The possibilities shown by the tabulated data need little comment. As mentioned above, the amount of entropy under the control of the magnetic field is large compared to the amount concerned in vibration. For this reason conditions appear favorable to the production of extremely low temperatures even if several members of the magnetic octet are rendered inactive at such temperatures by energy differences comparable with kT. It is evident that the cooling effect available is not only sufficient for producing very low temperatures in the gadolinium sulfate octahydrate itself, but is also sufficient to cool simultaneously other materials in addition.

Summary

The heat capacity of $Gd_2(SO_4)_3 \cdot 8H_2O$ has been measured from 14 to 290°K. Extrapolation of the heat capacity results combined with the entropy of magnetization previously given has been used to determine the conditions for producing temperatures below 1°K. by reversible adiabatic demagnetization of gadolinium sulfate octahydrate.

The magnetic field-temperature isentropics have been tabulated. The data indicate that the demagnetization of gadolinium sulfate at the temperatures of liquid helium not only provides enough cooling effect to produce temperatures considerably below 1° absolute, but that in addition other substances may be cooled by gadolinium sulfate for investigation of their properties.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

THE CONDUCTIVITY OF SOLUTIONS OF GERMANIC OXIDE[1]

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There are known to exist several modifications of germanium dioxide, the physical and chemical properties of which differ very definitely.[2] The ordinary form—the so-called "hydrolyzed" oxide—is soluble in water and is obtained by the hydrolysis of the tetrachloride. When solutions of this modification are evaporated to dryness, ignition of the residue gives varying yields of a very insoluble variety—the amount depending on the conditions under which the evaporation is carried out and on the temperature at which the residue is ignited. Only traces of this insoluble form can be obtained by directly igniting large quantities of the "hydrolyzed" oxide, whereas repeated evaporations and ignitions of the "evaporated" oxide bring about complete conversion of the soluble to the insoluble

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[1] From a thesis presented by C. E. Gulezian in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Müller and Blank, THIS JOURNAL, **46**, 2358 (1924).

variety.[3] Finally, a very soluble, transparent and "glassy" form results on quickly cooling melted germanic oxide obtained from any other variety. This form is amorphous and a true glass, as is indicated by the absence of lines in its x-ray spectrograph and the lack of a sharp break in its heating or cooling curves. Recently, R. Schwarz and E. Huf,[4] from a study of the properties of this oxide both in the solid condition and in solution, conclude that there are three true modifications—two crystalline and one amorphous. The "evaporated" oxide, according to their data, is homogeneous and not a separate variety.

This observed allotropy of germanium dioxide should, therefore, be taken into consideration in any study of the solutions of this substance. Roth and O. Schwartz,[5] in their study of the physical properties of this oxide in solution, give the earliest data on its conductivity. Their work, however, covers only solutions of the above-named "hydrolyzed" oxide, for the specific conductivity of which they obtained values showing very wide differences, depending on whether the solution of the oxide was prepared in the hot or cold. Furthermore, their lowest value for the primary dissociation constant of germanic acid, 1.2×10^{-7}, calculated from their conductivity data, is approximately fifty times the value given by Pugh,[6] 2.5×10^{-9}, and obtained from a potentiometric determination of the hydrogen-ion concentration in solutions containing sodium acid germanate. R. Schwarz and Huf,[4] working with solutions of the fused or "glassy" oxide, found 0.5×10^{-7} for this constant, which, though less than the value of Roth and Schwartz, is still about twenty times that of Pugh. The present study was undertaken in order to determine the conductivity of this substance in solution under different conditions with special reference to the influence, if any, of polymorphism on the conductivity, and also to determine the more probable of the above-mentioned values for the dissociation constant of the acid formed when the oxide is dissolved in water.

Preparation of Pure Germanium Dioxide

As will be seen from the experimental data to be given later, solutions of pure germanic oxide have an extremely low conductivity, which makes it imperative that the solid be prepared in such a way that it will be absolutely free of foreign ions capable of contributing to conductance. Considerable difficulty was experienced at first in getting concordant results with what was thought to be very pure oxide. When the sample was re-purified, such difficulties were overcome; and since, in an investigation such as this, the most important single factor affecting the final results seems to be the purity of the material used, considerable information will be given concerning its source and method of purification.

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[3] Müller, *Proc. Am. Phil. Assoc.*, [3] **65**, 183 (1926).

[4] Schwarz and Huf, *Z. anorg. allgem. Chem.*, **203**, 188 (1931).

[5] Roth and Schwartz, *Ber.*, **59A**, 338 (1926).

[6] Pugh, *J. Chem. Soc.*, 1994 (1929).

"Hydrolyzed" Germanic Oxide (Lot 1).—The original sample of oxide used in this investigation was obtained from germanite. The mineral was decomposed with nitric acid and the undissolved residue containing germanic oxide, siliceous gangue, etc., heated with concentrated hydrochloric acid, the crude germanium tetrachloride distilling out in the usual manner. The tetrachloride was then redistilled and the product hydrolyzed to oxide—most of which was deposited as the difficultly soluble solid. The acid filtrate from this hydrolytic decomposition was purposely discarded in order to eliminate rapidly most of the arsenic. This yield of solid oxide was then dissolved in water and the remaining traces of arsenic removed by rendering the solution faintly acid and adding hydrogen sulfide. The snow-white disulfide was then precipitated in the filtrate in the presence of 6 *N* sulfuric acid and the solid hydrolyzed to oxide by boiling with water in the absence of air. This residue of oxide was once more converted to chloride and the final transformation to oxide effected by collecting the chloride under ice water and warming. The solid so obtained was washed with cold water and then repeatedly moistened and ignited at 950° until no test for chloride ion was observed on dissolving two gram samples in water.

(Lot 2).—The solutions prepared from Lot 1 and used in all the preliminary experiments were combined and concentrated by slow evaporation to about one liter. The germanium was distilled out as chloride in a current of pure hydrogen chloride and the chloride collected, this time, not under water, but under ice cold, concentrated hydrochloric acid.

The advantages of this method will be discussed fully in a forthcoming contribution by Mr. E. R. Allison of this Laboratory. The lower layer of chloride was then run, drop by drop, from the ice-jacketed separatory funnel in which it had been collected into a large platinum dish containing about 300 cc. of conductivity water heated to 45–50° and kept in constant agitation. No solid oxide separated out at first—even after the addition of about forty grams of chloride. Then the apparently clear dispersion of chloride and water gave way to a very finely divided and heavy precipitate of germanium dioxide. The solid appeared uniform in structure, the absence of cakes or lumps of the oxide being especially noticeable. The precipitated oxide was filtered, washed with cold water and warmed with about 50 cc. of conductivity water. After a second filtration, the residue remaining on the filter was washed until apparently clear of chloride ion. This entire behavior was strikingly different from that observed when the chloride is hydrolyzed according to the usual method of adding it in bulk to water and gradually warming. The small amount of chloride lost by volatilization in the method described is more than compensated for by the improved condition of the oxide obtained, which makes subsequent purification much less difficult. Even though the wash water gave a negative test for chloride ion, large samples of the solid when dissolved in water gave good positive tests. The removal of the final traces of hydrogen chloride was effected only by ignition of the moistened oxide at temperatures above 900°. Only about five or six such ignitions are required when the oxide is obtained in the manner described, whereas at least twice as many are necessary when it is prepared by the other method.

(Lot 3).—A third yield of "hydrolyzed" oxide was prepared indirectly through the sulfide. Pure oxide solutions obtained from Lot 2 were made 6 *N* with hydrochloric acid and the sulfide precipitated with hydrogen sulfide obtained from liquid hydrogen sulfide. The filtered disulfide was washed with 6 *N* acid saturated with hydrogen sulfide, then with hydrogen sulfide water and finally with conductivity water. After drying in a desiccator over soda lime for three days, the sulfide was changed to chloride by Winkler's method[7] with the use of pure mercuric chloride. The distillate collected in a cooled receiver was redistilled and the portion boiling below 84° collected, as before,

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[7] Winkler, *J. prakt. Chem.*, **36**, 188 (1887).

under pure concentrated hydrochloric acid. The subsequent transformation to oxide and purification of the latter were carried out exactly as in the preparation of Lot 2.

"Glassy" Germanic Oxide.—"Hydrolyzed" oxide from Lot 2 or 3 was placed in a platinum boat and the temperature raised to about 1250° in an electrically heated platinum resistance furnace. After removal from the furnace and quick cooling in the air, the sample was dissolved, without grinding, in conductivity water.

Germanic Oxide from the Sulfide.—About six grams of "hydrolyzed" oxide was dissolved in conductivity water and precipitated as sulfide from 6 *N* sulfuric acid solution. After thorough washing of the sulfide—as previously indicated—until visible peptization occurred, it was transformed into oxide in a quartz flask by the hydrolytic method.[8] Superheated steam was passed through the liquid until the escaping vapors gave no test for hydrogen sulfide. Evaporation of the liquid to dryness in a platinum dish and ignition at 950° for eight hours gave a residue of oxide, 2-g. samples of which in conductivity water showed no visible test for sulfate ion.

Germanic Oxide Crystallized at 1050°.—"Hydrolyzed" oxide was melted as above, but instead of removing and cooling the melt quickly, the sample was cooled slowly in the furnace to 1050 ± 5°, and kept at this temperature for about five hours. When removed and broken up, observation of the solid under an ordinary microscope indicated the presence of a mass of large well-formed crystals. As the oxide obtained in this way dissolved much more slowly than the other samples, it was finely powdered in a quartz mortar before addition to water.

Insoluble Germanic Oxide.—The material was a 10-g. sample prepared in a previous investigation.[3] It was repeatedly treated with boiling conductivity water in order to remove all traces of soluble matter—the boiling being carried out in a quartz flask. A redetermination of the solubility of the material thus obtained showed that 2.3 milligrams dissolved per liter at 25°.

Conductivity Measurements

Apparatus and Reagents.—The usual Kohlrausch set-up was used with a thousand cycle microphone hummer as the source of alternating current. The slide was a Gray instrument with the scale divided into a thousand divisions. The variable resistance was a Leeds and Northrop instrument accurate to 0.1%—as checked against L. and N. standard resistances. A variable air condenser was placed in parallel with the resistance box to compensate for capacitance in the conductivity cell. All readings, except those on conductivity water, were taken with the end-coils of the slide wire in the circuit, thereby greatly increasing the accuracy of the bridge reading.

The thermostat was maintained at 25.00 ± 0.02°, the temperature being read with a calibrated thermometer.

All glassware was thoroughly cleaned and steamed before use, and all measuring apparatus calibrated. The heating of all germanic oxide solutions used in the measurements was carried out either in platinum dishes or quartz vessels.

The conductivity cell was made of Pyrex glass with the exception of a ground-glass stopper and the supporting tubes through which the electrodes were sealed. The electrodes were about three centimeters in diameter and about four millimeters apart. The cell constant, 0.02564, was checked frequently during the determinations and the change found to be inappreciable.

The potassium chloride was a sample of Kahlbaum's best grade recrystallized from conductivity water and heated to 300° for two to three hours just before use. The solutions necessary for the determination of the cell constant were prepared according to the data given in the "International Critical Tables."[9]

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[8] Müller and Eisner, *Ind. Eng. Chem., Anal. Ed.*, **4**, 134 (1932).

[9] "International Critical Tables," Vol. VI, p. 230, Table I.

The specific conductivity of the water used was in all cases below 1.0×10^{-6} mho per cm. The water was kept in well steamed and seasoned Pyrex flasks which were always kept filled with water until immediately before use, all samples of water being used within ten hours after collection.

Preliminary Experiments.—(a) In this and in all the other preliminary experiments, the conductivity measurements were made at 30° with samples of the oxide taken from Lot 1. Solutions of the "hydrolyzed" oxide of the same concentration (2.276 g. per liter) were prepared at 0° and at 100°. The specific conductivity was approximately the same for solutions made at both temperatures—between 6.5 and 8.0×10^{-6} mhos per cm. At the same concentration—but at 18°—Roth and Schwartz[5] obtained a value of about 17×10^{-6} mhos per cm. for the solution prepared in the cold and of about 35×10^{-6} mhos per cm. for that prepared in the hot (the temperatures at which the solutions were prepared not being stated in either case). Our experiments were easily duplicated and indicated that extremes of temperature in the preparation of such solutions had very little, if any, effect on the conductivity. After being kept in Pyrex flasks for several days, the solutions were found to be quite stable. only very slight changes in conductivity being observed.

(b) Samples of a similar solution of "hydrolyzed" oxide were then sealed up in previously cleaned and steamed quartz bulbs of 25-cc. capacity, and heated continuously for seven days in a boiling water-bath. A bulb was removed every twenty-four hours and the conductivity of its contents determined. Throughout the entire period, no changes over 1% were observed. The same experiment was carried out for solutions of the "glassy" form—the original solution in this case being prepared at 0°. Water blanks were also prepared and kept in the same bath throughout the run. After an initial slight increase—equal to that in the case of the water in the blanks—the values observed were constant over a period of five days. Solutions kept thus for four days at temperatures of 0, 30 and 65° also showed a similar stability.

(c) The sample of oxide used in the preparation of all these solutions had been ignited at 950° in order to remove traces of hydrogen chloride. It was thought that, perhaps, on heating, the germanic oxide had undergone some change in its physical condition that was responsible for its low conductivity when placed in solution. Attempts were then made to remove the hydrogen chloride from the hydrolyzed oxide at lower temperatures. The material was repeatedly extracted with boiling conductivity water; it was moistened and ignited at various temperatures up to 700°; superheated steam was passed over it at temperatures up to 500°; it was moistened several times and heated *in vacuo* at 500°; but, no matter what method was used, the residues when dissolved in conductivity water still gave good positive tests for chlorine. All attempts to obtain chloride-free germanic oxide at temperatures much below 900° were then given up. That such a high temperature is required to remove all the hydrogen chloride is quite remarkable. It may be that the last traces leave only with the last traces of water, which Dennis, Tressler and Hance[10] have shown to be completely removed only on heating to 950°. It is, perhaps, due to this fact also that Roth and Schwartz obtained the results which they report, since they state that, in purifying the oxide, the final step consisted in heating to a "dull-red" heat—which is considerably below 900°. R. Schwarz and Huf[11] report more than 0.1% of chlorine in the oxide ignited at 600°, and succeeded in eliminating all the chlorine at 800°.

(d) The conductivity of solutions of the "evaporated" oxide was then studied in order to determine whether it differed from that of the hydrolyzed modification. Solutions of the hydrolyzed oxide were evaporated in electrically heated platinum dishes.

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[10] Dennis, Tressler and Hance, THIS JOURNAL, **45**, 2033 (1923)

[11] Ref. 4, p. 196.

The results of four such experiments indicated a drop in specific conductivity from 24 to approximately 7.5 $\times$ 10^{-6} mhos per cm. Enough of this "evaporated" oxide was then obtained to heat one-gram portions to various temperatures in order to change some of it to the insoluble form and then to determine the influence of such heat treatment on the conductivity of the unchanged solid. In each case, the insoluble oxide was rapidly filtered off with suction and the conductivity of the filtrates determined. The concentration of the solutions obtained was found—as in all previous cases—by evaporating accurately measured 50.0-cc. portions to dryness in a small quartz beaker and igniting in the same vessel to constant weight. Table I summarizes the observations made.

TABLE I

THE CONDUCTIVITY OF IGNITED SAMPLES OF "EVAPORATED" GERMANIC OXIDE

Nature of sample	$k \times 10^6$ mhos/cm.	Concn. g./liter	$k \times 10^6$ mhos/cm. (for 4.8 g./liter)
Hydrolyzed oxide	24.54	4.792	24.58
Evaporated oxide	7.94	4.786	7.96
Evaporated oxide (to 380°)	7.72	5.464	6.78
Evaporated oxide (to 700°)	5.13	4.948	4.98
Evaporated oxide (to 850°)	4.67	5.058	4.43
Evaporated oxide (to 1250°)	3.85	4.796	3.85

In the last column are shown values for the specific conductivities of all the solutions at the same concentration—calculated on the assumption that, between such small limits, a straight line relationship exists between concentration and specific conductivity.

Either one of two explanations was thought capable of accounting for these results: (1) the portion of the oxide not transformed to the insoluble variety may be so changed as a result of the increasingly high temperatures to which it is subjected that on subsequent solution it is hydrated in a continually different manner, or (2) there may have been present in the hydrolyzed oxide an impurity removable by evaporation and ignition—the impurity being completely driven out on heating to the melting point (approx. 1100°).

(e) It was then decided to repurify the oxide used. This was done as described above for the preparation of Lot 2 of the hydrolyzed oxide. The evaporations of this especially pure material were carried out in a quartz flask closed to the air and immersed in a thermostat kept at about 60°. The evaporation was aided by passing air through a purifying train containing silver nitrate solution, concentrated sulfuric acid, concentrated sodium hydroxide, solid sodium hydroxide and blowing it across the surface of the evaporating liquid. The air was introduced through quartz tubes sealed into a tightly fitting quartz stopper, while the escaping air and water vapor passed out through a small indentation on the side of the stopper. Under these conditions the changes observed in the specific conductivity when the "evaporated" oxide was redissolved in water were very small—about 2 to 3% of the original values, which, as shown in Table II, were themselves extremely low. Successive evaporations had, likewise, little or no effect on the conductivity.

Final Determinations.—These determinations were made on solutions of the oxide prepared from Lot 2 or 3. They were all obtained by boiling a weighed sample in a quartz flask with conductivity water until a clear solution was formed, cooling the solution to room temperature and determining the specific conductivity at 25°. The concentration was then determined accurately, as described above, on a carefully measured volume of the solution—the sample being taken at 25°. Table II gives a summary of these observations.

TABLE II

THE SPECIFIC CONDUCTIVITY OF GERMANIC OXIDE AT 25°

	Source of sample	Concn., g./liter	$k \times 10^6$ (mhos/cm.)	$k \times 10^6$ mhos/cm. (for water)
1	Hydrolyzed (Lot 2)	4.720	2.91	0.96
2	Hydrolyzed (Lot 2)	4.720	2.99	.93
3	Hydrolyzed (Lot 3)	4.720	2.74	.92
4	Glassy (Lot 2)	4.658	2.78	.89
5	1050° (Lot 2)	5.520	5.41	1.00
6	From sulfide (Lot 3)	4.845	4.57	0.90

Table III shows the calculated values for the degree of dissociation, the equivalent conductivity and the primary dissociation constant of germanic acid as obtained from each of the observations recorded in Table II.

TABLE III

THE DEGREE OF DISSOCIATION, EQUIVALENT CONDUCTIVITY AND PRIMARY DISSOCIATION CONSTANT OF GERMANIC ACID

	Concn., mole/liter	$k \times 10^6$ mhos/cm.	$k \times 10^6$ mhos/cm. (corr.)	$\alpha \times 10^4$	Λ	$K_1 \times 10^9$
1	0.04513	2.91	2.73	1.59	0.0606	1.14
2	.04513	2.99	2.87	1.67	.0636	1.26
3	.04513	2.74	2.61	1.52	.0578	1.04
4	.04453	2.78	2.65	1.56	.0595	1.09
5	.05277	5.41	5.34	2.66	.101	3.73
6	.04632	4.57	4.50	2.55	.0970	3.00

In the case of each of the above solutions, dilutions were made and the specific conductivities determined at each concentration. The dissociation constants calculated decreased for all the solutions with decreasing concentration and remained fairly constant within the range 0.95 and 1.1×10^{-9}.

The only added electrolyte in all these solutions was the germanic oxide, which in the presence of water forms germanic acid. The specific conductivity of the water used was close to the value 0.85×10^{-6} mho per cm. found by Kendall[12] for "equilibrium water," and therefore we can make the assumption that the entire conductivity of the water was due to carbonic acid. In view of the very low conductivities observed, it is impossible to ignore the mutual effect of the two acids, carbonic and germanic, on their dissociation. A correction must be applied for this effect, and in making the above calculations this correction was determined by the method of Walker and Cormack.[13] Column 3 of the last table gives the corrected value for each of the specific conductivities recorded. The value of Λ_∞ for germanic acid which is needed in these calculations was

[12] Kendall, THIS JOURNAL, **38**, 1480 (1916).

[13] Walker and Cormack, *J. Chem. Soc.*, **77**, 5 (1900).

taken as 381.2, and was obtained by adding the mobilities of the hydrogen ion and the bigermanate ion. The value for the hydrogen ion, 349.9 at 25°, was taken from the "International Critical Tables,"[9] while the value for the bigermanate ion, 31.3, was obtained from measurements on the conductivity of sodium bigermanate—the data for which are given in the following paper. The dissociation constant of carbonic acid at this temperature was taken as 3.5×10^{-7}, and the concentration of carbon dioxide in equilibrium water at this temperature as 1.4×10^{-5} mols per liter.[12]

In order to complete the study of the conductivity of solutions of the allotropes of germanic oxide, several experiments were carried out with the insoluble variety—obtained as already described. The purified sample was boiled repeatedly with conductivity water in a quartz flask. The specific conductivity of solutions thus boiled in the presence of the solid for varying lengths of time up to four hours showed no appreciable increase over the value for the conductivity water used in preparing the solutions. This is to be expected in view of the very low solubility of the α modification and the extremely low conductivity of even saturated solutions of the soluble varieties.

Discussion

The results obtained indicate that solutions of germanic oxide are quite stable, at least over a period of a week at the concentrations studied. Extremes of temperature do not seem to bring about any changes in the fundamental equilibria set up when the oxide is first dissolved in water, no matter whether an amorphous or crystalline variety is involved in the equilibria. Furthermore, the fact that at similar concentrations, solutions of the "evaporated" and "hydrolyzed" oxides have similar conductivities lends support to the conclusion of R. Schwarz and Huf that they are not distinct modifications, in spite of the observed differences in density and in their behavior on ignition. On the other hand, it is difficult to explain the fact that solutions of the "glassy" and "hydrolyzed" forms give practically the same conductivity—since it has been shown[3,4] from x-ray spectrographic data that the one is amorphous and the other crystalline. It may be that the low values for these two varieties are due entirely or in large part to electrically charged colloidal particles, whereas, in the cases of the oxide obtained from the sulfide and that crystallized at 1050°, the amount of colloid in solution is relatively small. The higher conductivities observed in the solutions of the latter two samples would then be due almost entirely to dissociated germanic acid. In other words, all solutions of germanic oxide—no matter from what source—contain both molecularly and colloidally dispersed material with the one or the other in greater amount depending on the source and manner of preparing the solutions. This would explain the small differences in conductivity observed for the different samples and would be in agreement with the conclusion to which Schwarz and Huf arrived on the basis of their data concerning anomalies in the solubility of the oxide.

In any event, the very low conductivities observed in all the cases indicate a very high degree of purity for all the samples, and should serve to place a definite upper limit for the value to be assigned to the primary dissociation constant of germanic acid. Both the high and low values agree very well with the average value of Pugh, *i. e.*, 2.5×10^{-9}; and when it is considered that Pugh's average was obtained from the three values 1.75, 3.2 and 2.1×10^{-9}, the agreement of our values with his seems to be quite satisfactory. However, in view of the very low conductivities measured, it was thought advisable to determine the value of the constant by other and independent methods. These are discussed in a subsequent paper.

Summary

1. The importance of exceptionally pure germanic oxide in conductivity work has been discussed and a description given of the method used to obtain such material.

2. The conductivity of solutions of the oxide from various sources has been measured and the values in all cases found to be much lower than those already in the literature.

3. In contrast to the work of Roth and O. Schwartz, the conductivity of these solutions was found to be practically unaffected by changes in temperature—either during their preparation or after.

4. Small differences in conductivity of solutions of the several varieties were observed and the possible cause for such differences discussed.

5. The dissociation constant of germanic acid was calculated from the conductivity data obtained, and found, at different concentrations, to lie between 1.0 and 3.0×10^{-9}. These values were in close agreement with those of Pugh.

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