oxidize the purple solution to a colorless solution. Zinc amalgam spirals reduced the colorless solution back to a purple solution.

Dissolution of titanium in hydrofluoric acid in Pyrex test-tubes proceeds at a moderate rate to produce a purple solution. This reaction moderates, then proceeds vigorously to a green solution which is more stable to air than the purple, but also yields a colorless solution when in contact with oxygen, permanganate or ceric ions. The green solution is regenerated by placing zinc amalgam spirals in the colorless solution. Moreover, simply pouring some of the purple solution (from the polyethylene bottle) into a Pyrex test-tube produces the green solution. Quantitative oxidations with ceric ions show that both the green and purple solutions contain trivalent titanium while the colorless solutions contain tetravalent titanium. It appears that the green solution is a titanium–silicon–fluoride complex.

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WACO, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ANTIOCH COLLEGE]

Hydrothermal Reactions in the Na_2O-GeO_2 System[1]

BY ELWOOD R. SHAW, JAMES F. CORWIN AND JAMES W. EDWARDS

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The hydrothermal reactions between GeO_2 and water and water solutions containing sodium hydroxide have been studied at temperatures between 100 and 400°, and in the time range from 1 to 384 hours. The reaction of GeO_2 with water resulted in no new crystalline forms, but with solutions containing sodium hydroxide two crystalline forms having the proposed formulas $Na_3HGe_7O_{16}\cdot 4H_2O$ and $Na_2Ge_4O_9$ were prepared in such quantity that optical recognition and properties were easily established. The anhydrous material has heretofore been prepared by ignition only. On the basis of chemical analysis and *p*H determination mechanisms for the formation of these crystals are proposed.

Introduction

The early work[2,3] in the Na_2O-GeO_2 system consisted of studies of the melting point diagrams of mixtures. Eutectics were found at Na_2O-GeO_2 ratios of 1:1, 1:2 and 1:4 corresponding to compounds with the general formulas Na_2GeO_3, $Na_2Ge_2O_5$ and $Na_2Ge_4O_9$, respectively. The metagermanate and the tetragermanate have been prepared, but only the hydrated metagermanate has been characterized in the literature.[4-7]

Our studies of the products of hydrothermal reactions of $NaOH-GeO_2$ mixtures have shown that a condensed, anhydrous sodium germanate can be prepared in three crystalline habits and occurs as a single phase in the products of the reaction. Thus, the compound can be physically characterized and the structure determined.[8] By varying the conditions of the reaction the sodium hydrogen germanate described earlier by Nowotny and Wittmann[6] has been prepared in crystals of somewhat less regular habit. This hydrogen germanate is shown by X-ray studies to be the same compound precipitated at room temperatures from $NaOH-GeO_2$ mixtures containing NaCl. Infrared studies have shown the compound to be a definite hydrate so that the formula $Na_3HGe_7O_{16}\cdot 4H_2O$[6] is confirmed as preferable to $Na_2Ge_5O_{11}$.[9,10]

Ignition of this sodium hydrogen germanate at 900° caused a loss of 10.6% water and produced a compound with an identical X-ray pattern to that of the condensed anhydrous germanate synthesized hydrothermally from $NaOH-GeO_2$ mixtures and to that of a compound formed when a $Na_2CO_3-GeO_2$ mixture in the molar ratio 1:4 was fused at 900°.

From somewhat parallel reactions described by Nowotny and Wittmann,[6] and on the basis of Na_2O-GeO_2 analysis, the condensed germanate is identified as sodium tetragermanate.

By a similar hydrothermal reaction the ammonium and potassium hydrogen germanates were prepared; however the methods used for the hydrothermal conversion of sodium hydrogen germanate to the corresponding tetragermanate had no effect on the ammonium compound.

Hydrothermal runs in the GeO_2-H_2O system for purposes of familiarization with the products for optical identification confirmed the work of Laubengayer and Morton[11]; however new indices of refraction are proposed for the soluble form. Also, runs which were quenched produced birefringent, fibrous crystals with an average index of 1.66, close to that found for the commercial[12] GeO_2, 1.64–1.65, and to that reported in a handbook[13] for GeO_2, 1.65.

Experimental

Reagents.—Reagent grade chemicals were used in all cases unless otherwise described below. The germanium dioxide[12] was either in the form of a microcrystalline powder, 99.99% pure, or a fused glass in chunks of 5 mm. or less in

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF 18(600)1490. Reproduction in whole or in part is permitted for any purpose of the United States Government.

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[7] A. Wittmann and H. Nowotny, *ibid.*, **87**, 654 (1956).

[8] This work is being readied for publication by Dr. John F. White, Department of Geology, Antioch College.

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[11] A. Laubengayer and D. Morton, THIS JOURNAL, **54**, 2303 (1932).

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diameter. All solutions or mixtures were made using distilled, demineralized water and were stored in stoppered polyethylene bottles. Acidic solutions only were allowed to remain in glassware for more than 0.5 minute except during centrifugation when the high GeO_2 and Na_2O content minimized the effect of any possible contamination. Silica-free NH_3 water was prepared by bubbling NH_3 through distilled water in a polyethylene container. This solution or dilute H_2SO_4 was used in *p*H adjustments during analysis.

Equipment and Procedure.—Hydrothermal runs were made in 10-ml. stainless steel autoclaves with wedge caps held down by screw caps. Germanium dioxide analyses were run colorimetrically on a Beckman DU spectrophotometer. This method was checked on each type of sample by use of the gravimetric procedure of Hecht and Bartelmus.[14]

The sodium analyses were performed using a Weichselbaum–Varney Flame Photometer with sodium chloride standards.

Water was determined gravimetrically by ignition of samples to 900° after drying at 110°. No appreciable water was detected by infrared analysis in samples shown by gravimetric procedures to be anhydrous.

In the exploratory runs analytical control was not attempted. Two NaOH–GeO_2 mixtures were prepared in which the *p*H was adjusted to 10.4 with enough excess GeO_2 to precipitate solid material. The first mixture, which drifted to *p*H 7.8 and became gelatinous in five months, was found by later analysis to have a GeO_2/Na_2O molar ratio of 3.8. The second mixture drifted to *p*H 9.7 in several months and was found to contain a GeO_2/Na_2O molar ratio of 3.3.

A series of quantitative reactions also was run. The ratio of Na_2O/GeO_2 was held constant and the time of run varied. The resulting solutions and solids were analyzed to determine the molar ratio of GeO_2/Na_2O. A constant ratio was taken to indicate that equilibrium had been reached between the solution and solid phases.

Results

Tables I and II show the results of the reaction of NaOH–GeO_2 mixtures at 12 atmospheres pressure. In each case an attempt has been made in the tables to equate the optical description with the phases detected by X-ray methods. To check the possibility that Unknown II was the other form of $Na_2Ge_4O_9$ reported by Nowotny and Wittmann[6] some of Unknown I and also a 1:4 Na_2CO_3–GeO_2 mixture were fused at 1054° and cooled slowly. A crystalline compound with the indices of refraction N_O = 1.740, N_E = 1.76–1.77 resulted as a single phase in each case. Analysis by X-ray methods indicated that no detectible amount of any previously prepared germanate was present. The infrared pattern resembled somewhat that for the tetragermanate; however, there were additional bands not present in any other pattern. Identification of this form is in progress.

TABLE I

REACTIONS OF *p*H 7.8 NaOH-GeO_2 MIXTURE AT 200°

Time, hr.	Final *p*H	Analysis Optical Crystals	Index	X-ray
2	7.6	Octagonal prisms	1.690, 1.695	Unknown I only
2^a	6.5	Cubes[b]	1.695, 1.72	Soluble form
		Oct. prisms	1.690, 1.695	Unknown I Unknown II
2^c	8.0	Rectangular solids	1.690, 1.695	Strong—unk. 1
		Irregular crystals (Isotropic)	1.63–1.64	Medium—$NH_4H_3Ge_2O_6$[d]
43	7.9	Rect. solids	1.690, 1.695	Unknown I only
2	7.9	Rect. solids	1.690, 1.695	Strong, unk. I
		Irregular crystals	1.63–1.64	Faint $NH_4H_3Ge_2O_6$
		Twinned crystals[e]		Weak—unk. II

[a] GeO_2 glass was added to this run. [b] Exhibit diagonal extinction. [c] Quenched in cold water. [d] Obviously the sodium salt; however only ammonium pattern is available. [e] The twinned crystals extinguish diagonally. Top indices 1.690, 1.695; side 1.695, 1.72.

TABLE II

REACTIONS OF *p*H 9.7 NaOH–GeO_2 MIXTURE

Time, temp.	Final *p*H	Analysis Optical		X-Ray
2 hr. 200^c	9.5	Isotropic crystals	1.63–1.64	(S) $NH_4H_3Ge_2O_6$[a]
8 da. 200	11.8	Large dipyramids (40–50 microns)	1.690, 1.695	(S) Unknown I
12 da.[b] 200	10.2	Small dipyramids (10–14 microns)	1.690, 1.695	(S) Unknown I
26 da. 110	9.8	Isotropic crystals Very small crystals[d] (birefringent)	1.63–1.64	Note *e*
13 da. 150	11.2	Same as at 110^c Many more birefringent crystals.		

[a] See note (d) Table I; (S) = strong. [b] Germanium dioxide glass added. [c] Infrared analysis gave same pattern as 200°-hr. run. [d] Very few—not detected on infrared pattern. [e] X-Ray analysis indicates a mixture of two $MH_3Ge_2O_6$, (M = metal which in this case could be only Na).

The results of the analyses of three runs which X-ray methods had shown consisted of the same single phase are shown in Table III. As the high GeO_2/Na_2O ratio was noted in several analyses, a series of quantitative reactions was run using 1:4 Na_2O–GeO_2 mixtures at 200° and with increasing time of reaction in order to determine the ratio at equilibrium. The progress of the reaction was followed by optical, infrared and X-ray analyses of the solid products, and by colorimetric analysis of the solutions. After 2 hours the solid product was found to contain roughly equal amounts of sodium tetragermanate and the hexagonal crystalline modification (soluble form) of germanium dioxide with a lesser amount of sodium hydrogen germanate. At this stage the crystals of the tetragermanate could be seen forming in and on the larger glassy hydrogen germanate crystals. A trace only of germanium dioxide remained after 12 hours and only a small amount of hydrogen germanate completely surrounded by tetragermanate crystals was detected. After 24 hours at 200° only the tetragermanate could be detected by X-ray analysis.

TABLE III

ANALYSIS OF RUNS WHICH BY X-RAY ANALYSIS CONTAIN A SINGLE PHASE

Crystal	Na_2O, %	GeO_2, %	H_2O, %	Molar ratio GeO_2/Na_2O
Octagonal prism	11.5	85.5	0.33	4.42
Rectangular prism	12.6	85.3	.50	4.01
Dipyramidal	12.2	87.5	.51	4.25
Calcd. $Na_2Ge_4O_9$	12.9	87.1	..	4.00

The molar ratio of GeO_2/Na_2O in the solid product came to equilibrium at 4.3–4.5 and in the solution at 1.2–1.4. The average *p*H rose from 11.65 for the two hour runs to a maximum of 11.85 for the 12-hour runs, then fell to 11.55 after 24 hours with little further variation regardless of the reaction time. A check run which was allowed to stand 30 days before raising to temperature had a final *p*H of 10.48 for a 2-hour run and no germa-

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(14) F. Hecht and G. Bartelmus, *Mikrochem.*, **36/37**, 466 (1950).

nium dioxide remained in the product, only tetragermanate. This give some indication of the reason for the variation of the results reported in Tables I and II from those of the series of runs just above.

After two months standing a precipitate formed in the hydrothermal run solutions having a GeO_2/Na_2O ratio greater than 1.2. The ratio dropped to 1.0 with a corresponding average drop of 0.4 unit in *p*H. According to X-ray analysis the precipitate now contained a mixture of two $MH_3Ge_2O_5$, one with too large a lattice constant to be $NaH_3Ge_2O_6$. This same X-ray pattern with double peaks was obtained for the solid product of a 110° run as shown in Table II, for the precipitate formed when a sodium hydroxide solution of germanium dioxide was saturated with sodium chloride, and for the product of a run in which an attempt had been made to prepare the tetragermanate hydrothermally at 200° from sodium metagermanate.[6] As the infrared patterns indicate no new crystalline forms present, and also since the acid germanates are known to be zeolitic,[6] the slight variation in patterns is at present attributed to two definite states of hydration.

Crystals of the tetragermanate with 5 ml. of water reacted at 200° for 2 days. There was no visible change in the crystals and the GeO_2/Na_2O ratio in the solution was 1.0 and the *p*H 11.5. A run of 30 days under the same conditions resulted in the unusual combination of 10 mg. Na_2O/100 ml. with 860 mg. GeO_2/100 ml. (*p*H 10.7) in the liquid phase. The solid product contained only tetragermanate.

Attempts to prepare the tetragermanate hydrothermally at 200° from the metagermanate[6] resulted in only the acid germanate. From a run which leaked dry slowly, long birefringent needles with indices N_O = 1.58–1.59, N_E 1.59–1.60, presumably Na_2GeO_3 (anhyd.)[15] were obtained. From another run which leaked to 1 ml., crystals of index 1.50, presumably hydrated sodium metagermanate, was the only solid phase obtained.

For aid in spectral identification, since only the XRD pattern for $NH_4H_3Ge_2O_6$ appears in the A. S. T. M. Card File, some of the ammonium compound was prepared hydrothermally at 200° using a $NH_4OH–GeO_2$ mixture. It was confirmed[6] that the X-ray pattern very closely resembled that for the corresponding sodium compound; however their infrared patterns had distinct differences. The sodium compound gave very strong absorption bands at 3.10 and 6.1 μ (water), and at 13.0 μ; while the ammonium compound gave similarly strong bands at 3.15–3.20 and 7.10 μ (NH_4) and at 12.75 μ. A small shoulder only was visible at 3.00–3.05 on the first strong ammonium band and a small broad band at 6.1 that would indicate a small amount of water present either as hydrate water or molecular water. The infrared pattern for the potassium hydrogen germanate also showed by a weak band at 3.05 μ only a small amount of water present, but had the same strong broad band at 13.0 μ found in the corresponding sodium compound.

Runs at 300° using the $NH_4OH–GeO_2$ mixture produced only the insoluble form of GeO_2. With GeO_2 glass present and runs at 200° a lower *p*H resulted, but with no visible effect on the formation of ammonium germanate. The glass was converted *in situ* to the soluble form in 1 day with a resulting *p*H of 9.95; while in 19 days the glass was converted to the insoluble form (*p*H 10.8).

Discussion

Since DTA analysis[7] and infrared analysis show that the hydrated condensed germanate contains molecular water, as well as water of hydration, the formula $Na_3HGe_7O_{16}\cdot 4H_2O$ will be used here in preference to $Na_2Ge_5O_{11}$. The former is also preferable to the general formula $NaH_3Ge_2O_6$[6] since conversion of the hydrogen germanate to the tetragermanate by ignition also produced enough GeO_2 to be detected by X-ray and infrared analysis. This confirmed equation 1 as proposed by Nowotny

$$2Na_3HGe_7O_{16}\cdot 4H_2O \rightleftharpoons 3Na_2Ge_4O_9 + 9H_2O + 2GeO_2 \quad (1)$$

and Wittmann,[4] except no evidence was found that an equilibrium is reached, at least when the conversion is at high temperatures.

The ease of precipitation of polymeric germanates from basic GeO_2 solutions is said to indicate that polymeric germanate ions are present in solution.[16] The slight acidity of aqueous GeO_2 solutions also has been attributed to an equilibrium similar to equation 2 which is displaced well to the

$$7H_4GeO_4 \rightleftharpoons (HGe_7O_{16})^{3-} + 12H_2O + 3H^+ \quad (2)$$

left.[9] A rise in *p*H should increase the contribution of the polymeric ion. The fact that the $NaOH–GeO_2$ mixture of Table I at *p*H 7.8 became gelatinous after several months standing confirms this.

Potentiometric titration of a 0.048 *M* GeO_2 solution by 0.2 *N* NaOH resulted in a curve[17] with a readily determined end-point at *p*H 10.75 and at a GeO_2/Na_2O ratio of 1.97. From this it is apparent that at the end-point the major germanate ion is $(H_3GeO_4)^-$ with a small contribution from $(H_2GeO_4)^{2-}$. Since the polymeric germanate can be precipitated from solutions at this *p*H merely by adding NaCl there is undoubtedly some polymeric germanate present according to equation 3. Any decrease in *p*H should increase the amount.

$$7(H_3GeO_4)^- \rightleftharpoons (HGe_7O_{16})^{3-} + 8H_2O + 4OH^- \quad (3)$$

The first step in hydrothermal reaction of $NaOH-GeO_2$ mixtures is the conversion of any excess polymeric germanate (gelatinous or otherwise) to crystalline form probably by removal of water. Since this does not disturb the small amount of hydrogen germanate in equilibrium in equations 2 and 3 the *p*H does not change. However, in longer runs in which the insoluble tetragermanate is formed, $(HGe_7O_{16})^{3-}$ ions are removed from the equilibrium. As is seen from Table II the *p*H then rises two *p*H units. It is evident from the final *p*H of 11.5–12.0 and solution ratio GeO_2/Na_2O = 1 that the major ion in solution after the run is $(H_2GeO_4)^{2-}$.

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[15] "Handbook of Chemistry and Physics," 37th Ed., Chemical Rubber Pub. Co., Cleveland, Ohio, reports 1.59.

[16] P. Souchay, *Bull. soc. chim., France*, 395 (1953).

[17] Identical curves to those of Carpeni, *ibid.*, 1010 (1952), for KOH titrations of GeO_2 were obtained for NaOH.

The pH of the solutions in Table I does not change when the tetragermanate is formed. As can be seen from equation 3 the concentration of $(H_3GeO_4)^-$ would be small at this pH. Removal of $(HGe_7O_{16})^{3-}$ from the equilibrium then would produce little shift to the right and a corresponding rise in pH. Also the small amount of GeO_2 produced according to equation 1 would be of much greater importance.

There was no evidence of $(Ge_4O_9)^{2-}$ ions in solution. The precipitate from the run solutions contained a very small amount of birefringent material which could not be the acid germanate. Infrared and X-ray analyses indicated another compound present in small amount; however, it was unidentifiable with known patterns.

Since both the hydrogen germanates and tetragermanates prepared showed no noticeable tendency to absorb moisture from the air it is presumed that the hygroscopic product described by Nowotny and Wittmann[5] contained residual metagermanate.

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YELLOW SPRINGS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CLARKSON COLLEGE OF TECHNOLOGY]

The Molecular Weight of the Phosphotungstic Acids by Light Scattering[1]

BY MILTON KERKER, DOROTHY LEE AND ADAM CHOU

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The light scattering of 12-phosphotungstic and 9-phosphotungstic acids in a number of organic solvents and water has been determined. In the organic solvents, the molecular weight calculated for the former corresponds to the monomer, $H_3PW_{12}O_{40}$, while that of the latter corresponds to the dimer, $H_6P_2W_{18}O_{62}$. This is consistent with crystal structure studies by X-rays. The usual treatment is not adequate to interpret the data from aqueous solutions where these acids are strong.

Since the discovery of ammonium phosphomolybdate by Berzelius in 1826, the heteropoly acids and their salts have provided a fruitful testing ground for the theories of structural inorganic chemistry. The bewildering variety of species proposed in the literature and the lack of a critical evaluation of the great amount of experimental work at the turn of the century has necessitated a new look with the aid of modern structural tools.[2]

The best characterized of the phosphotungstic acids are those with empirical formulas $H_3PW_{12}O_{40}$ and $H_3PW_9O_{31}$, 12-phosphotungstic acid and 9-phosphotungstic acid. The complete structure for these in the solid state has been elucidated by Keggin[3] and Dawson.[4] Dawson found that the unit cell of 9-phosphotungstic acid consists of the dimeric ion $P_2W_{18}O_{62}^{-6}$. This agrees with the finding of Souchay[5] who proposed, on the basis of cryoscopy of the sodium salt in sodium sulfate at its transition point, that 9-phosphotungstic acid is the dimer, $H_6P_2W_{18}O_{62}$, whereas 12-phosphotungstic acid is monomeric, $H_3PW_{12}O_{40}$.

Although the structure of these acids in the solid state has been well established, the state of molecular aggregation in solution is hardly known. This knowledge constitutes the starting point for an understanding of the various aggregation, degradation and equilibrium phenomena encountered in solution. It is the purpose of this work to investigate the molecular weight of the 12- and 9-phosphotungstic acids in solution by means of light scattering in order to determine whether these species consist of monomers, dimers or higher polymers.

Experimental

Preparation and Analysis of Compounds. 1. **12-Phosphotungstic Acid.**—The reagent grade chemical, commercially available from J. T. Baker Company, was used. The purity was checked by analysis of P_2O_5 and H_2O content, assuming the difference was WO_3. After conversion to the Na salt by Na_2CO_3 fusion, the usual method of precipitation of phosphate with magnesia reagent and ignition to the pyrophosphate was used. The loss in weight at 600° was assumed to correspond to the water content. The W/P ratio was found to be 11.7 ± 0.1. Considering the errors resulting from possible coprecipitation of WO_3 with the phosphate and the volatilization of P_2O_5 above 250°, the above accuracy was considered satisfactory.

2. **9-Phosphotungstic Acid.**—The method of Souchay[6] which is a modification of that first reported by Wu[7] was used. One hundred g. of Na_2WO_4 was dissolved in 350 ml. of hot water and brought to a boil. One hundred and fifty ml. of 85% H_3PO_4 was added slowly to the boiling solution and the whole mixture was refluxed for 5 hr. or overnight

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[1] Supported in part by U. S. Atomic Energy Commission Contract Number AT(30-1)-1801.

[2] The standard treatises such as J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1927–1937; J. Newton Friend, "Textbook of Inorganic Chemistry," Charles Griffin and Company, London, 1924–1930; and "Gmelins Handbuch der Anorganische Chemie," Verlag Chemie, Berlin, from 1926, summarize the literature to the early 1930's. The structural problem is stated in modern terms in such textbooks as W. Hückel, "Structural Chemistry of Inorganic Compounds," by Elsevier, New York, N. Y., 1950, p. 179; H. B. Jonassen in Bailar's "Chemistry of the Coördination Compounds," Reinhold Publ. Corp., New York, N. Y., 1956, Chapter 14; and A. F. Wells, "Structural Inorganic Chemistry," Oxford, 1950, p. 348. For present directions in research in this field see the preprints of papers read at the symposium on "Structure and Properties of Heteropoly Anions," at the National Meeting of the A.C.S., Division of Physical and Inorganic Chemistry, Atlantic City, N. J., September 17, 1956.

[3] J. F. Keggin, *Nature*, **131**, 908 (1933); **132**, 351 (1933); *Proc. Roy. Soc.* (*London*), **A144**, 75 (1934); J. W. Illingworth and J. F. Keggin, *J. Chem. Soc.*, 575 (1935); A. J. Bradley and J. W. Illingworth, *Proc. Roy. Soc.* (*London*), **A157**, 113 (1936).

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