

[CONTRIBUTION FROM THE GRASSELLI CHEMICALS DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS &amp; CO. INC.]

## The Reaction of Low Molecular Weight Silicic Acids with Molybdic Acid

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RECEIVED JUNE 11, 1953

The rate of reaction of molybdic acid with monosilicic, disilicic and low molecular weight polysilicic acids is quantitatively reproducible and varies inversely with the degree of polymerization of the silica. The polysilicic acids were prepared from sodium silicates of different  $\text{SiO}_2:\text{Na}_2\text{O}$  ratios by reaction with acid under such conditions that the rate of polymerization is negligible. In the polysilicic acid solutions so obtained, the average number of silicon atoms per polysilicic acid molecule is about 1.5 to 1.8 times the  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio of the silicate used.

### Introduction

Dienert and Wandenbulecke<sup>1</sup> and Harmon<sup>2</sup> have stated that "soluble silica," but not "colloidal silica" will react with molybdic acid to form the yellow silicomolybdate complex. Weitz, Francke and Schuchard<sup>3</sup> have thrown further light on this point by the discovery that silica in the monomeric state (as indicated by a molecular weight determination by the freezing point method) will react with molybdic acid completely within 75 seconds at 20° while disilicic acid reacts completely in about 10 minutes and higher polysilicic acid requires even longer.

Based on the reactivity of silicate but not colloidal silica with molybdate and acid, Snell<sup>4</sup> has described an analytical method for the determination of silicate in the presence of colloidal silica.

This investigation has dealt with the reactions of monosilicic, disilicic and low molecular weight polysilicic acids with molybdic acid reagent under controlled conditions of temperature and silicic and molybdic acid concentrations, and indicates how the rates of these reactions are related to the degree of polymerization of silicic acids and soluble silicates in aqueous solution.

### Experimental

#### Colorimetric Method for Determining Soluble Silica.—

The colorimetric method for the formation of the silicomolybdic acid complex was patterned after that described by Thompson and Houlton,<sup>5</sup> except that a color developing solution was first prepared, and this was then mixed with the silicic acid solution. By following this method, the  $\beta$ -silicomolybdic acid complex described by Strickland<sup>6</sup> is formed.

**Standard Solutions.**—One hundred grams of ammonium molybdate,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ , is dissolved in distilled water and diluted to one liter.

Molybdic acid color-developing reagent is prepared from this solution just prior to use by adding 40 ml. of this reagent to about 500 ml. of water, then adding 100 ml. of 1 *N* sulfuric acid and diluting the entire solution to 1 liter.

**The Color Reaction.**—The silicomolybdate yellow complex is formed by mixing one ml. of a solution containing about one mg. of  $\text{SiO}_2$  with 49 ml. of the color developing solution. A Beckman Model DU photoelectric quartz spectrophotometer with a thermostatically controlled cell holder (25°) was used to follow the increase in optical density of the sample due to the formation of the colored silicomolybdic

acid complex. The optical density is measured at a wave length of 400  $m\mu$ , with a slit width of 0.04  $m\mu$ ; under these conditions and when complete reaction is obtained between the two reagents, 1.00 mg. of silica per 50 ml. of solution gives an optical density of 0.720.

Immediately upon mixing the silicic acid or silicate solution with a color developing reagent, the sample is placed in a standard cell and the color reading is noted at 30-second intervals for approximately a ten-minute period, or until a constant value is obtained. For samples containing 1.00 mg. of  $\text{SiO}_2$ , the ratio of silicic acid which has reacted with molybdic acid at any given time to the total silicic concentration is equal to the ratio of the optical density obtained at that time to 0.720.

Blank readings in the colorimetric method were kept negligibly low by using freshly prepared distilled water and color developing reagent.

**Preparation of the Silica Sample for Analysis.**—When the sample consisted of silicic acid, the pH was adjusted to 2.0  $\pm$  0.5, and the sample diluted, if necessary, to a silica concentration of 1 mg. of  $\text{SiO}_2$ /ml. of solution. When the sample was a solution of sodium silicate or an alkaline silica sol, it could be converted to free silicic acid by adding the solution in a very thin stream from a pipet to a violently agitated solution of cold sulfuric acid in an amount to give a final pH around 2.5 and a silica concentration preferably about 0.1%, following the method for the preparation of monosilicic acid as described by Iler<sup>7</sup> and Alexander.<sup>8</sup> It has been observed that, upon dilution in alkaline solution of pH about 11 or above, silica depolymerizes very rapidly. Thus, the state of polymerization of silicic acid obtained from silicate of fixed  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio has been found to vary with the concentration of the silicate solution from which the acid was prepared. However, once silicate has been converted to the corresponding silicic acid, both polymerization and depolymerization at pH 2.5 and 0.1%  $\text{SiO}_2$  are quite slow, not changing appreciably in 10 minutes at ordinary temperature.

**The Reaction of Monosilicic Acid.**—Three solutions containing silicic acid which was essentially monomeric were prepared: (a) as described by Alexander,<sup>8</sup> by the reaction of crystalline sodium metasilicate hydrate with an aqueous slurry of ion-exchange resin, (b) from methyl orthosilicate: a 3% solution of this compound in methanol was hydrolyzed at room temperature in 0.005 *M*  $\text{H}_2\text{SO}_4$  to give a solution of silicic acid containing 0.120 mg. of  $\text{SiO}_2$  per ml.; after standing for 5 minutes, 5 ml. of the silicic acid solution was treated with 45 ml. of color developing reagent solution, and (c) from a solution of sodium orthosilicate: 2 ml. of a dilute solution of sodium orthosilicate (0.50 mg.  $\text{SiO}_2$ /ml.) was added directly to 48 ml. of the molybdic acid reagent in a very thin stream and with vigorous stirring. When this addition was made under conditions of vigorous agitation, reproducible results were obtained.

Typical readings for these experiments are shown in Table I.

**The Reaction of Disilicic Acid.**—Disilicic acid was obtained: (a) by hydrolyzing hexaethyl disilicate by treating 712 mg. of the disilicate with 500 ml. of 0.002 *M*  $\text{H}_2\text{SO}_4$  for two hours at 25°; 2 ml. of this solution was treated with 48 ml. of molybdic acid reagent, and (b) polymerizing monosilicic acid in a solution of pH 2.10 and 2° until the cryoscopic method indicated disilicic acid was present.

(7) R. K. Iler, U. S. Patent 2,588,389, assigned to E. I. du Pont de Nemours & Co., Inc.

(8) G. B. Alexander, *THIS JOURNAL*, **75**, 2887 (1953).

(1) F. Dienert and F. Wandenbulecke, *Compt. rend.*, **176**, 1478 (1928).

(2) R. W. Harmon, *J. Phys. Chem.*, **31**, 616 (1927).

(3) Ernst Weitz, Heinz Francke and Marianne Schuchard, *Chem. Z.*, **74**, 258 (1950).

(4) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. 1, 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1936, p. 517 ff.

(5) T. G. Thompson and H. G. Houlton, *Ind. Eng. Chem., Anal. Ed.*, **5**, 417 (1933).

(6) J. D. H. Strickland, *THIS JOURNAL*, **74**, 872 (1952).

TABLE I  
RATE OF COLOR DEVELOPMENT OF MONOSILICIC AND DISILICIC ACIDS

DP <sup>a</sup> Time, min.	Mono- silicic acid 1.2	Methyl ortho- silicate unknown	Na <sub>4</sub> SiO <sub>4</sub> soln. unknown	Polymerizing monomer		Dimer from hexa- ethyl silicate un- known
				1.6	2.1	
				Total color developed, %		
1.0	85	89	90	60	54	59
1.5	94	96	96	75	65	74
2.0	98	99	99	83	75	84
2.5				89	81	89
3.0	100	100	100	93	86	93
4.0				97		97
5.0				98		99
6.0				99		100

<sup>a</sup> DP, Degree of polymerization or silicon atoms per molecule, as measured by cryoscopic method.<sup>8</sup>

The rate of reaction comparing these silicic acids can be seen in Table I.

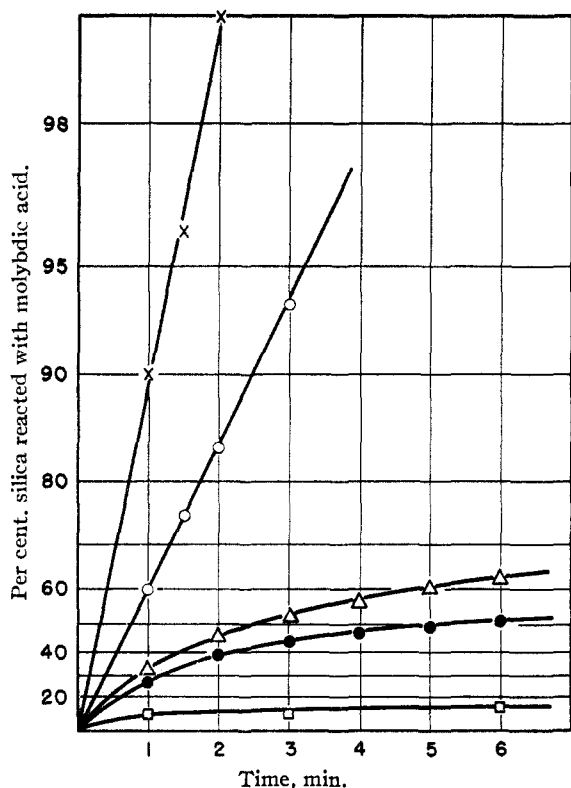


Fig. 1.—Reaction of sodium silicate solution with molybdc acid at 25°

Designation	SiO <sub>2</sub> :Na <sub>2</sub> O Ratio	DP
X	0.5	..
○	1.0	1.5
△	3.25	4.7
●	4.0	6.7
□	10.0	18

**The Reaction of Sodium Silicate Solutions.**—Solutions of sodium silicate of different SiO<sub>2</sub>:Na<sub>2</sub>O ratios and containing 2% SiO<sub>2</sub> were prepared from (a) crystalline Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O (J. T. Baker C.P.), (b) sodium silicate solution "JM" Technical (E. I. du Pont de Nemours and Co.), or by (c) treating colloidal silica solutions prepared according to Bird<sup>9</sup> with NaOH solution, as described by Bechtold and

(9) P. G. Bird, U. S. Patent 2,244,325.

Snyder<sup>10</sup> to adjust the SiO<sub>2</sub>:Na<sub>2</sub>O ratio to the desired value. By adding these sodium silicate solutions directly to molybdc acid reagent, it was possible to determine the relative rates of color development as related to SiO<sub>2</sub>:Na<sub>2</sub>O ratio. Results of these experiments are plotted in Fig. 1.

From these data, it is concluded that in solutions of sodium metasilicate, the silicate ion exists at least partially as a polymer (dimer). This accounts for the observation that monosilicic acid cannot be prepared from solutions of sodium metasilicate.<sup>8</sup> Moreover, it is concluded that in solutions of silicates having an SiO<sub>2</sub>:Na<sub>2</sub>O ratio of 3.25 or higher, most of the silica is in a polymeric state.

This latter observation was confirmed by converting silicates in these solutions to silicic acids by a technique similar to that used for the preparation of monosilicic acid.<sup>8</sup> The silicate solution containing 2% SiO<sub>2</sub> was added through a capillary tube to a slurry of 0.01 M H<sub>2</sub>SO<sub>4</sub> and an excess of "Nalcite" HCR ion-exchange resin in the hydrogen form. During the reaction, the temperature was maintained at 2° and the pH below 2.5. By determining the degree of polymerization of the resulting silicic acid solution by the cryoscopic method,<sup>8</sup> it was found that the ratio of the degree of polymerization divided by the SiO<sub>2</sub>:Na<sub>2</sub>O ratio was 1.6 ± 0.2.

### Discussion

With excess molybdc acid reagent, the rate of reaction with monosilicic acid follows a first-order reaction law, since there is a linear relationship between the logarithm of the concentration of unreacted silicic acid and reaction time; see Fig. 1, the reaction of 0.5 ratio SiO<sub>2</sub>:Na<sub>2</sub>O silicate with molybdc acid. Apparently, in the presence of an excess of molybdc acid, the rate of reaction is determined by the concentration of monosilicic acid remaining in the solution at any given time. With disilicic acid obtained from hexaethyl disilicate or by polymerizing monomer, the reaction is also first order, but the rate is decreased; see Table I. In this case, it is postulated that the rate of reaction is primarily dependent on the rate of depolymerization of dimer to monomer prior to reaction of monosilicic acid with molybdc acid. For higher polymers the rate of color formation is still slower. The rate of these reactions can be expressed mathematically as

$$-\frac{dP_x}{dt} = k_x P_x$$

where  $P_x$  is the concentration of the monomer or dimer at time,  $t$ , and  $k_x$  is the corresponding specific reaction rate constant. It is expected that this equation may be general for any given silicic acid polymer, and that the rate constant will vary not only with the degree of polymerization (the number of silicon atoms in the molecule), but also with different isomers. Thus, a ring trimer would probably react at a different rate than a linear trimer.

The  $k_x$  values at 25° for monomer and dimer are estimated to be 2.3 and 0.9 min.<sup>-1</sup>, respectively. The value for dimer is based on the rate of reaction of the silicic acid obtained by hydrolyzing hexaethyl disilicate. It may be that, during the conversion, polymerization or depolymerization occurred, and because of the uncertainty of the DP of this silicic acid, the  $k_x$  value for dimer should be considered as an approximation. Because of this, and since these  $k_x$  values are of the same order of magnitude, a quantitative determination of monomer in the presence of dimer is difficult. Re-

(10) M. F. Bechtold and O. E. Snyder, U. S. Patent 2,574,902, assigned to E. I. du Pont de Nemours and Co., Inc.

action rate constants for higher polymers have not been determined. Thus, although the molybdate curve for a given mixture of polysilicic acids is quantitatively reproducible, it gives only a qualitative picture of the relative distribution of monomer, dimer, and higher polymers.

It is of interest to note that the degree of polymerization of 4.7 of polysilicic acid from 3.25 ratio sodium silicate corresponds to a molecular weight of 282 on an anhydrous  $\text{SiO}_2$  basis. Earlier work

by Iler<sup>11</sup> indicated such silicic acid to have a number average molecular weight of around 200, while Debye and Nauman<sup>12-14</sup> found, in solutions of 3.3 ratio sodium silicate, a molecular weight of 325 by light scattering.

(11) R. K. Iler, *J. Phys. Chem.*, **57**, 604 (1953).

(12) P. Debye, *ibid.*, **53**, 1 (1949).

(13) P. Debye and R. Nauman, *J. Chem. Phys.*, **17**, 664 (1949).

(14) R. V. Nauman and P. Debye, *J. Phys. Colloid Chem.*, **55**, 1 (1951).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

## The Preparation and Properties of Molybdenum-Germanium Compounds<sup>1,2</sup>

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RECEIVED JUNE 15, 1953

An X-ray diffraction investigation has established the existence of the phases  $\text{Mo}_3\text{Ge}_2$ ,  $\text{Mo}_2\text{Ge}_3$ ,  $\alpha\text{-MoGe}_2$  and  $\beta\text{-MoGe}_2$  in addition to the phase  $\text{Mo}_5\text{Ge}$  which has already been reported. The high temperature form of  $\text{MoGe}_2$  is tetragonal with unit cell dimensions  $a = 3.313 \pm 0.003 \text{ \AA}$ . and  $c = 8.195 \pm 0.005 \text{ \AA}$ . It belongs to space group  $D_{2h}^{17}\text{-I } 4/mmm$ . Reactivities of the molybdenum germanides toward some common reagents are reported.

The germanides of transition metals have received little attention until very recently. Apparently there is still no published information on the chemical properties of any transition metal-germanium compounds, although a few transition metal-germanium phase diagrams have been studied.

The available information shows that germanides of the transition metal often have compositions and structures similar to those of the silicides of the same transition metals.

Since the molybdenum silicides have recently been shown to be stable and high melting compounds,<sup>4</sup> it seemed of interest to investigate the nature of molybdenum-germanium compounds.

The remark by Wallbaum<sup>5</sup> that  $\text{MoGe}_2$  does not have the same crystal structure as  $\text{MoSi}_2$  is apparently the only reference to any molybdenum germanide compound prior to our own investigations. We have recently reported the preparation of  $\text{Mo}_3\text{Ge}$  and the determination of its structure.<sup>6</sup>

**Experimental.**—Samples for X-ray diffraction analysis were prepared by heating thoroughly mixed germanium and molybdenum powders in carbon crucibles. The molybdenum was obtained from Fansteel Metallurgical Corporation in the form of 200 mesh powder. The germanium was obtained from Eagle-Picher Company both in lump form and in the form of 200 mesh powder. Spectrographic analysis of the germanium showed it to contain essentially no metallic impurity, but the powder was found by X-ray diffraction investigation to contain a few per cent. germanium dioxide. Two series of samples were made: a series prepared by heating to  $980^\circ$  in a resistance-heated nickel tube furnace under an atmosphere of argon, and a second series prepared by heating to  $1350^\circ$  in an induction furnace under vacuum.

Molybdenum powder gave negligible weight losses when

heated alone under conditions comparable to those of our preparative runs. Germanium powder lost a few milligrams per 100 mg. under the same conditions. The compositions of the molybdenum-germanium alloys after heating were calculated by assuming that the small weight losses that occurred were due exclusively to vaporization of germanium, perhaps as germanium monoxide. Substitution of crushed lump germanium reduced losses of germanium to 5 or 6 mg. for heating periods of 6 hr. at  $980^\circ$ . For samples heated at  $1350^\circ$ , excessive loss of germanium was avoided by covering the crucibles with tight-fitting lids. These lids were drilled with  $1/32$ -inch holes to allow the escape of non-condensable gases. When lids were used, the loss of germanium at  $1350^\circ$  was never more than 2 mg. per hour even for samples of high germanium content. Samples prepared at  $980^\circ$  were all cooled at a rate of about  $100^\circ$  per hour while samples prepared at  $1350^\circ$  were cooled from  $1350$  to  $700^\circ$  in 3 or 4 min.

X-Ray diffraction patterns of the powdered products were obtained in a camera of 114.57 mm. diameter. Copper  $K\alpha$  radiation (wave length  $\alpha_1 = 1.540522 \text{ \AA}$ ,  $\alpha_2 = 1.544367 \text{ \AA}$ ) was used.

**Discussion.**—Examination of the variation in diffraction patterns with composition revealed the existence of four molybdenum-germanium phases in the set of samples heated to  $980^\circ$ . The presence of three or more phases in a sample after heating would constitute evidence that equilibrium had not been reached. Samples which had been heated for at least one-half hour at  $980^\circ$  never yielded diffraction patterns of more than two phases. Maximum intensities of the four phases were obtained at compositions  $\text{MoGe}_{0.85} \pm 0.05$ ,  $\text{MoGe}_{0.7} \pm 0.1$ ,  $\text{MoGe}_{1.5} \pm 0.2$  and  $\text{MoGe}_{2.1} \pm 0.25$ . The phases were, therefore, identified as  $\text{Mo}_3\text{Ge}$ ,  $\text{Mo}_3\text{Ge}_2$  (or  $\text{Mo}_5\text{Ge}_3$ ),  $\text{Mo}_2\text{Ge}_3$  and  $\text{MoGe}_2$ . Details of this method of fixing phase compositions are presented in previous publications.<sup>4,6</sup>

Samples of less than 60 atomic % germanium which had been prepared at  $1350^\circ$  were indistinguishable from those prepared at  $980^\circ$ , but samples of more than 60 atomic % germanium always yielded the pattern of a new phase. Since the maximum intensities for the pattern of this phase were always obtained along with a pattern of the phase identified as  $\text{MoGe}_2$ , the new phase was

(1) From a thesis presented by Robert J. Peavler in partial fulfillment of the requirements for the Ph.D. degree.

(2) Work supported by the Metallurgy Branch of the Office of Naval Research.

(3) Purdue Research Foundation Fellow 1950-1952.

(4) L. Brewer, A. W. Searcy, D. H. Templeton and C. H. Dauben, *J. Am. Ceram. Soc.*, **33**, 291 (1950).

(5) H. J. Wallbaum, *Naturwissenschaften*, **32**, 76 (1944).

(6) A. W. Searcy, R. J. Peavler and H. J. Yearian, *THIS JOURNAL*, **74**, 566 (1952).