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

THE ALLOTROPY OF GERMANIUM DIOXIDE[1]

BY JOHN HUGHES MÜLLER AND HORACE R. BLANK

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In previous investigations on germanium and its compounds carried out in this Laboratory, it was noticed that quite frequently when germanium dioxide solutions were evaporated and the residues ignited over a Bunsen or Meker burner, a part of the residual oxide did not appear to be soluble in water or in ammonium hydroxide, and adhered very firmly to the containing vessel. This aroused the suspicion that the oxide might exist in another modification having a much lower solubility than the ordinary form.

A large number of preliminary experiments were carried out on 0.5g. samples of the oxide prepared by evaporation of the aqueous solution. It was found that when the sample was not subjected to any further heating after evaporation, complete solution resulted upon treatment with boiling water. Fusion of this material in the oxy-gas flame also gave a completely soluble form of the oxide. On the other hand, when the oxide obtained by evaporation was heated to any temperature between these two extremes, in every case a small amount of insoluble material remained even after prolonged boiling for several days with fresh portions of pure water. Several attempts were made to prepare this insoluble material by heating the original germanium dioxide (prepared by hydrolysis of the pure tetrachloride) directly, without first dissolving it and evaporating the aqueous solution but, with one or two exceptions described below, all of them met with failure.

Identification of the Insoluble Residue as Germanic Oxide.—To make certain that the insoluble residues were really germanium dioxide, a sample was repeatedly washed by boiling with water and decanting, and then dried in a platinum dish and fused over a blast lamp. The glassy mass so obtained was found to dissolve completely in an excess of boiling water, and from this solution the white germanium disulfide was precipitated in the presence of 6 *N* sulfuric acid. After oxidation to germanium dioxide with nitric acid, and ignition, this precipitate amounted to 99.4% of the original insoluble material. It was concluded that this insoluble substance must be essentially germanium dioxide.

Possible Allotropy of Germanium Dioxide.—The existence of a variety of germanium dioxide having such an extremely low solubility in water suggested that this oxide might exhibit allotropy. While in the present

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[1] From a thesis presented to the Faculty of the University of Pennsylvania, 1924, by Horace R. Blank, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

investigation this has not yet been established beyond all question, the experimental results which have been obtained seem rather difficult to explain from any other point of view.

Variation in Behavior of Germanium Dioxide toward Water

Germanium dioxide differs very greatly in its behavior toward water and various chemical reagents with the method employed for its preparation. The oxide obtained by the hydrolysis of the tetrachloride, which may for convenience be designated in this paper as "hydrolyzed" germanium dioxide, agrees in properties with that described by Winkler.[2] When mixed with water it always forms a milky suspension in the cold, which after a few minutes' boiling suddenly becomes clear. This oxide dissolves quickly in hydrofluoric acid with evolution of much heat and with a hissing noise, a fact observed by Krüss and Nilson,[3] and is also easily attacked by hydrochloric acid.

The oxide obtained by evaporating an aqueous solution of germanic oxide may be called, for the purposes of this paper, "evaporated" germanium dioxide. This evaporated material always retains a small amount of water. It is extremely slowly soluble in cold water, but dissolves in hot water after a short time.

"Insoluble" germanium dioxide is obtained by heating the "evaporated" oxide to any temperature between 200° and its melting point (about 1100°), and then boiling the mass thoroughly with water to remove the unconverted "evaporated" oxide. This form settles quickly from suspension in water, in which it is quantitatively insoluble. Qualitatively examined it did not dissolve in hydrochloric acid, sodium hydroxide, and ammonium hydroxide, even when boiled with these reagents. It was also insoluble in hydrofluoric acid, which is in striking contrast to the behavior of the hydrolyzed oxide.

That the inactivity of this form of germanium dioxide toward water is not due to a very slow rate of solubility was shown by placing a weighed portion of it in a flask with pure water and boiling from time to time for 120 hours in all. The insoluble material was then recovered by filtration through a Gooch crucible. *The result indicated that only 10 mg. per liter had dissolved,* whereas the solubility of the "hydrolyzed" oxide is 10.9 g. per liter[2a] at 100°.

Formation of a Soluble Glass by Fusion of Insoluble Oxide

All forms of germanic oxide, regardless of their behavior with water, melt at high temperatures to a viscous liquid, which solidifies to a glass-like mass on cooling. The unground glass is only very slowly affected by

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[2] (a) Winkler, *J. prakt. Chem.*, **34** (N. F.) 211 (1886). Its solubility at 25° has been recently redetermined by (b) Müller and Iszard, *Am. J. Med. Sci.*, **163**, 364 (1922).

[3] Krüss and Nilson, *Ber.*, **20**, 1696 (1887).

cold water, but dissolves easily and completely when digested with boiling water. It never, even when finely ground, forms a milky suspension with water before dissolving, as does the "hydrolyzed" oxide.

In consequence, the insoluble form of germanium dioxide may again be rendered soluble by fusion, but up to the present time it has not been found possible to reconvert it to a soluble modification in any other way.

Possible Differences in Crystalline Form

Differences in crystalline form between the "hydrolyzed," "evaporated," and "insoluble" germanium dioxide have not yet been established, for under the microscope no distinct crystals were observable in our preparations. In the case of the "evaporated" oxide the lack of visible crystalline structure may have been due to rapid evaporation, for when examined in polarized light between crossed Nicol prisms numerous illuminated spots were seen, indicating that even when evaporated rapidly it is anisotropic. The oxide obtained by hydrolysis and the insoluble form showed perfectly dark fields when examined in the same way.

Effect of Temperature on Yield of Insoluble Germanium Dioxide

Further evidence suggesting allotropy was obtained in an attempt to determine the most favorable temperature for the production of insoluble germanium dioxide from the evaporated oxide. Approximately 0.5g. samples of the latter were heated at a number of different temperatures for a fixed period of time (four hours), and the amount of insoluble oxide formed was determined in each case. The results are shown in Fig. 1, where the yield of insoluble germanium dioxide is expressed in percentage of the evaporated oxide used. The following procedure was adhered to in these experiments.

A large volume of an aqueous solution of germanic oxide was evaporated in a platinum dish until a fairly thick crust of the evaporated material had been obtained. This was separated from the dish by bending the metal back and forth. It is quite a difficult matter to detach the evaporated oxide from any rigid vessel. The oxide was then powdered and the entire series of experiments was run on 0.5g. portions from this same lot (Lot 1). Each sample was weighed in a porcelain boat, and was heated to the desired temperature in a small, platinum-wound resistance furnace. Since the evaporated oxide could not be prepared anhydrous, and always retained water[4] up to 800–900°, it was found necessary to weigh the samples again after heating. The average water content (1.73% on Lot 1) of the samples heated to high temperatures, found in this manner, was used to calculate the weight of anhydrous germanium dioxide present in those samples heated to lower temperatures, and from which in consequence only part of the contained water was driven off during the experiment. Uniformity was secured in the rate of heating and cooling by first bringing the furnace to the desired temperature, then inserting the boat, removing it quickly after the proper time, and finally allowing it to cool quickly in the open to below redness. It was then placed in a desiccator and weighed

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[4] Dennis, Tressler and Hance [(a) THIS JOURNAL, **45**, 2033 (1923)] state that a temperature of 900° is necessary to dehydrate germanium dioxide completely.

when completely cooled, after which it was allowed to stand overnight in about 300 cc. of water. The mass disintegrated more quickly when treated in this manner than when boiling was begun at once. The mixture was then kept at the boiling point on the hot plate for the next two days (16 hours' boiling). The residue was allowed to settle, and the clear supernatant liquid was decanted while hot through a weighed Gooch crucible. Fresh water was then added to the residue and the boiling continued for four hours more. The residue of insoluble oxide was then filtered through the same crucible, dried at 110–120° and weighed. Drying for two hours at this temperature always gave constant weight. Although upon investigation it was found that the insoluble oxide retains about 0.5% of its weight of water to a very high temperature, it will be seen that the correction which could be applied would hardly be appreciable, and that all of these determinations are directly comparable with one another.

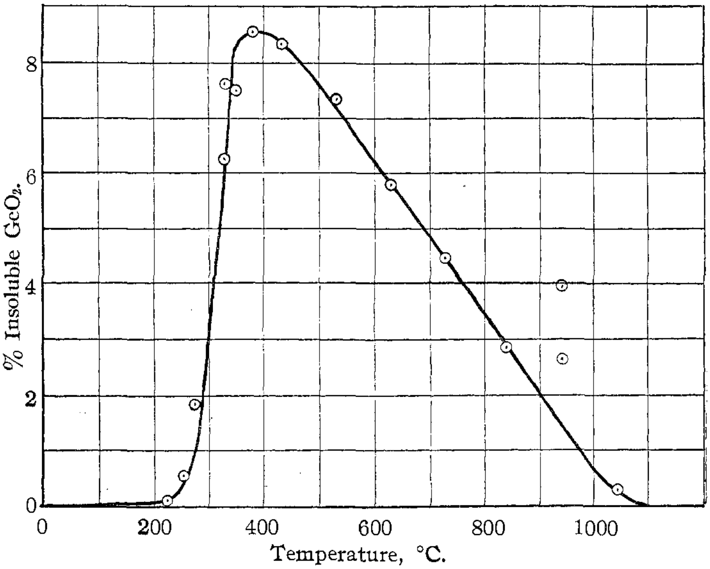

Fig. 1.—Yields of insoluble GeO_2 at various temperatures in four hours.

From Fig. 1 it will be observed that a slight conversion of the evaporated oxide into the insoluble form was noticed at 225° in four hours. The amount converted in this given time increased rapidly with rising temperature to a maximum at 380°, and then decreased gradually, but some conversion could be observed at any temperature from 225° up to the melting point.

Maximum Velocity of Transformation at 380°

Since in all cases of allotropy the metastable form always has the greater solubility, the "insoluble" germanium dioxide must be the stable modification at ordinary temperatures. The amounts of the stable insoluble dioxide produced from the metastable evaporated oxide at different temperatures in the same length of time should be proportional to the velocities of transformation at these temperatures. Then from Fig. 1 it may be concluded that the velocity of transformation of the evaporated oxide into the insoluble form increases with rising temperature to a maximum at about 380°, under the conditions of this experiment, and then decreases gradually from this temperature to the melting point. It would therefore appear that the transition point between the two forms should lie close to, if not above, the melting point, for the transformation in question should not take place at all except at temperatures where the insoluble form is stable. It must not be forgotten, however, that in all of these experiments at high temperatures it was necessary for the evaporated material to pass from room temperature through the temperature of maximum velocity of transformation before reaching the temperature of the furnace, and that this fact may possibly have affected the yields of the insoluble oxide at temperatures above 380°. Attention should also be called to the two anomalous results at 940°, which represent two separate experiments under as nearly as possible the same conditions, and which cannot be explained from the data thus far secured.

Effect of Time of Heating on Yield of Insoluble Germanium Dioxide at 280°

If the formation of insoluble germanium dioxide is the result of the transformation of one allotropic modification into another, the time of heating, as well as the temperature, might affect the yield of the insoluble form produced. This was very soon found to be the case. The effect of heating eleven 0.5g. samples of the evaporated oxide for different periods of time at the constant temperature of 280° is shown in Fig. 2, where the percentage yields of the insoluble modification are plotted against the time.

Great care was exercised to make the time the only variable factor in this experiment. The samples were all taken from the same lot of evaporated germanium dioxide (Lot 2) which, however, due to the necessity of preparing more material, was not the same as that used for the experiments shown in Fig. 1. The water content was determined on a separate sample of the same material. All eleven samples were heated simultaneously in a specially constructed furnace, in which their radial arrangement permitted equal exposure to the source of heat. Each sample was withdrawn from the furnace at the expiration of the proper time, and the yields of insoluble dioxide were determined in the manner already described.

Suggestion of Three Allotropic Forms of Germanium Dioxide

If germanium dioxide exists in only two allotropic modifications, one of which is soluble in water and the other insoluble, the evaporated oxide, being completely soluble, must be homogeneous. The complete transformation of this metastable form into the stable insoluble form should only require the lapse of a sufficient time. The curve obtained by plotting the yields against the time should therefore be asymptotic to 100%. But a prolongation of the curve in Fig. 2 indicates that in this case the reaction would probably come to completion when only about 15% of the evaporated oxide had been converted into the insoluble form. As a possible explanation of this behavior it may be suggested that the evaporated dioxide may not be homogeneous, and that only part of it may be convertible into the insoluble oxide with a velocity measurable in such an experiment as this. This would necessitate three allotropic forms of germanium dioxide, two of which would be soluble in a large excess of boiling water. The insoluble form would be the stable one at ordinary temperatures.

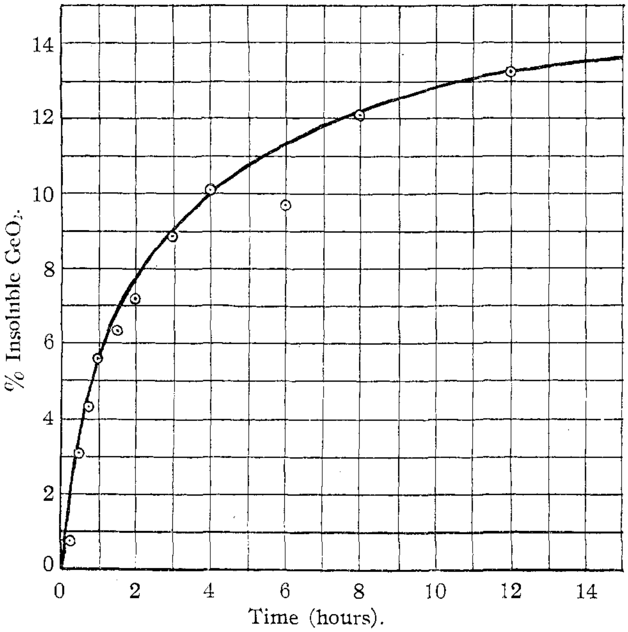

Fig. 2.—Yields of insoluble GeO_2 at 280°.

Other Experiments

An experiment entirely similar to that illustrated by Fig. 2 was carried out on eleven samples of Lot 1 of evaporated dioxide, except that a constant temperature of 530° was employed. Yields varying from 6.5 to 7.2%, averaging 7%, of the insoluble oxide were obtained for periods of heating ranging from 15 minutes to 12 hours. Considering the errors due to irregularities in temperature to which this experiment must be subject, this represents a practically constant yield of the insoluble dioxide regardless of the time of heating. The yield for 530° in Fig. 1, determined from the same material, also agrees with the average yield in this experiment. The temperature of 530° is apparently above the temperature of maximum velocity of transformation for this particular material (Lot 1 of evaporated oxide), but the full significance of these results is not yet understood.

As previously mentioned, repeated attempts to prepare the insoluble form of germanium dioxide by heating 0.5g. portions of the "hydrolyzed" oxide directly, without first dissolving it in water and evaporating the solution, resulted in failure. But when larger quantities (10 to 20 g.) of the hydrolyzed oxide, and also of the oxide prepared by the oxidation of germanium disulfide, were ignited to high temperatures for about 36 hours in the effort to expel chlorides and sulfates, on one or two occasions the insoluble dioxide was formed in sufficiently large amounts to be easily identified. It is evidently much more difficult to prepare the insoluble oxide directly from these sources than from the product of the evaporation of aqueous solutions, but beyond this fact the exact conditions for its direct formation are as yet undetermined.

Further Discussion

If it is supposed that germanium dioxide may exist in three allotropic modifications, the "evaporated" dioxide may be regarded as a mixture of two soluble metastable forms, one of which is converted into the stable insoluble form much more rapidly than the other, in the range of temperature in which we have experimented. In the experiments described, the transformation of this rapidly converted form seemed to reach its maximum velocity at about 380°. Since different preparations of the evaporated oxide gave quite different amounts of insoluble dioxide when heated under similar conditions, it may be inferred that the composition of the mixture varies according to the conditions of the evaporation. The temperature of maximum velocity of transformation may also be affected by these conditions. Our experience appears to indicate that the more rapid the evaporation, the smaller will be the subsequent yield of the insoluble oxide at any particular temperature. In one case of particularly rapid evaporation only a few tenths of 1% was formed at temperatures where the maximum yield, according to Fig. 1, would be expected. Unfortunately, scarcity of material has prevented the repetition of experiments involving both constant temperature with varying time, and constant time with varying temperature on the same large lot of evaporated dioxide, which would make results such as those in Figs. 1 and 2 quantitatively comparable.

While the highest proportion of the easily convertible form in the material used in any of the above experiments would seem to be about 15%, none of the evaporations has as yet been conducted with a view to allowing the greatest freedom for crystallization. It seems not unlikely that the orthorhombic crystals of germanium dioxide described by Haushofer,[5] of the existence of which in our material we have some slight optical evidence, may prove to be the readily convertible form in a pure state. Therefore, if it should prove possible to prepare large quantities of these crystals, their nearly complete conversion into the insoluble form might be anticipated.

The supposition that there are three allotropic forms of germanium dioxide is not inconsistent with the fact that, as above noted, it is much more difficult to prepare insoluble dioxide by heating "hydrolyzed" dioxide than by heating the evaporated oxide. According to this view the hy-

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[5] Haushofer, *Sitz. Bayer. Akad. Wiss. München*, 17, 133 (1887).

drolyzed material may be regarded as composed entirely of that metastable form which is the more slowly converted into the insoluble modification. However, the conditions under which this latter conversion reaches its maximum velocity still remain to be investigated.

If the formation of the insoluble form of germanium dioxide were simply a surface phenomenon due to sintering on heating, fusion of this mass could hardly increase its solubility; but the insoluble dioxide can be fused to a glass which is easily soluble in hot water. From the point of view of allotropy the glass, which from its physical nature would be expected to represent a metastable phase, ought to be more soluble than the stable "insoluble" modification. Consequently allotropy seems to us to be the most reasonable explanation for this behavior.

The Melting Point of Germanium Dioxide

While it has long been known that germanium dioxide melts to water-like drops at a high temperature, no attempt has been made to determine the melting point until recently, when Nichols,[6] while studying the luminescence of the oxide at various temperatures, obtained results indicating its melting point as 1400°. Since preliminary experiments had led us to believe that the melting point was close to 1100°, it seemed necessary to make a more detailed investigation.

Accordingly, 9.87 g. of carefully purified germanic oxide were packed around a platinum platinum-rhodium thermocouple in a transparent silica tube, which was then placed within the tube of a platinum-wound electric furnace. The space between the two tubes was filled with quartz sand to prevent rapid radiation.

The temperature was now raised until all of the powdered oxide had melted. Four successive cooling curves were taken between 1300° and room temperature, with readings at 15-second intervals, but the rate of cooling was perfectly regular and no retardation was noticed at any point. It may therefore be concluded that no crystallization takes place when the oxide solidifies, unless the heat change with 10 g. of the material is too small to be observed in this experiment.

Between 1200° and 1300° molten germanium dioxide is a very viscous liquid, which regularly becomes thinner as the temperature is raised. It can be drawn out in thin flexible threads resembling those obtained from molten glass. Like glass, the fused oxide cracks easily when suddenly cooled. Pure fused germanium dioxide does not appear to attack silica chemically at all, but it firmly adheres to a silica vessel and almost always causes the destruction of the latter when the molten mass is quickly cooled. Threads of the dioxide glass of approximately 0.3 mm. diameter were

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[6] Nichols, *Proc. Nat. Acad. Sci.*, 9, 248 (1923). In a private communication Dr. Nichols has explained that his material was heated in direct contact with the hydrogen flame, which may have caused some change in its composition.

suspended in a resistance furnace and very slowly heated. By attaching small weights they were made to elongate indefinitely at temperatures as low as 740°. These behaviors are exactly what would be expected if the germanium dioxide which has solidified quickly from a state of fusion is a true glass.

The melting point of powdered germanium dioxide prepared in various ways was arbitrarily determined by placing a little of the dry powder in a thin-walled silica tube adjacent to the thermocouple in the electric furnace, and noting the temperature below which the fine particles did not coalesce into minute globules, as observed under a magnification of 14 diameters. The purest germanium dioxide, which had been ignited to 950° but which had never been fused, showed globules at 1096–1099°. The ground glass, the same material as that used in the experiment described in the preceding paragraph, also coalesced at 1096–1099°. This is interesting in comparison with the behavior, as above noted, of the same glass before grinding. The "insoluble" form of the oxide when examined in the same way yielded globules at 1090–1091°. It therefore seems that the melting point of any form of germanium dioxide, as arbitrarily defined in this experiment, should be placed between 1090° and 1100°.

The platinum platinum-rhodium thermocouple and millivoltmeter used in these experiments were calibrated by a determination of the melting points from the cooling curves of pure bismuth, lead, zinc, antimony and silver. The temperatures given are believed to be correct within ±5°.

Purification of Germanium Dioxide

The germanium dioxide used in the experiments described above had been freed from arsenic and other metals by repeated distillation in chlorine from hydrochloric acid solution, and precipitation from the distillates by hydrogen sulfide. The final distillations of the tetrachloride gave a product from which the oxide was prepared by simple hydrolysis. Germanium dioxide made by the hydrolysis of the tetrachloride contains detectable amounts of chloride, and the oxide prepared by the oxidation of the sulfide by nitric acid retains appreciable amounts of sulfur. It is usually assumed that these impurities will be removed by continued ignition, but larger quantities of the oxide are not readily freed from either of them by this method. Germanic oxide may therefore readily be prepared free from either chlorides or sulfates, but it is rather difficult to eliminate both of these impurities from the same portion of material.

Sulfates can be removed by ignition alone, provided it be continued for a very long time at a very high temperature. Prolonged ignition over a Meker burner was found insufficient when 10 g. or more of the oxide was involved. Immediate fusion at about 1100° also failed to produce a pure oxide, as sulfates could be detected in the aqueous solution of the resulting glass. Ignition above 950° for about 36 hours in an electric furnace completely removed the sulfates from 10 or 15 g. of the oxide.

The ignition described above was found insufficient for the removal of the last traces of chlorine from 10–15 g. of material. Heating the oxide in a current of superheated steam slowly carries out much hydrogen chloride, as may be seen by treating the condensed steam with silver nitrate. Repeated moistening of the oxide with water, followed by evaporation and ignition at 950°, was finally found to be an effective method. It seems probable that the small quantity of water tenaciously held by germanium dioxide[4a] up to 900° plays an important part in completing the hydrolysis of the chloride, for unless this water was repeatedly renewed and expelled, the oxide did not lose all of its retained chlorine even at 950°.

Germanium dioxide thus purified completely from chlorides and sulfates was used for the determination of the melting point. A portion was also converted into the insoluble form. While much of the material used in the other experiments described in this paper still contained traces of these non-metallic impurities, it is evident that the presence of chlorine or sulfur is not essential to the formation of "insoluble" germanium dioxide.

Summary

As a result of the following observations, the suggestion is made that germanium dioxide probably exists in two or more allotropic modifications.

1. When an aqueous solution of germanium dioxide is evaporated carefully and the residue heated to any temperature between 225° and 1100°, part of the oxide is converted into a form insoluble in water and very inert toward acids and alkalies.
2. This "insoluble" germanium dioxide becomes soluble again after fusion.
3. The yield of insoluble germanium dioxide, formed by heating portions of the "evaporated" oxide at different temperatures for the same period of time, increased up to 380° and then decreased to the melting point. It is therefore suggested that 380° may represent the temperature of maximum velocity of transformation under these conditions.
4. When the time of heating was varied at the constant temperature of 280°, the yield of the insoluble form increased in such a manner as to suggest that the conversion could never reach 100%. For this reason, and because the yields of the insoluble form varied greatly with different preparations of the "evaporated" oxide, it is suggested that three allotropic forms of germanium dioxide may exist, the "evaporated" oxide being a mixture of two of them.
5. The melting point of any form of germanium dioxide appears to lie between 1090° and 1100°.
6. A description of the purification of germanium dioxide from chlorides and sulfates is given.

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