the "cell constant" curve, which value is assumed to remain fixed in the measurements with the acid solutions.

6. Extrapolation of the results upon the assumption that the mass-action law is approached as a limiting form at infinite dilution, gives a value of Λ_0 for hydrochloric acid of 425.69. Assuming that the value of Λ_0 for the chloride ion at 25° is 75.8, a value of 349.89 for the hydrogen ion at that temperature is obtained. By comparing this with the value 349.93 obtained by Kraus and Parker for iodic acid, the value 349.89 ± 0.05 is deduced as the most probable value for the hydrogen ion at 25°—the basis for the "cell constant" being more firmly established in the measurements with hydrochloric acid. The mass-action constant corresponding to this extrapolation has a value of 0.105.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM.[1] VI. METALLIC GERMANIUM. REDUCTION OF GERMANIUM DIOXIDE. PREPARATION OF FUSED GERMANIUM. PHYSICAL AND CHEMICAL PROPERTIES

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Material.—The germanium that was used in these investigations was prepared by the reduction of pure germanium dioxide that was practically free from other metals, including arsenic.[3]

Dehydration of Germanium Dioxide

Since it was desirable that germanium dioxide be thoroughly dehydrated before experiments were made upon its reduction, the lowest temperature at which complete dehydration resulted was ascertained by heating germanium dioxide that had been dried at about 100° to successively higher temperatures until constant weight was obtained. It was found that the dioxide is completely dehydrated when heated to a temperature of 950° for about 3 hours, and that there is no volatilization of germanium dioxide at a temperature of 1250°. The dehydration may be effected rapidly by heating the oxide over a gas-air blast flame, and the product that is formed is not hygroscopic.

[1] This article is based upon the theses presented to the Faculty of the Graduate School of Cornell University by Katharina M. Tressler and F. E. Hance in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] The experimental work of this investigation was carried on separately and not jointly by Miss Tressler and Mr. Hance.

[3] Dennis and Papish, THIS JOURNAL, **43,** 2131 (1921). Dennis and Johnson, *ibid.,* **45,** 1380 (1923).

Reduction of Germanium Dioxide by Aluminum

The heat of formation of aluminum oxide is far greater than that of silicon dioxide or of stannic oxide, and since germanium lies between silicon and tin in the fourth group of the Periodic Table, it is clearly apparent that metallic aluminum will easily reduce germanium dioxide.

Forty g. of germanium dioxide and 14 g. of granular aluminum were mixed and placed in a small iron crucible that was thickly lined with aluminum oxide. The reaction was started with an ignition mixture of magnesium and barium dioxide and proceeded quietly through the mass. A dense white cloud was, however, given off, and this was found to consist chiefly of germanium dioxide. A button of bright, lustrous metal was obtained, but as this represented a yield of only 61%, further study of this reaction was abandoned for the present.

Reduction of Germanium Dioxide by Hydrogen

Winkler[4] found that germanium dioxide is reduced by hydrogen at red heat but that the reduction is not always complete.

Müller[5] stated that the ratio GeO_2:Ge was not suited to the determination of the atomic weight of germanium, both because of impurities in the germanium oxide that he used, and because of loss that he thought resulted from the formation and escape of germanium hydride.

In our study of this reaction, the following procedure was employed. A small sample of germanium dioxide that had been dehydrated at about 950° was weighed into a porcelain boat which was heated to definite temperatures in hydrogen. The hydrogen was first passed through spirals of red-hot copper gauze and then through drying towers filled with calcium chloride. A quartz tube drawn out to a fine tip was joined to the exit end of the quartz combustion tube.

After the air in the apparatus had been displaced by hydrogen, the temperature of the combustion furnace was slowly raised. At 500° the surface of the white germanium dioxide began to turn gray, and when the temperature had risen to 540°, the whole surface of the dioxide had taken on this gray color. The temperature was maintained at this point for 45 minutes, the powder changing in that time to a very dark gray. The heat was then turned off, the boat was allowed to cool in hydrogen, and the hydrogen was displaced by air. The weight of the boat showed that reduction was not complete. It was, therefore, re-inserted in the combustion tube and heated in hydrogen for 90 minutes more at from 500° to 540°. The weight of the residual germanium now coincided with the calculated amount (at. wt., Ge = 72.5).

[4] Winkler, *J. prakt. Chem.*, **142,** 177 (1886); **144,** 188 (1887).

[5] Müller, THIS JOURNAL, **43,** 1085 (1921).

	G.
Wt. GeO_2 taken	0.3498
Heated in hydrogen at 500–540° for 45 minutes, loss	.0909
90 minutes longer, additional loss	.0162
Total loss in 2¼ hours	.1071
Calculated loss in weight, $GeO_2 - Ge$	.1071

The boat and its contents were then heated for 2¼ hours longer in hydrogen at 500–540°, and the temperature was finally raised to 900°. No change in weight resulted.

During the reduction of the oxide, a porcelain dish was repeatedly held in the hydrogen flame burning at the quartz tip, but at no time was there formed a mirror of metallic germanium nor did any deposit appear within the quartz combustion tube beyond the boat. The above results indicate that a comparatively small amount of germanium dioxide is quantitatively reduced by about 2 hours' heating in hydrogen at 540°, and that no volatilization of germanium or of any compound of the element takes place under these conditions.

Metallic germanium prepared in this manner is a dark gray powder without metallic luster.

When, however, attempt was made to reduce larger amounts of germanium dioxide that completely filled 4 porcelain boats, there appeared on the walls of the quartz tube beyond the boats a deposit that was black nearest the heated area, and shaded off through brown to yellow toward the cold end of the tube.

Total charges of from 10 to 14 g. always yielded an amount of germanium that was below the calculated quantity.

Preparation of Fused Germanium

A preliminary trial of Winkler's method[4] of fusing powdered germanium, prepared by reducing germanium dioxide in hydrogen under a layer of borax glass showed that a small amount, about 1 g., could be fused to a bead that was free from boron and sodium. When, however, a larger sample of 26 g. of germanium was heated with 30 g. of borax glass in a covered porcelain crucible over the blast lamp to a temperature of about 930°, the germanium did not coalesce. About 5% of boric acid was then added to a fresh portion of this mixture, and upon fusion there resulted small granules of germanium from 1 to 3 mm. in diameter which were coated with a black powder. The flux also was deep black in color, and when digested in water it yielded a reddish-brown, flocculent residue, consisting chiefly of hydrated germanous oxide.

When the cover of the crucible was lifted during the heating of powdered germanium under borax glass, a white cloud of germanium dioxide rose from the crucible. This misled Winkler into believing that the "vaporization temperature of germanium lies only slightly above its melting point."

As a matter of fact, metallic germanium, as will be shown later, is not volatile at a temperature 300° above its melting point, and the white cloud that rose from the open crucible is doubtless due, as Biltz[6] has also pointed out, to oxidation of volatile germanous oxide that is formed by the action of molten borax upon germanium.

Powdered germanium was next fused under a layer of anhydrous sodium sulfate. Small samples yielded bright, silvery granules of germanium and a larger sample, about 40 g. of germanium, gave a button of brilliant luster that was distinctly crystalline in character. The button was surrounded by a yellow, transparent, glass-like material that evolved hydrogen sulfide when treated with hydrochloric acid and contained 48.94% of germanium. The weight of the button was only 73.8% of the powdered germanium that was used.

Some of this metal from the first fusion was again fused under sodium sulfate at temperatures rising from 829° at the beginning to 1050° at the end of the 10 minutes' heating. Reduction of the sodium sulfate again resulted and the metallic regulus weighed only 77.7% of the fused germanium that was employed.

These results made it clear that salts of oxy-acids are not suitable as fluxes for this purpose. The compound that is employed as a flux should have a somewhat lower melting point than germanium, but should not appreciably volatilize or dissociate at a temperature that would ensure fluidity of the metal. Sodium chloride seemed to meet these requirements.

Fig. 1.—(Actual size)

A porcelain crucible 7 cm. in diameter was charged first with a layer of pure, dry sodium chloride to a depth of about 15 mm., then with a layer of a mixture of equal parts of salt and powdered germanium that had been ground together, and finally with salt nearly to the top. It was then covered and placed upon a short, perforated cylinder of asbestos board which rested on an iron ring. The crucible was surrounded by 3 concentric tubes of asbestos board through the walls of which passed a long asbestos tube which permitted the reading of the temperature of the crucible by means of an optical pyrometer. The crucible was heated by the direct flame of 2 blast lamps, and the temperature was brought to from 980° to 1000° and was held there for about 30 minutes. The crucible was

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[6] Biltz, *Z. anorg. Chem.*, **72**, 313 (1911).

allowed to cool and was then broken. The germanium was found as a single, brilliant, crystalline button. (Fig. 1.) Adhering salt was removed by digesting the metal in hot water. This solution was alkaline, probably because of the presence of sodium germanate which resulted from the fluxing off of the small amount of the oxides of germanium in the powdered metal. The yields from 3 fusions, in which 24, 38 and 41 g. of powdered germanium were used, were 96%, 96.05% and 96.30%, respectively. Arc spectrograms of the preparations showed that they were free from other metals.

Behavior of Germanium when Heated in Hydrogen

Müller states[5] that germanium dioxide is completely reduced to the metal by heating in hydrogen to 700°, but that there is always loss of weight when the metal is further heated in hydrogen at the above temperature. In a later article[7] he adds that "metallic germanium is slowly but appreciably volatile in hydrogen at elevated temperatures," and he gives these temperatures as 750–800°. He ascribes the loss in weight to the direct formation of a volatile hydride, the evolution of which was indicated by the formation of a slight black precipitate when the escaping hydrogen was "passed through a solution of a silver salt." He gives no description of his method of preparing metallic germanium, nor of the manner in which its purity was tested.

Since it seemed possible that the loss in weight of germanium when heated in hydrogen, as reported by Müller, might be due to the presence of oxides of germanium in the metal and the consequent volatilization of germanous oxide, detailed experiments were made with the object of first freeing the germanium from all trace of oxide and then heating this product in pure hydrogen to ascertain whether loss in weight and the formation of a volatile hydride resulted.

The germanium that was used was prepared by reduction of very pure germanium dioxide in hydrogen, fusion of the powdered germanium under pure sodium chloride, pulverizing the fused germanium and repeating the fusions under salt until the solution of the flux proved to be neutral to litmus. The final button was pulverized, the powder was digested several times in boiling water to remove the salt, and the product was then heated for 8 hours at 1000° in a current of carefully purified hydrogen.

A sample of this metal weighing 8.93 g. was placed in a porcelain boat which was then inserted in a quartz tube that rested in a combustion furnace. Hydrogen prepared by electrolysis was passed through a purifying chain containing, in the order given, alkaline potassium permanganate, calcium chloride, concd. sulfuric acid, platinized asbestos heated to 260°, soda lime, calcium chloride, concd. sulfuric acid and phosphorus pentoxide.

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[7] Müller, THIS JOURNAL, **44**, 1909 (1922).

The hydrogen then entered a Y-tube, part of it passing through the quartz combustion tube, and the remainder directly through two Wagner absorption flasks containing a 0.25 *M* solution of silver nitrate. The hydrogen issuing from the quartz tube passed through a small tube with 3 constrictions, and then through 2 Wagner flasks containing a solution of silver nitrate of the above-mentioned concentration.

After the air in the apparatus had been displaced by hydrogen, the germanium was heated to 760–800°. The temperatures were measured by a thermocouple, the hot junction of which was in the quartz tube directly beside the boat.

In the first run, the solution of silver nitrate in both pairs of Wagner flasks was blackened and a small amount of germanium was found in the flasks connected to the combustion tube. The constricted tube was not heated during this first experiment. Since the silver nitrate was reduced not only by the hydrogen that passed over the germanium but also by that which came directly from the purifying chain, 2 spiral gas-washing bottles containing a 0.25 *M* solution of silver nitrate were inserted at the head of the chain and the metal was then heated in the current of hydrogen on 5 successive days. The introduction of silver nitrate into the purifying chain stopped the reduction of the silver nitrate by the hydrogen that entered it directly from the chain.

The run, each day, consisted in first passing the hydrogen over the germanium at 760–800° for from 2 to 4 hours (see Table I) and through the heated, constricted tube and the solution of silver nitrate beyond, then allowing the furnace to cool, weighing the germanium and the constricted tube and testing the silver nitrate for germanium. The germanium was then replaced in the quartz tube, the apparatus was connected, air was swept out by hydrogen, and the temperature of the furnace was raised to 960–1000° to melt the germanium in the boat. The furnace temperature was then lowered until the germanium solidified, and was then immediately raised again until the metal melted. The metal was in this manner alternately melted and solidified about 10 times each day with the object of repeatedly exposing fresh surfaces of it to the action of hydrogen and thus gradually reducing all oxide of germanium that might be present. During the first 3 days, the germanium lost weight, but the loss steadily became less. There was a correspondingly decreasing amount of germanium deposited in the heated, constricted tube, but no reduction of silver nitrate was observed after the first day. Four hours' heating on the fourth day gave no loss in weight of germanium and no evidence of germanium passing out of the combustion tube. For the fifth day's run, a new quartz tube was used so that the formation of a deposit in the tube beyond the boat, which would be due to the presence of germanous oxide, might clearly be observed. No such deposit was seen, the germanium did not lose weight, no deposit was formed in the constricted tube, and no reduction of the solution of silver nitrate resulted.

When, however, hydrogen was passed over *molten* germanium the metal invariably lost weight and germanium was found in the flask that contained the solution of silver nitrate.

Table I

Results Obtained when a Sample of Germanium Was Heated in Hydrogen

Day	Duration of heating each day 760–800° Hrs.	Total duration of heating 760–800° Hrs.	Loss in weight of germanium G.	Gain in weight of constricted tube G.	Germanium present in $AgNO_3$ solution
1	3	3	0.0090	Tube broke	Trace
2	2	5	.0066	0.0054	None
3	4	9	.0020	.0004	None
4	4	13	.0000	.0000	None
5	4	17	.0000	.0000	None

The above experiments seem to warrant the conclusion that metallic germanium which is free from oxide does not lose weight when heated in hydrogen to a temperature not exceeding 800°, but that volatilization of germanium does take place when hydrogen is passed over the molten metal.

The Physical Properties of Germanium

Melting Point.—Determinations of the melting point were made by melting the metal in a graphite crucible that rested in an electric-resistance furnace, measuring the temperature by means of a platinum-platinum-rhodium couple and a potentiometer indicator, and plotting the cooling curve. The metal was purified by several fusions under pure sodium chloride and then repeatedly melting and cooling it in a current of hydrogen. It was finely pulverized and 105 g. of it was packed in the graphite crucible around the quartz protection tube of the thermocouple, being firmly tamped down to exclude air as completely as possible. The crucible was next filled to the top with tightly packed sugar carbon, placed in the electric furnace and heated to about 980°. The current was then turned off, and temperature readings were made at 1-minute intervals as the metal cooled. A constant value of 958.5° was obtained over a period of 10 minutes. Repetition of the determination gave the same result. The germanium was then removed from the crucible, pulverized, melted in a current of hydrogen, again pulverized, and its melting point redetermined as above. The results were identical with the first value. An arc spectrogram of the metal was then made and the material was found to be free from impurities.

The Sprouting of Germanium.—When germanium is melted and is then quickly cooled, the "sprouting" of the metal, as noted both by Winkler and by Biltz,[6] is very pronounced. Winkler ascribes the phenomenon to the great increase in volume of the metal when it crystallizes from the molten condition.

In one of our early experiments, 1 g. of the powdered metal, when fused under borax, solidified to a small button about 4 mm. in diameter, from the top of which projected a cone-shaped protuberance with a needle-sharp point about 3mm. high. When a larger amount, about 30 g., was fused under sodium sulfate and more slowly cooled, there resulted a circular regulus about 40 mm. in diameter and 10 mm. thick, from the middle of the upper surface of which there had been extruded a mass about $^1/_4$ the size of the main button. The whole surface was beautifully crystalline.

When germanium was melted in a small porcelain boat in an atmosphere of nitrogen, it was found that the sprouting along the surface was very prominent. It was noticed that when the heating was stopped and the asbestos housing around the quartz tube was removed, the metallic germanium retained its redness after the quartz tube and the porcelain boat had resumed normal appearance. The metal then gradually darkened, but suddenly there appeared within the ingot one or two bright spots which rose to the surface and then, with the suddenness of the bursting of a bubble, became dark. This observation seems to support Winkler's explanation of the "sprouting" of germanium. The exterior of the molten metal cools and solidifies first, and when the molten interior solidifies, the resulting expansion of the metal causes it to burst through the surrounding shell. This usually occurs on the upper surface where the shell is thinnest. When the regulus is slowly cooled from the molten condition, the sprouting is much less pronounced and the surface of the metal then shows a beautiful, coarsely crystalline structure.

Since it was possible that the sprouting of germanium might be due to absorption of the gas in contact with which it was melted and the expulsion of this gas upon solidification, as is the case with silver when melted in an atmosphere of oxygen, the metal was melted in a porcelain crucible that rested in a special, closed steel crucible which was exhausted of air. The steel crucible was then cooled as quickly as possible, and although the sprouting was not so marked as when the chilling was more rapid, 3 large protuberances appeared on the sides of the button. Winkler's explanation of the sprouting of the metal, therefore, appears to be correct.

Specific Gravity.—Crystalline germanium that had carefully been purified for the determination of the melting point (see above) was melted in porcelain boats in hydrogen in such a manner as to yield small, compact globules of the metal about 2 mm. in diameter. Two pycnometers were used, one of 10cc. capacity and the other of 25 cc. After the germanium and water had been placed in the pycnometer, the instrument was placed in a desiccator under diminished pressure for several hours. The results of the two determinations were the same, d_{20}^{20}, 5.35. This value agrees very closely with that obtained by Dr. Albert W. Hull who used a sample of the same preparation of germanium. He wrote: "The density given by X-ray analysis is 5.36. This is correct within one-half of one per cent., and should agree with the density found by other methods for chemically pure germanium free from holes."

Hardness.—Metallic germanium is extremely brittle. However, attempts to determine the hardness of crystalline germanium were kindly made for us by Professor H. Diederichs. Both the Brinell test and the Shore Scleroscope hammer test were separately applied to blocks of polished germanium. In both cases the metal was so thoroughly shattered that even approximate estimation of the hardness could not be made.

A compact specimen of very pure germanium, weighing about 12 g., was then submitted to Professor A. C. Gill, who found that it scratched a well crystallized piece of adularia, but made no mark on epidote. This fixes its hardness number between 6 and 6.5 at, say, 6.25.

Crystal Form.—When a considerable amount of germanium is fused in a large porcelain crucible under a thick layer of salt and is slowly cooled it shows beautiful crystallization on the upper surface. Professor A. C. Gill examined the preparation shown in Fig. 1, and states that it is an aggregate of elongated crystals that are bounded in some cases by octahedral faces. Some of the crystals exceed 3 cm. in length, and occasionally are notched or covered with small dendritic branches. He adds that this particular form of surface crystallization seems to be peculiar to germanium, although it resembles to a certain degree that of antimony.

Electric Resistance and Thermoelectric Power.—For the determination of these two values it was necessary to prepare a small bar of germanium about 25 × 5 × 5 mm. This was first attempted by fusion of the metal in a small porcelain boat in an atmosphere of nitrogen. The cool ingot, however, adhered tenaciously to the porcelain, and the bar of germanium could not be removed without fracture because of the very great brittleness of the metal.

To obviate this difficulty, the boat was lined with a paste of germanium dioxide which was then thoroughly dried. The boat was filled with powdered crystalline germanium and was heated in nitrogen in a quartz tube as before. When the temperature of the melting point of germanium was reached, the tube filled with a thick, dark colored vapor. Heating was at once stopped, and examination of the contents of the tube after cooling showed that the germanium dioxide had turned black where it had been in contact with the metal, and that there had been considerable volatilization of this black substance which is most probably germanous oxide. This observation is directly in accord with the statement of Winkler that germanous oxide results when germanium and germanium dioxide are heated together under a layer of borax glass, and contradicts the assertion of

Biltz[6] that germanium dioxide is not reduced by germanium when a mixture of the two is heated to 1000° in a current of nitrogen.

Since the heat of formation of aluminum oxide is more than twice that of silicon dioxide, and this in turn is undoubtedly greater than that of germanium dioxide, it seemed obvious that germanium might be melted in contact with aluminum oxide without reacting upon it. Consequently a porcelain boat was filled with a paste made by grinding aluminum oxide with a little water, a small bar of wood of the size of the desired ingot was pressed down into this paste and the whole was dried. The piece of wood was then removed and the mould was filled with crystalline germanium. This was melted in nitrogen and a bright bar of the metal was obtained. So far as could be seen, there was no reaction whatever between the germanium and the aluminum oxide. The uneven, upper surface of the bar was smoothed with emery paper and was then used for the determination of the electric resistance and thermoelectric power of the metal.

These determinations were made by Professor C. C. Bidwell of the Department of Physics at Cornell University, and the results appeared in full in *The Physical Review*, **19,** 447 (1922). They are here shown graphically in Fig. 2. He found that in respect to its electric resistance and thermoelectric power, germanium conforms to its position in the Periodic Table.

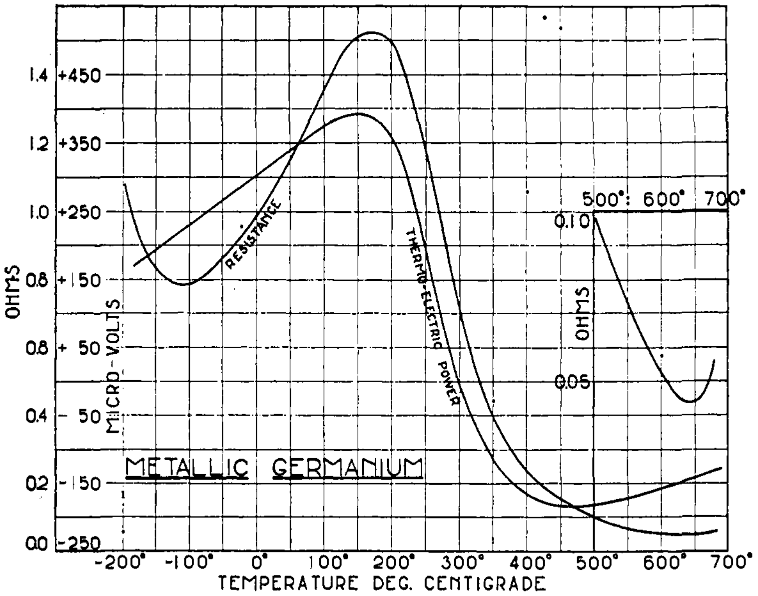

Fig. 2

The Molecular Inversion of Germanium.—Bidwell's results cited in the foregoing paragraph show that the thermoelectric power of germanium is a linear function of the temperature, and the resistance is an exponential function of the form, $\log R = \log A + aT + Q/kT$, except in the range 100° to 600°. Between these temperatures there appeared to be a slow, reversible transformation whose completion apparently depended only upon the temperature and not upon the time.

Mr. Hance studied this inversion using the differential method of Roberts-Austen.[8] This procedure consists in the measurement of the heat effect of the test specimen simultaneously with that of a neutral body.[9]

The general arrangement of the apparatus is shown in Fig. 3. The neutral body was made from a block of pure copper that was obtained from the United States Mint at Philadelphia. It was cylindrical in shape and of about 2cm. diameter. A hole 4 mm. in diameter was bored into it to half its depth.

Germanium is so brittle that it was impossible to drill holes into it. For this reason it was cast in a special mould in the form of a circular block with 2 holes extending halfway through the block. The weights of the blocks of copper and germanium were made such that the two would have very nearly the same heat capacity. Each block was inserted in a thin-walled graphite shell which in turn was surrounded by a cylinder of asbestos board. The two were then placed side by side in an alundum electric furnace core of 7.5 cm. bore. In the grooves of this was laid Nichrome wire which was then covered with refractory cement.

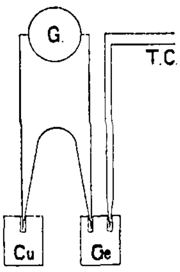

Fig. 3

After the wires from the galvanometer G and the thermocouple T.C. were inserted into the openings in the blocks as shown in Fig. 3, the openings and the space around the blocks were tightly packed with asbestos wool. Each block was then covered with a layer of sugar carbon, and the alundum core was next tightly packed to its top with asbestos wool. The cup, thus charged, was placed in a circular box of asbestos board 25cm. wide and 22cm. high, which was then packed with the wool.

After connections with the galvanometer and thermocouple had been made, the heating current was thrown on. The temperature was raised very gradually until 850° was reached, which took about 90 minutes. Readings of the galvanometer deflections and of the temperature of the germanium were made throughout this period at 1-minute intervals. The results are shown in Fig. 4. Inversion began at 117° and reached a maximum at 560°. The experiment was repeated and data concordant with those of the first run were obtained.

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[8] We are greatly indebted to Professor Bidwell for many valuable suggestions during the progress of these determinations.

[9] Hoyt, "Principles of Metallography," McGraw-Hill Book Company, **1920,** Part I, pp. 151–156.

It thus appears that germanium passes through a gradual molecular inversion with two or more modifications between the temperatures of 117° and 560°.

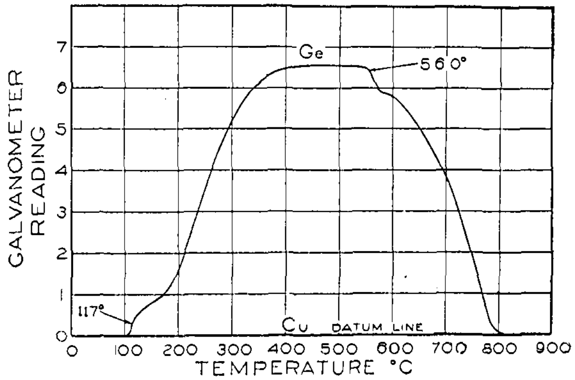

Fig. 4

Chemical Properties of Germanium

I. Behavior toward Various Gases

Oxygen.—Finely divided amorphous germanium, prepared by the reduction of germanium dioxide in hydrogen, was heated in a porcelain boat in a quartz tube in a current of purified oxygen. The metal was not attacked at 600° even when the temperature was held at this point for 30 minutes. Oxidation began at 605° and proceeded very rapidly at 615°, but was not complete even when the temperature was raised to 900°. The gain in weight at 750° was about 50% of that calculated, and about 90% at 900°. When heated to this latter temperature, the material in the boat was found to be fused to the porcelain and was light gray in color.

These experiments were then repeated with purer germanium that had been fused under sodium sulfate and then finely pulverized. The temperature of the furnace was slowly raised, but no oxidation was observable until the temperature rose to 714°. At this point the powdered metal glowed brightly and white germanium dioxide formed along the edges of the charge and in spots on the top of it. The heating was continued for 30 minutes at 730° and the material was then allowed to cool in oxygen. The product showed a glazed surface and was black in color, with a fine white powder, germanium dioxide, around the edges and distributed irregularly over the top of the mass. The gain in weight of the charge was found to be only 50.8% of that calculated, and the residue in the boat evidently contained germanous and germanic oxides, and metallic germanium. The boat and its contents were then again heated in oxygen, the temperature being gradually raised above 730°. At 900° a white sublimate began to condense in the cool end of the quartz tube. Since germanium dioxide is not volatile at this temperature, it is evident that the sublimate must be due to the volatilization of germanous oxide which is then further oxidized to the dioxide.

It appears, therefore, to be impossible under the conditions here described, to oxidize germanium quantitatively to the dioxide at a temperature of 730° or lower. At higher temperatures, there is loss of material from the boat through volatilization of germanous oxide.

Hydrogen Sulfide.—Winkler states that when vapor of sulfur is led over germanium that is heated to "incipient redness" (presumably about 600°), the two elements combine to form germanous sulfide, GeS.

Hydrogen sulfide begins to dissociate between 400°[10] and 440°.[11] To ascertain whether germanium is acted upon by hydrogen sulfide below this dissociation temperature, some of the finely powdered metal was heated in a current of dry hydrogen sulfide at slowly rising temperatures.

No action was apparent up to 290°. At that temperature a slight, yellowish-white deposit appeared in the cool portion of the tube. At 350° this deposit had become heavy. When the temperature dissociation of hydrogen sulfide was reached, the interior of the boat was coated with a yellow deposit and white fumes issued from the tube. At the end of the experiment, 692°, the interior of the tube was so heavily coated with the yellow deposit that the boat was invisible. Minute black crystals were mixed with this yellow coating.

The residue in the boat presented a glazed surface and was of a deep purple color, which persisted when the material was powdered. There was copious evolution of hydrogen sulfide when the material was treated with concd. hydrochloric acid.

The results of the experiment indicate that germanium is not attacked by hydrogen sulfide at temperatures below 200°, and that the action of the gas upon the metal is comparatively slight until dissociation of the hydrogen sulfide begins, when the reaction becomes that between sulfur and germanium with the formation of germanous sulfide as noted by Winkler.

Sulfur Dioxide.—Finely pulverized germanium was heated in a current of sulfur dioxide which had been dried and freed from sulfur trioxide by passing it through concd. sulfuric acid. The temperature was gradually raised to 672°.

When cool, the boat was withdrawn and examined. Its contents were yellowish-gray in appearance, and the end of the boat which was farthest from the sulfur dioxide inlet was covered with a heavy coating of a fine white powder. The cool end of the quartz tube was also coated with a heavy white deposit. When heated with hydrochloric acid, both the white powder and the yellowish-gray material in the boat gave off hydrogen sulfide.

[10] Myers, *Ann.*, **159**, 124 (1871).

[11] Pelabon, *Compt. rend.*, **124**, 35, 686 (1897).

The results show that sulfur dioxide acts upon crystalline germanium at a temperature somewhat below 500°, that this action is rapid between 510° and 530°, and that the disulfide and the dioxide of germanium are formed in the reaction.

II. Behavior in Various Liquid Reagents

Small weighed pieces of fused germanium were immersed in the reagents listed below. They were allowed to stand at room temperature for 1 week, and were then removed, washed with distilled water, dried at 110° and weighed.

Weighed samples were then placed in the same reagents which were maintained at a temperature of 90° for 8 hours. The samples were again washed, dried and weighed.

At room temperature and at 90°, water, a 50% solution of sodium hydroxide, 1:1 hydrochloric acid, concd. hydrochloric acid or 1:1 sulfuric acid did not act upon the metal, which remained bright and lost no weight. The germanium was slightly tarnished by a 10% solution of sodium hydroxide, both cold and warm, and lost about 0.5% in weight. Dilute nitric acid, 1:1, acted upon the metal superficially with the formation of white germanium dioxide, and the loss in weight amounted to about 7% at room temperature and 1.6% at 90°. Concd. nitric acid darkened the surface of the metal, but there was no appreciable loss in weight. The metal was not attacked by concd. sulfuric acid at room temperature, but lost 1% in weight at 90°. Hydrofluoric acid, 19 *N*, caused a loss in weight of only 0.1% at room temperature, and about 0.8% at 90°. Immersion in a 3% solution of hydrogen peroxide at room temperature for 1 week resulted in a loss of weight of about 40%, and at 90° for 8 hours the loss in weight was about 70%.

When finely powdered germanium is digested in a 3% solution of hydrogen peroxide at about 100°, it finally dissolves entirely and the product, germanium dioxide, dissolves in the water present. This solubility of germanium in hydrogen peroxide, which was first observed by us early in 1921, appears to offer an excellent method for determining the atomic weight of germanium by means of the ratio $Ge:GeO_2$. This will be studied in the near future in this Laboratory.

III. Behavior of Germanium when Fused with Various Solid Reagents

Potassium Hydroxide.—Ten g. of potassium hydroxide was melted in a nickel crucible and was heated until water had been expelled. A small piece of fused germanium weighing 0.0992 g. was then dropped into the molten mass. It began to dissolve immediately with the copious evolution of tiny bubbles. The mass was kept molten and in 10 minutes the reaction ceased and the metal had entirely disappeared. When dissolved in water, the material gave a clear, colorless solution.

Sodium Hydroxide.—The reaction was similar to that with potassium hydroxide.

Potassium Hydrogen Sulfate.—A small particle of germanium weighing 0.1534 g. was dropped into a platinum crucible containing 10 g. of molten potassium hydrogen sulfate and allowed to remain there for 10 minutes. No visible reaction occurred. The sample, however, lost 6% in weight, showing that the metal is slowly attacked by this reagent.

Sodium Carbonate.—Fragments of crystalline germanium were dropped into molten sodium carbonate. The metal was rapidly attacked, with the evolution of gas and with the projection of bright sparks from the surface of the reagent. The metal was eventually dissolved.

Potassium Cyanide.—Molten potassium cyanide was without action.

Potassium Chlorate.—Molten potassium chlorate very slowly attacked germanium, and at the end of 30 minutes a small amount of metal had passed into the solution.

Potassium Nitrate.—When small pieces of germanium were dropped into the molten potassium nitrate, there was immediate reduction of the nitrate and evolution of gas. The germanium was oxidized and was found to be present in the water solution of the residue.

Sodium Peroxide.—The reagent was carefully melted and a small amount of germanium was dropped into it. Vigorous reaction at once took place and continued until the germanium had entirely passed into solution.

Germanium Carbide

Preliminary experiments upon the formation of a carbide of germanium analogous to silicon carbide, SiC, led to negative results. When a mixture of finely powdered germanium and sugar carbon was heated in a small electric furnace, part of the germanium vaporized and burned in the air, and part of it condensed on the upper portion of the crucible as brown germanous oxide. The germanium that remained in the crucible was found to have fused into globules, but there was no evidence of combination of the metal with carbon. The experiments will be continued.

Summary

This article deals with the dehydration of germanium dioxide, the reduction of germanium dioxide by aluminum and by hydrogen, the preparation of fused germanium, the behavior of germanium when heated in hydrogen, the melting point, specific gravity, hardness, crystal form, electric resistance, thermoelectric power, molecular inversion and sprouting of germanium, and the behavior of the metal toward various gases, liquid reagents and molten solid reagents.

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