrasodium pyrophosphate of equivalent concentrations. The pH values measured with indicators may be as much as 0.4 unit lower than those measured with the hydrogen electrode in concentrated solutions of the more siliceous silicates. This may be due at least partially to preferential sorption of one form of the indicator. The alkali-resistant glass electrode after suitable correction and standardization gives values agreeing well with those of the hydrogen electrode except at high concentrations of the most alkaline silicates.

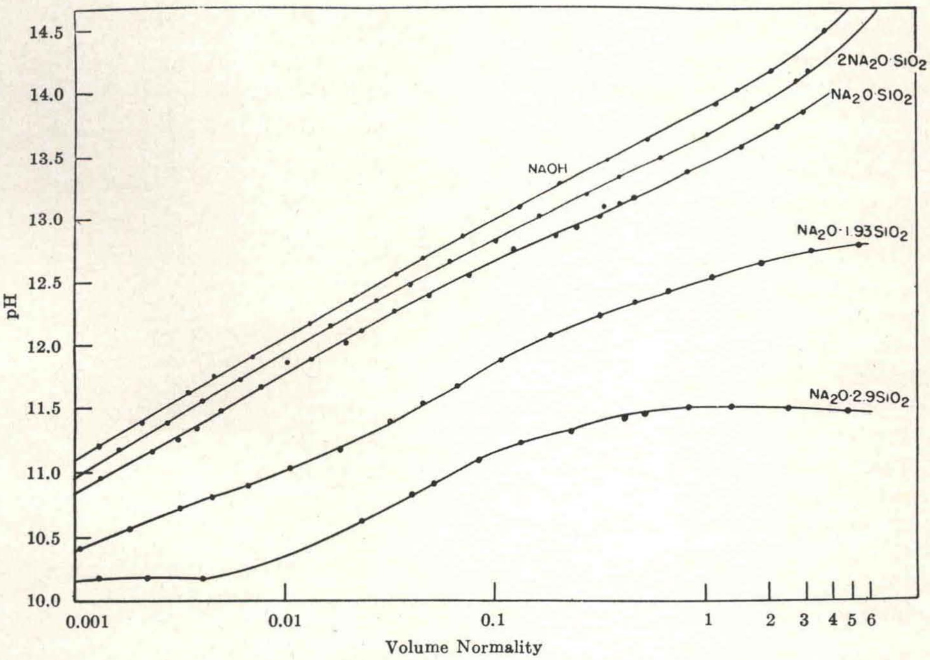


Figure 5. pH vs. Concentrations (Log Scale) for Caustic Soda and Ortho, Meta, 1:2, and 1:2.9 Sodium Silicates at 20°C.

Titration curves of sodium metasilicate indicate

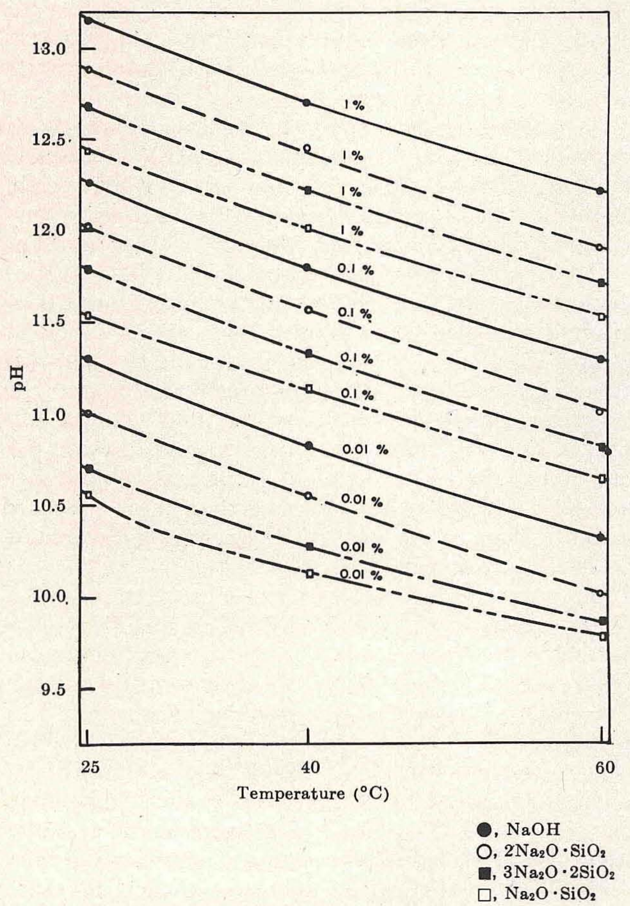


Figure 6. pH of 0.01, 0.1, and 1.0 Per Cent Alkali Solutions as a Function of Temperature [Data from Kuentzel, Hensley, and Bacon, *Ind. Eng. Chem.*, 35, 1286 (1943)]

the formation of an acid silicate ion, $HSiO_3^-$. From the electrometric titration curve and the extent of hydrolysis the first dissociation constant of the hypothetical metasilicic acid is calculated as 2×10^{-10} and the second as 9.5×10^{-16}.

Viscosities of varying weight normalities of different ratio silicates are shown in Figure 7. The viscosity at a given normality increases with the silica to alkali ratio. At ratios of three or greater the viscosity rises very rapidly above a certain normality. This concentration is lower and the rise more abrupt for the more siliceous silicates. The rise in viscosity is illustrated by the data for a 3.2-ratio silicate. A solution containing 37.6 per cent solids has a viscosity of 1.8 poises at 20°C. At 38.7 per cent solids the viscosity is 7.5 poises, at 39.0 per cent 11.1 poises, at 39.4 per cent 100 poises, and at 40.3 per cent of the order of 1000 poises. At the latter concentration the system is essentially a semisolid. The viscosity of solutions of the same concentration by weight is a minimum for a silica to alkali ratio just above two. Potassium silicates are usually more viscous than the corresponding sodium silicate at the same concentration by weight.

The apparent viscosity of concentrated solutions of the siliceous silicates varies quite considerably with the rate of shear. Absolute viscosities of such solutions are not given by the Ostwald or flow types of viscometers. The falling ball or rotating cylinder types will give absolute viscosities under the proper conditions, providing suitable corrections are made. The indication of "structural viscosity" in fairly concentrated systems of the siliceous silicates is in agreement with the colloidal nature of these systems.

As expected, temperature decreases the viscosity of silicate solutions. The effect is larger for the more siliceous silicates. A common explanation for the marked decrease with temperature in the viscosity of lyophilic colloids, such as the siliceous sodium silicates, is that the hydration layer of the micelle or the amount of bound water is reduced.

Crystalloidal and Colloidal Silicates. The physical properties of solutions of the soluble silicates are in agreement with the theory that the alkaline silicates are crystalloidal, forming only simple ions in solution, whereas the siliceous silicates are colloidal. Colloidal properties begin to appear above a silica to alkali ratio of about two and are particularly evident above a ratio of three. This gradual transition from crystalloidal to colloidal is indicated by a decrease in the activity coefficient of the silicate determined by freezing-point lowering, boiling-point elevation, vapor pressure, and determinations of the sodium-ion activity with the sodium-amalgam electrode. Transport numbers of the silicate also increase with the silica ratio to a high value, indicative of an aggregation of simple ions with or without colloidal silica or of a definite complex colloidal ion. The electrical conductivity of silicate solutions

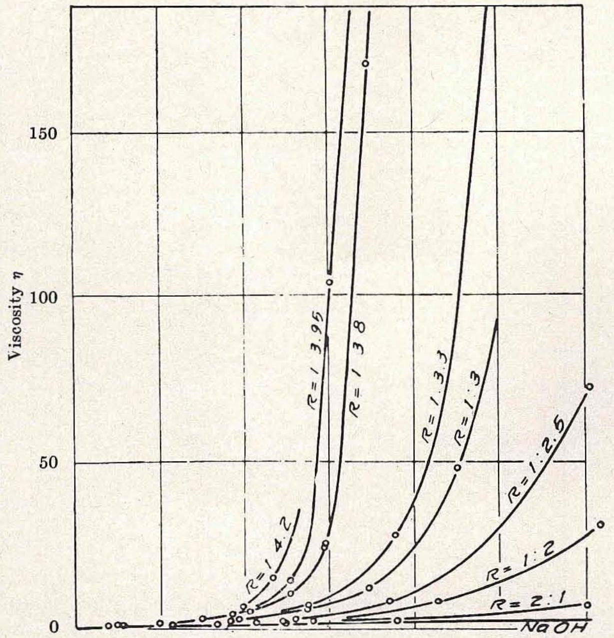


Figure 7. Viscosity of Silicate Solutions of Different Ratio as a Function of Normality (From J. G. Vail, "Soluble Silicates in Industry," Chemical Catalog Company, New York, 1928, p. 148)

decreases greatly with silica to alkali ratio up to about two; the decrease in conductivity with silica to alkali ratio above this point is very small. The temperature coefficient of conductivity increases with ratio up to two; above this ratio it decreases slightly.

The gradual transition from crystalloidal to colloidal silicates is further shown by light scattering and membrane diffusion methods. The Tyndall scattering of 2 molar sodium silicate solutions is small and practically constant below a silica to alkali ratio of 2.5. Above this ratio it increases greatly, indicating the presence of colloidal particles which increase rapidly in size. The more siliceous silicates contain some silica in a form which does not diffuse through a parchment or collodion membrane. The amount is not large, except for the most siliceous silicates, indicating that the colloidal particles are either quite small or in equilibrium with simple ions or relatively small complex particles. Donnan-membrane equilibrium calculations have indicated that the average silicate micelle contains some nondiffusible sodium, but this has not yet been proved.

The colloidal particles in the siliceous silicates are visible in the ultramicroscope. The change of ratio on diffusion shows the presence of several ionic species in all but the most alkaline silicates.

Ammonium molybdate reacts with the crystalline silicates, forming a greenish yellow silicomolybdate. Colloidal silica sols show no color with this reagent. The intensity of the color developed by the soluble siliceous silicates is far less than that expected on the basis of their silica content and decreases with the silica to alkali ratio. Although this reaction has been used to estimate the proportion of crystalloidal matter in silicate solutions, no complete study has been made of the ions producing the reaction nor of the relation between concentration and intensity of color under various conditions.

The soluble silicates may, like the soaps, be regarded as colloidal electrolytes. However, unlike the soaps and synthetic detergents, a variety of ions may be involved, and the equilibrium between simple ions and micelles is reached only very slowly. When one of the siliceous silicates is diluted, several hours are required for the pH and electrical conductivity to become constant. The slow reaction between the more siliceous silicates and sodium hydroxide can be followed by observing the decrease in light scattering and number of ultramicroscopically visible particles, and the change in pH, electrical conductivity, and color formed with ammonium molybdate as a function of time. Very little quantitative work has been done on reactions of this type.

Chemical Properties. Silicates of soda are precipitated by most salts of the heavy metals but seldom, if ever, is a stoichiometric definite metal silicate produced, even with the crystalline metasilicate. The precipitate may contain varying ratios of colloidal silica, a basic salt, a hydroxide or hydrous oxide of the metal, or a colloidal complex or floc. For example, the color of the precipitate formed by the reaction between tenth molar copper sulfate and sodium metasilicate varies from light blue-green to deep blue. X-ray investigations indicate that this precipitate consists of varying proportions of two basic copper sulfates—$4CuO{\cdot}SO_3{\cdot}3H_2O$ and $3CuO{\cdot}SO_3{\cdot}2H_2O$—and amorphous silica. Electron diffraction studies show that thin membranes made by the reaction of sodium metasilicate with copper sulfate, ferric chloride, and lead acetate contain "hydroxides" of these metals.

When crystals of readily soluble heavy metal salts are placed in moderately concentrated silicate solutions, they become encased in a gel-like covering. This soon bursts or deforms due to the osmotic pressure of the concentrated solution formed by water diffusing through the membrane. This salt solution thus exposed is again covered with a membrane and this process repeated. Long filaments and curious growths are formed. Colored salts of copper, nickel, cobalt, manganese, iron, and uranium form "silicate gardens" of great variety and beauty.

Alcohol, glycerin, acetone, strong ammonia, and salt brine precipitate the silicates. These precipitates can be partially redissolved, but the solutions formed differ somewhat in viscosity from the original.

Solid zinc oxide, amorphous calcium carbonate or oxide, and some clays react with the soluble silicates, forming insoluble products. The reaction is more rapid with the alkaline silicates. Because of their alkalinity silicate solutions react with aluminum and zinc, liberating hydrogen. In solutions of the siliceous silicates, the metal soon becomes coated with a silicate film which essentially stops the reaction.

Sols and Gels. The ability to form sols and gels is one of the most interesting and characteristic properties of the soluble silicates. When a solution of any one of them is mixed with a solution of an acidic material, the mixture gradually becomes opalescent and, if the silica concentration is above one to two per cent, sets to a gel. Solutions with a lower concentration of silica form silica sols whose highly hydrated colloidal particles are negatively charged except in moderately concentrated acid solutions. All acids or acid-forming materials, such as chlorine, sulfur dioxide, ammonium salts, bisulfates, and bicarbonates, form sols or gels under these conditions. Sodium aluminate, zincate, and plumbate solutions also form gels with soluble silicate solutions.

The time of set of the gel mixture increases with silica concentration, and, except above a pH around 8.0, with temperature. For acetic acid gels at a fixed temperature and pH, it appears to be inversely proportional to the square of the silica concentration. The logarithm of the time of set is proportional to the reciprocal of the absolute temperature. The activation energy thus obtained of 17,000 calories per mol in acid and neutral solutions and 24,700 calories per mol in basic solution suggests that the rate-determining step of this gelation is a chemical process. The time of set is in some cases a minimum at a pH near that corresponding to complete neutralization of the alkalinity of the silicate with acid. It is roughly proportional to the hydrogen-ion concentration in acid solution and to the hydroxyl-ion concentration in basic solution. Added salts decrease the time of set. Nonelectrolytes have little effect except in fairly large amounts. Some, such as dulcitol, decrease the rate of set. Others, as methyl alcohol, increase the rate of set, whereas still other nonelectrolytes, for example glycerol, retard setting at some pH's and increase it at others. Light appears to have no effect on the time of set.

No change in conductivity and practically no thermal effect occurs as the gels set. Freshly set gels show syneresis effects. Some silicic acid gels containing 1 to 2 per cent silica are thixotropic. Gels formed in acid or neutral solutions are firm, semisolid, elastic, and slightly opalescent; those formed in basic solutions are softer, probably because some silica dissolves above a pH of 8.

According to the most widely accepted theory of gelation, the low molecular weight silicic acid first produced by neutralization of the silicate alkalinity by acid condenses to form very large polysilicic acid molecules. These heavily hydrated, long, branched molecules form an interlaced fibrillar or brush heap structure which enmeshes the liquid.

Silica sols are now finding commercial applications in water and textile treatments. Since dry silica gels absorb large amounts of many materials, they are used industrially as desiccants, catalysts, adsorbents, and for solvent recovery.

17-19-M-253Ad.

Printed in U.S.A.

THIS is a reprint of a paper prepared from studies made by Philadelphia Quartz Co. Chemical Dept. If you abstract or quote from it, please credit the author and the company. Additional copies available on request.

PHILADELPHIA QUARTZ COMPANY

Manufacturers PQ Silicates of Soda, Silicates of Potash, Metso Detergents

General Offices: Public Ledger Building, Philadelphia 6, Pa.

Chicago Sales Off. 205 W. Wacker Drive

Distributors in over 65 cities

PQ WORKS

ANDERSON, IND.
BALTIMORE, MD.
CHESTER, PA.

GARDENVILLE, N. Y.
JEFFERSONVILLE, IND.
KANSAS CITY, KANS.

RAHWAY, N. J.
ST. LOUIS, MO.
UTICA, ILL.

SOME REFERENCES ON THE CHEMISTRY OF THE SOLUBLE SILICATES

cf. Paper in J. Chem. Ed., 24, 262 (1947)

The pictures of the sesquisilicates and metasilicate hexahydrate shown in the frontispiece were taken by Sprauer and Pearce (J. Phys. Chem., 44, 909 (1940). The other metasilicate hydrate pictures were taken by C. L. Baker (Am. Mineralogist, **18**, 206 (1933). The photograph of tetrasilicate crystals was taken by J. H. Wills.

References
to Text

Page	Col.	Line	
262	2	14	Pliny, Historiae Naturalis, **36**, 66 (A. D. 77)
262	2	16	Porta, C. B., Magia Naturalis, Neapoli (1567)
262	2	17	Agricola, G., De Re Metallica, Basillae (1621)
262	2	18	Van Helmont, J. B., De Lithiase, Amstelodami, **28** (1644)
262	2	24	Glauber, J. R., Furni Novi Philosophici Franckfurt, **107** (1648)
262	2	26	Von Fuchs, J. N., Kastners Arch. **5**, 385 (1825); Ber. Akad. Munchen, 66 (1824)
262	2	30	Vail, J. G., Soluble Silicates in Industry, Reinhold Publishing Co., New York (1928)
262	2	35	Howarth, J. T., and Turner, W. E. S., J. Soc. Glass Tech. **14T**, 402 (1930)
262	2	35	Howarth, J. T. Maskill, W., and Turner, W. E. S., J. Soc. Glass Tech. **17**, 25T (1933)
262	2	35	Huttig, G. F., and Dimoff, K., Ber. **75B**, 1573 (1942)
262	2	35	Kroger, C. and Fingas, E., Z. Anorg. Allgem. Chem., **213**, 12 (1933); **225**, 1 (1935)
262	2	35	P. Niggli, J. Am. Chem. Soc., **35**, 1693 (1913)
262	2	35	Tschernobaef, M. D., Rev. Met. **2**, 729 (1905)
262	2	40	Gibson, G. and Ward, P., J. Am. Ceram. Soc. **26**, 239 (1943)
262	2	43	Morey, G. W., J. Am. Chem. Soc., **36**, 215 (1914)
262	2	43	Nutting, E. G., U. S. Patent 2,374,035 (April 17, 1945)
262	2	43	Riggs, W. S. and Buckhardt, C. W., U. S. Patent 2,230,909 (February 4, 1941)
262	2	43	Soderberg, P. W., U. S. Patent 2,211,733 August 13, 1940)
262	2	43	Zintl, E., Alien Property Custodian Serial No. 370,863, April 27, 1943; U. S. Patent 2,351,385 (July 4, 1944)
262	2	43	Zintl, E., and Leverkus, H., Z. Anorg. Allgem. Chem., **243**, 1 (1939)
263	1	3	Weyl, W. A., J. Soc. Glass Tech., **28**, 267 (1944)
263	1	19	Chirkov, S. K., Kinyakh, A. I., and Lobanov, E. V., J. Chem. Ind. (USSR) **13**, 1300 (1936); C. A. **31**, 1964 (1937)
263	1	22	Hitchen, C. S., Bull. Inst. Min. Met. No. 364 (1935) 26 pp.; C. A. **29**, 4294 (1935)
263	1	22	Romenskii, A. A., Zhur. Khim. Prom. **17** (10), 39 (1940); Khim. Referat Zhur. **4** (5), 88 (1941); Ceram. Abst. **22**, 128 (1943)
263	1	24	Codd, L. W., U. S. Patent 1,557,491 (Oct. 13, 1925); U. S. Patent 1,562,940 (Nov. 24, 1925)
263	1	24	Pshenitsyn, P. and Lavrovich, S., Zhur, Khim. Prom. **6** (5) 459 (1940); Khim. Referat Zhur., 4, 100 (1941)
263	1	28	Jaubert, G. F., 15th Congr. Chem. Ind. (Brussels, Sept. 1935) p. 1222 (1936)
263	1	28	Laschakov, L., J. Applied Chem. Russ., **9**, 455 (1936)
263	1	36	Iler, R. K., and Tauch, E. J., Trans. Am. Inst. Chem. Engrs. **34**, 853 (1941)
263	2	28	Kracek, F. C., J. Phys. Chem., **34**, 1583 (1930)
263	2	28	Morey, G. W., and Bowen, N. L., J. Phys. Chem., **28**, 1167 (1924)
263	2	30	D'Ans, J., and Loffler, J., Z. Anorg. Allgem. Chem. **191**, 1 (1930)
263	2	32	Zintl, E., and Marawietz, Z. Anorg. Allgem. Chem., **236**, 372 (1938)
263	2	43	Kracek, F. C., Bowen, N. L., and Morey, G. W., J. Phys. Chem. **41**, 1183 (1937)
263	2	43	Morey, G. W., J. Am. Chem. Soc. **39**, 1173 (1917)
265	1	8	Baker, C. L., U. S. Patent 2,145,749, (Jan. 31, 1939)
265	1	8	Morey, G. W., U. S. Patent 1,948,730 (Feb. 27, 1934)
265	1	14	Jorissen, et. al., J. Am. Chem. Soc. **63**, 889 (1941)
265	1	18	Fritzche, E., Pogg. Amn. Physik and Chem., **131**, N. S. **43**, 135 (1838)
265	1	20	Jordis, E., Zeit, Angew. Chem. **20**, 1410 (1907)
265	1	21	Baker, C. L., Woodward, H. T., and Pabst, A., Am. Mineralogist, **18**, 206 (1933)
265	1	24	Baker, C. L., U. S. Patent 1,898,707 (Feb. 21, 1933)
265	1	24	Baker, C. L., U. S. Patent 2,017,561 (Oct. 15, 1935)
265	2	11	Wegst., W. F., and Wills, J. H., U. S. Patent 2,179,806 (Nov. 14, 1939)
265	2	17	Vesterberg, K. A., Zeit, Anorg. Chem. **110**, 48 (1920); Medd. Vet. Nobel-Inst. **5**, 30 (1919)
265	2	18	Sprauer, J. W. and Pearce, D. W., J. Phys. Chem., **44**, 909 (1940)
265	2	19	Goranson, R. W. and Kracek, F. C., J. Phys. Chem., **36**, 913 (1932)
265	2	19	Kracek, F. C., J. Am. Chem. Soc., **61**, 2863 (1939)
266	1	10	Bichowsky, F. R., and Rossini, F. D., "Thermochemistry," Reinhold Publishing Co., New York (1936)
266	1	10	Kelley, K. K., J. Am. Chem. Soc., **61**, 471 (1939)
266	1	10	Kelley, K. K., U. S. Bureau of Mines, Bull. No. 393, 166 pp. (1936)
266	1	16	Baker, C. L., and Jue, L. R., J. Phys. Chem., **42**, 165 (1938)
267	1	4	Jander, G. and Heukeshoven, W., Z. Anorg. Allgem. Chem., **201**, 361 (1931)
267	1	29	Cann, J. G. and Gilmore, K. E., J. Phys. Chem., **32**, 72 (1928)
267	1	29	Harman, R. W., J. Phys. Chem. **29**, 1155 (1925); **30**, 359, 917, 1100 (1926); **31**, 355, 511, 616 (1927); **32**, 44 (1928)
268	1	10	Burgess, L. L. and Krishnamurti, K., Trans. Faraday Soc., **26**, 574 (1930)
268	1	26	Ray, R. C., Ganguly, P. B. and Lal, A. B., Trans. Faraday Soc., 38, 104 (1942)
268	2	3	Anderson, H. V. and Hochgesang, J. Phys. Chem., **44**, 439 (1940)
268	2	8	Fordham, S. and Tyson, J. T., J. Chem. Soc. 483 (1937)
268	2	50	Hurd, C. B., J. Chem. Ed., **14**, 84 (1937); Chem. Reviews **22**, 403 (1938)