

substances would lead us to believe that the manner of swelling was similar in all cases. Different conditions and materials give the same general type of curve, but with maximum and minimum values coming at somewhat different concentrations. In all cases the swelling seems to increase with addition of acid or alkali up to a certain point, when it decreases again. The authors believe that a further study of anomalous osmose and its relation to the swelling of colloid materials should find important applications in various problems of biology; also in such every day problems as tanning, the preservation of fruits, meats, etc.; in fact in all problems in which the direction of flow of solutions through membranes cannot be predicted from a knowledge of the isotonic values of the solutions concerned.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY.]

GERMANIUM. III. GERMANIUM TETRABROMIDE AND GERMANIUM TETRACHLORIDE.¹

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Germanium Tetrabromide.

Winkler² prepared what he assumed to be germanium tetrabromide by heating germanium in vapor of bromine, and also by heating a mixture of pulverized germanium and mercuric bromide. He stated the product to be a mobile, fuming liquid which solidified at 0° or slightly below that temperature to a white crystalline mass. He did not analyze or make a detailed study of the compound because of lack of material.

The present investigation describes the preparation and further study of this substance.

Material.—Germanium was prepared in finely divided form by reducing³ germanium dioxide in a current of hydrogen at temperatures between 550° and 600°. Toward the end of the reduction the temperature was raised to 900°.

Bromine was purified by first digesting it with calcium bromide and zinc oxide,⁴ then distilling the bromine, converting the middle fraction to hydrobromic acid by treating it with sulfur dioxide in the presence of water, distilling the hydrobromic acid, and liberating the bromine from this by means of pure manganese dioxide. This bromine was redistilled, was next dried over phosphorus pentoxide, and was then again distilled. The middle fraction was used.

Preparation of Germanium Tetrabromide.—Powdered germanium was placed in alundum boats which were inserted in a tube of Jena glass lying in an electric combustion furnace. A thermometer was laid in the combustion tube beside the boats.

¹ The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

² Winkler, *J. prakt. Chem.*, **144** (N. S. **36**), 193(1887).

³ Further details concerning this reaction will be given in a later article.

⁴ Richards and Merigold, *Proc. Am. Acad. Arts Sci.*, **37**, 387 (1901-2).

To the front end of this tube was attached an inverted T-tube. The upright arm of the T-tube was sealed to a separatory funnel containing bromine. The further end of the T-tube was joined to a chain of apparatus supplying purified nitrogen. The exit end of the combustion tube was brought well within a long adapter which in turn was fused to the inlet tube of the first of 2 small, all-glass distilling bulbs.⁵ The side arm of the second bulb was connected with a U-tube containing calcium bromide, and this to a water suction-pump and manometer.

In beginning the procedure, nitrogen was started flowing slowly through the apparatus. Slightly diminished pressure was maintained throughout the run by suitable adjustment of the suction pump. When the whole apparatus was filled with nitrogen, bromine was slowly admitted into the T-tube. A small alcohol lamp placed beneath this tube hastened the volatilization of the bromine. A freezing mixture of ice and salt was brought up around the bulb that served as the first receiver.

Reaction between the bromine and germanium began at once in the unheated tube (26°), small, colorless globules of oily liquid appearing on the inner surface of the tube. Combination of the two elements apparently ceased after a short time, and vapor of bromine passed over into the receiver. The temperature of the tube was then slowly raised. At 180° slow union again was discernible. At 220° germanium bromide was rapidly produced, and it was found that bromine could now be admitted at the rate of 20 drops per minute without any appreciable amount of it escaping combination with the germanium. The temperature was maintained at 220° until the interaction apparently had ceased and free bromine appeared in the receiver. During the experiment, an oily liquid had steadily passed over, and had collected entirely in the first of the receiving bulbs. The admission of bromine was now stopped and the apparatus was allowed to cool in the current of nitrogen. During this interval the distillate in the cooled receiver solidified to a yellowish-white solid.

There remained in the alundum boats a grayish-white residue which proved to be chiefly germanium dioxide. The reasons for its occurrence here will be discussed in a later article.

The flask containing the distillate was disconnected from the chain, a U-tube filled with calcium bromide was attached to the side-arm, and the neck of the flask was tightly stoppered. The contents was warmed until it melted, and about 2 cc. of mercury was then introduced. Agitation of the flask soon removed the free bromine, and the supernatant liquid became clear and colorless. Later analysis showed that the product is germanium tetrabromide. Before making the analysis to establish its identity, the liquid was purified by fractional distillation and its boiling point was determined.

The germanium tetrabromide was siphoned from the mercury into a dry distilling flask, the substance being carefully protected from moisture during the transfer. It was then twice distilled, but a sample of the second distillate showed on spectroscopic examination the presence of a slight amount of mercury. For this reason a second preparation of the germanium tetrabromide was made, and from this the free bromine was removed by repeated fractional distillation instead of by the use of mercury. A large middle fraction that passed over at about 183° was then used for the determination of the boiling point and 71 readings, taken at 1-minute intervals, gave a constant boiling point of 183.0°, the total weight of the germanium tetrabromide that distilled over at this temperature being 97.47 g. The corrected boiling point was then calculated according to the formulas given by Young.⁶ There is no formula that is generally applicable to the accurate correction of the observed boiling point to that under standard

⁵ See Dennis and Bridgman, *THIS JOURNAL*, **40**, 1543, Fig. 5 (1918).

⁶ Young, "Fractional Distillation," MacMillan and Co., **1903**, pp. 12, 14.

pressure. Young states that quite precise results are, however, obtained by the use of the formula $\Theta = K(760 - P) / (273 + t)$. Provided the value of the constant K is determined experimentally, Θ is the correction in centigrade degrees to be added to the observed boiling point t , and P is the barometric pressure corrected to 0° . Young gives the value of K for several substances among which are silicon tetrachloride and tin tetrachloride. He further states that the value of the constant is not altered by replacing one halogen by another. Inasmuch as germanium lies between silicon and tin in the fourth group of the periodic table, the value of K for germanium tetrachloride and germanium tetrabromide may be assumed to lie midway between the value for silicon tetrachloride, 0.000126, and that for tin tetrachloride, 0.000121. The boiling point of germanium tetrabromide thus corrected is 185.9° .

Analysis.—Portions of about 2 g. each of the substance were introduced into small glass capsules of known weight and the capsules were then sealed and weighed again. A capsule was broken under absolute alcohol and the solution was diluted to 250 cc. with absolute alcohol. Two portions of this solution were used for the analyses. The bromine was determined by precipitation as silver bromide. The filtrate was freed from silver by the addition of hydrobromic acid in very slight excess. The silver bromide was filtered off, conc. hydrochloric acid was added to the filtrate until the acidity was 6 *N* and the germanium was then precipitated by hydrogen sulfide. The germanium sulfide was washed with alcohol, was then oxidized with nitric acid, was ignited at red heat to constant weight, and was weighed as germanium dioxide.

In calculating the results of the analyses, 72.5 was used as the atomic weight of germanium.

Wt. of GeBr ₄		Wt. of Ge		Wt. of Br	
G.	Calc. G.	Found G.	Calc. G.	Found G.	
0.2158	0.0398	0.0403	0.1759	0.1753	
0.2158	0.0398	0.0399	0.1759	0.1756	

The results of the analyses, while not in very close accord with those calculated, suffice to establish the identity of the substance as germanium tetrabromide.

Melting Point.—About 90 g. of germanium tetrabromide of constant boiling point was brought into a large test-tube and its melting point was determined with the aid of an Anschütz thermometer that had been calibrated by the Bureau of Standards. The observed melting point was 26° . The corrected melting point was 26.1° .

Crystal Form.—A crystallographic examination of the substance was kindly made for us by Professor A. C. Gill of the Department of Mineralogy. Inasmuch as the substance could not be exposed to the air during observation under the microscope, a sample of about 1 cc. was sealed in a thin-walled glass tube and was cooled therein until it crystallized. The crystals were found to be brilliant, white, flattened octahedrons which

under polarized light proved to be isotropic, indicating that they belong to the regular system.

Index of Refraction.—An approximate determination of the index of refraction was first made using a microscope, Abbe condenser, and graduated screen. The germanium tetrabromide was placed in a small brass cell that was mounted on a cover glass. The cell was first calibrated with water, oil of cedar, and oil of cassia. The approximate value for the refractive index thus obtained was 1.61.

More accurate determinations of the index of refraction were then made with an Abbe refractometer. The super-cooling exhibited by germanium tetrabromide made it possible to obtain a series of readings at temperatures below the melting point of the substance.

Temperature ° C.	Index of Refraction
20.75	1.6296
21.10	1.6292
22.20	1.6283
24.00	1.6274
24.50	1.6272
25.50	1.6268

Index of Refraction of Germanium Tetrabromide at 25° = 1.6269.

Specific Gravity.—A pycnometer of 10cc. capacity was dried over phosphorus pentoxide and was then quickly filled with germanium tetrabromide. The measurements were made at 29° to keep the substance in a liquid state. At this temperature, $d_{29}^{29} = 3.1315$.

Electrical Conductivity.—An alternating current, 1000 cycles per second, was used. Resistance was measured by a Wheatstone bridge with telephone attachment. A conductivity cell of 18cc. capacity and 90 mm. between platinum electrodes, was filled with germanium tetrabromide and was at once sealed to prevent contact with the moisture of the air. The cell was placed in a bath that was maintained at a constant temperature of 30°. A resistance totaling 300,000 ohms was found to be insufficient to balance the resistance of the cell. This shows that the specific conductivity of germanium tetrabromide is less than 0.000078 mho.

Chemical Properties.—In the liquid form germanium tetrabromide is a colorless, mobile liquid which fumes when brought into contact with the air. It shows to a marked degree the property of super-cooling, and it was found that the liquid when not agitated could be chilled to a temperature of -18° before it solidified. The substance crystallizes in minute, white octahedrons. This crystalline mass gradually changes on standing into a clear, hard, transparent, glass-like material with fractures running through it like the fissures in a lump of cracked glass.

When a few drops of water were added to about 1 cc. of liquid germanium tetrabromide, hydrolysis at once took place with the evolution of heat. A layer of hydrated germanium dioxide formed at the surface, and if the tube was not agitated, two liquid layers appeared below this solid crust. The lower layer consisted of unchanged germanium tetrabromide and the upper layer of a suspension of germanium hydroxide.

When a drop of germanium tetrabromide was allowed to fall into water, a small, white ring of hydrated germanium dioxide was formed and further deposit of the white hydroxide around the circumference of this ring rapidly built up.

In one experiment 25 g. of germanium tetrabromide was poured into 50 cc. of water. The tetrabromide sank to the bottom of the tube, and at the surface of contact between the two liquid layers there was rapidly formed a heavy film of germanium hydroxide. Above this film there gradually appeared a fine suspension of this substance. The layer of germanium hydroxide protected the tetrabromide below it from further hydrolysis for more than 24 hours, the hydroxide forming a tough impervious stratum. The water above this layer of germanium hydroxide gradually cleared and this clear solution gave a decided acid reaction to litmus. When germanium tetrabromide is dropped into water, there is noted a slight but distinct crackling sound. It is scarcely audible and it would probably have escaped attention were it not for the fact that a similar phenomenon had already been noticed when germanium tetrachloride and water are brought together.

When a few drops of germanium tetrabromide were allowed to fall into 2 cc. of conc. sulfuric acid, the substance sank to the bottom of the tube and no reaction nor visible change took place during the several days that the tube was allowed to stand at room temperature. This behavior is similar to that of the tetrachlorides of tin and lead, elements which lie below germanium in Group 4 of the Periodic Table.⁷

When germanium tetrabromide was introduced into an aqueous solution of potassium hydroxide (1:4), reaction took place at once with the evolution of heat. Germanium hydroxide first separated and then quickly dissolved in the alkali. When carbon dioxide was passed through this solution of potassium germanate, a heavy white precipitate resulted.

When germanium tetrabromide was dropped into conc. nitric acid, it fell to the bottom of the tube and gradually became deep orange in color. The nitric acid above the tetrabromide became yellow and turbid and was rapidly reduced. The layer of germanium tetrabromide soon became dark brown in color and a disk of white germanium oxide formed between the two liquid layers. After about 15 minutes the color of the tetrabromide changed to black and the reaction between it and the nitric acid went on

⁷ Friedrich, *Ber.*, **26**, 1434 (1893).

slowly with copious evolution of nitric oxide. After the reaction had ceased, water was added to the contents of the tube whereupon there formed a precipitate that appeared to consist of white powder, a yellowish substance, and the black amorphous precipitate previously mentioned. The supernatant liquid was clear and of a pale yellow color. After standing for 24 hours, the precipitate in the bottom of the tube became entirely white.

With dry ammonia, germanium tetrabromide formed a white solid compound which is probably analogous to the corresponding compounds of ammonia with the tetrabromides of silicon and tin. This substance is now being subjected to further study.

Germanium tetrabromide was found to be soluble in absolute alcohol, carbon tetrachloride, benzene, and ether without decomposition. It dissolves in acetone but slow decomposition takes place with the liberation of bromine.

Germanium Tetrachloride.

Germanium tetrachloride was first prepared⁸ by Clemens Winkler in 1886. He found its specific gravity to be 1.887 at 18°, its boiling point 86°, and he adds that it did not solidify at -20°. In our investigations upon the compounds of germanium with the halogens, it seemed desirable to redetermine the above constants of germanium tetrachloride and to study somewhat further the properties of the compound.

Preparation.—In the preparation of germanium tetrabromide by the action of bromine upon germanium that had been prepared by the reduction of germanium dioxide in hydrogen, the very considerable residue of germanium dioxide that remained after action between the metal and bromine had ceased, showed that reduction of germanium dioxide by hydrogen is difficult to carry to completion when fairly large quantities of the oxide are employed. In the preparation of germanium tetrachloride, a large yield was obtained by employing crystalline, fused germanium⁹ that had been pulverized and thoroughly freed from any adhering flux.

This metallic germanium was heated in a current of chlorine in an apparatus quite similar to that used for the preparation of germanium tetrabromide, except that the lower boiling point of the tetrachloride rendered necessary a modification of the condensing tube. This was given the shape of a U-tube, to the bend of which there was fused a short tube that terminated in a bulb of about 60cc. capacity. The condensed germanium tetrachloride flowed down into this bulb and evaporation of the liquid by the nitrogen and chlorine flowing through the apparatus during the run was thus greatly lessened.

⁸ Winkler, *J. prakt. Chem.*, **142** (N. S. **34**), 177 (1886).

⁹ The manner of its preparation will be described in a later article.

About 30 g. of pulverized germanium was placed in boats in the combustion tube. Purified nitrogen was then passed through the apparatus. A freezing mixture of ice and salt was packed around the U-tube condenser, the current of nitrogen was turned off, and dry chlorine that had been freed from vapor of sulfuric acid by passage through glass wool was then passed through the apparatus. The temperature of the electric combustion furnace was gradually raised. Reaction between the germanium and chlorine began at about 80°, and at 180° there was rapid combination of the two elements, although the heat of formation of the chloride did not bring the metal to incandescence. When the temperature was raised to 360°, near the end of the experiment, the metal glowed brilliantly when the chlorine was rapidly passed through the tube.

The germanium tetrachloride was completely condensed in the U-tube. The yield was about 45 cc. A very slight reddish-brown residue remained in the porcelain boats. The passage of chlorine was now discontinued, and nitrogen was run through the apparatus while it cooled.

It was found impracticable to free the germanium tetrachloride from chlorine by fractional distillation. Five fractionations gave a final product that still contained some free chlorine. The chlorine was removed by placing the tetrachloride in a distilling flask that had a long neck that was constricted at its lower end and was provided with a side-arm close to its upper end. A cork in the neck carried a glass tube that reached downward into the liquid. The space between this tube and the wall of the neck of the flask was tightly packed with glass wool. The neck of the flask was cooled by a refrigerant on the outside to prevent volatilization of germanium tetrachloride. The side-arm of the flask was joined to a condenser, and this connected to a U-tube that was packed in a freezing mixture. Upon passing dry air through the liquid at room temperature for 7 hours, it was found that the germanium tetrachloride had been freed from chlorine and that only a very small amount of the tetrachloride had been carried over through the condenser.

The residual germanium tetrachloride was then fractionally distilled from the flask. The bulk of the product passed over between 85.2° and 85.8°, and a large middle fraction was obtained that showed a constant boiling point of 85.6°. This fraction was redistilled and all but a trace of residue passed over at 85.6°. The corrected¹⁰ boiling point of germanium tetrachloride is 86.5°.

Analysis.—Known amounts of the substance were sealed off in glass capsules. A capsule was broken under absolute alcohol, the solution was diluted with alcohol to 100 cc., and separate portions of this solution were used for the determination of chlorine by precipitation with silver nitrate, and for that of germanium with hydrogen sulfide.

Wt. of GeCl ₄	Wt. of Ge		Wt. of Cl	
	Calc.	Found	Calc.	Found
G.	G.	G.	G.	G.
0.04289	0.0145	0.0144
0.04289	0.0145	0.0145
0.1972	0.1304	0.1301
0.1970	0.1303	0.1303

The analysis identifies the substance as germanium tetrachloride.

Melting Point.—A preliminary determination with a pentane thermometer gave -49° as the melting point of the compound. The constant

¹⁰ See p. 300.

was then accurately determined under the direction and with the assistance of Professor C. C. Bidwell of the Department of Physics, and we take pleasure in expressing here our appreciation of his kindly coöperation.

The determinations were made with a gold resistance thermometer, the resistance being measured by the fall of potential method. The instrument was calibrated against the boiling points of sulfur and water, the ice point, and the freezing point of mercury.

A test-tube was filled with pure germanium tetrachloride to a depth of 8 cm. which sufficed to completely immerse the thermometer. A larger test-tube was brought up around the smaller one to protect the latter from direct contact with the refrigerating agent, liquid air, and to avoid too rapid rise of temperature of the frozen samples after the liquid air was removed.

The melting point of germanium tetrachloride was found to be $-49.5^{\circ} \pm 0.2^{\circ}$.

Index of Refraction.—The measurement was made with an Abbe refractometer, and the index of refraction at 27° was found to be 1.3606.

Specific Gravity.—A pycnometer of 25cc. capacity was thoroughly dried and was filled with germanium tetrachloride in a dry atmosphere; $d_{25}^{25} = 1.874$.

Chemical Properties.—Germanium tetrachloride is a colorless, mobile liquid that fumes strongly when brought into contact with the air. Our observations of the behavior of germanium tetrachloride when brought into contact with water, are substantially identical with those of Winkler.⁸ Of peculiar interest is the crackling sound that is emitted when the two substances interact. If the container is not shaken, this snapping persists for hours, and can be heard at a distance of 2 meters.

When germanium tetrachloride is dropped into conc. sulfuric acid of room temperature, it sinks to the bottom of the tube and is not attacked by the acid even on long standing.¹¹

Germanium tetrachloride reacts violently with a 1:4 solution of potassium hydroxide, the heat of reaction causing the distillation of some of the tetrachloride before interaction is complete. The germanium dioxide that forms and dissolves in the excess of the reagent is precipitable by carbon dioxide.

When germanium tetrachloride is dropped into conc. nitric acid, it sinks to the bottom and slow reduction of the acid takes place at the surface of contact between the two liquids. The tetrachloride becomes yellow in color but remains clear. Vigorous agitation somewhat hastens the reaction, but does not cause immediate decomposition of the tetrachloride. When the container is not shaken, a considerable portion of the tetrachloride still remains unattacked after 48 hours. Upon dilution

¹¹ See also H. Friedrich, *Monatsh.*, **14**, 505 (1893).

of the acid with half its volume of water, however, a slow but steady decomposition of the tetrachloride ensues.

When ammonia is passed into germanium tetrachloride, much heat is evolved and a white precipitate is formed. This substance is now being subjected to further study.

Germanium tetrachloride is soluble in absolute alcohol, carbon disulfide, carbon tetrachloride, benzene, chloroform, and ether. It dissolves in acetone with the formation of a light orange colored liquid.

Summary.

This article deals with the preparation and purification of germanium tetrabromide and germanium tetrachloride, the analyses determination of the boiling points, melting points, indexes of refraction, specific gravities, and some of the chemical properties of the two compounds, and the crystal form and electrical conductivity of germanium tetrabromide.

ITHACA, NEW YORK.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW HAMPSHIRE COLLEGE.]

THE ATOMIC WEIGHT OF YTTRIUM.

BY H. C. FOGG AND C. JAMES.

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This work was undertaken because the atomic weight of yttrium, the commonest member of the yttrium earths, varies considerably according to the results published by different workers. Among the publications concerning this work only those which appear to the writers to be of major importance are discussed below.

Clève¹ carefully purified yttria, first by means of the basic nitrate method, and finally by fractionally precipitating the oxalate from very acid solutions of the nitrate in order to remove the last traces of terbium. He found, as a result of 12 determinations by the synthesis of the sulfate, the value 89.12.

Jones² used yttrium oxide, very carefully purified by the sodium sulfate method to remove members of the cerium group and then by the ferrocyanide method to throw out erbium, etc. His ratio of yttrium oxide to sulfate gave an atomic weight of 88.96 as a mean of 10 determinations. A second series in which the sulfate was converted to oxide, yielded the value 88.98 as the average of 10 analyses.

Feit and Przibylla³ by means of a volumetric method obtained 89.346 as a mean of 6 runs.

Meyer and Wuorinen⁴ roughly separated the yttrium and cerium earths

¹ Clève, *Compt. rend.*, **95**, 1225 (1882).

² Jones, *Am. Chem. J.*, **14**, 154 (1895).

³ Feit and Przibylla, *Z. anorg. Chem.*, **50**, 262 (1906).

⁴ Meyer and Wuorinen, *ibid.*, **80**, 7 (1913).