

rapid to endanger the accuracy of analytical work with sodium trinitride as absorbent.

### Summary

1. The total absorbing power of a 1% solution of sodium trinitride for carbon disulfide vapor has been determined. This dilute solution absorbs irreversibly about 3.5 times its volume of the vapor, with quantitative formation of sodium azido-dithiocarbonate,  $\text{NaSCSN}_3$ .

2. Various mixtures of carbon disulfide vapor with air, or with oxygen, nitrogen, hydrogen, methane, and carbon monoxide have been analyzed, using 5% or saturated aqueous solutions of sodium trinitride as absorbent.

3. The solution of azido salt resulting from the interaction of absorbent and vapor has been found to possess no dangerously explosive qualities, but to decompose very slowly after long standing, with formation of nitrogen, sulfur and sodium thiocyanate.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

## GERMANIUM. IV. GERMANIUM TETRA-IODIDE<sup>1</sup>

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Winkler<sup>2</sup> prepared germanium tetra-iodide by heating pulverulent germanium in vapor of iodine that was carried over the metal by a slow current of carbon dioxide. He found it necessary to sublime the product repeatedly in carbon dioxide to remove free iodine. He describes the substance as highly hygroscopic, of orange color, yellow when powdered, possessing a melting point of 144°, and appearing to boil between 350° and 400°. He gives the results of an analysis of the compound, and adds that L. F. Nilson found that germanium tetra-iodide did not dissociate up to 440°, but showed considerable dissociation at 658°.

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

**Preparation.**—Powdered, crystalline germanium was placed in alundum boats which were then inserted in a tube of Jena glass lying in an electric combustion furnace. A thermometer was laid in the combustion tube beside the boats. The portion of the tube projecting beyond the furnace was drawn down to small diameter at 7 points 10 cm. apart. Each constriction was packed with glass wool. Into the other end of the combustion tube was inserted the neck of a 500cc. glass retort containing purified iodine. The tubulus of the retort was joined to an apparatus that supplied pure, dry carbon dioxide. An asbestos box was built around the retort, and this was heated from the outside to a temperature sufficiently high to keep the retort filled with vapor of iodine.

<sup>1</sup> 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.

<sup>2</sup> Winkler, *J. prakt. Chem.*, **142** [N. S. 34], 177 (1886).

The introduction of iodine into the combustion tube was regulated by the rate at which carbon dioxide was passed through the retort.

All air in the apparatus was first displaced by carbon dioxide, and then the retort and tube were gradually heated. Union of germanium and iodine began at 212°. When the temperature had risen to 250°, there appeared in the hot tube just before it emerged from the furnace a deposit of yellow and red crystals. At 360° very rapid combination of germanium and iodine took place, and the sublimate steadily increased until there had collected a considerable deposit of yellow crystals just beyond the boat, and beyond these a mass of orange-colored crystals on the upper side of the tube and a ruby-red liquid along the bottom of the tube.

The operation was continued for 30 hours, and at intervals during the run the product that had formed was caused to sublime through the constrictions beyond the furnace by gently heating the tube with a Bunsen flame. It was noted, however, that as the substance was driven through the successive constrictions, its color gradually changed from bright red (Mulliken's Color Standard<sup>3</sup> R, Shade 2) to a chocolate-brown (R. O. Shade 2). Inasmuch as this change of color indicated that the germanium tetra-iodide underwent decomposition when sublimed, the experiment was repeated with a tube that was not constricted, and the red liquid which collected just within and beyond the heated part of the combustion tube was allowed to cool in the tube at the end of the run, which was of 70 hours' duration. It solidified to a mass weighing about 50 g.

During this run there appeared on the walls of the tube, between the last boat and the red tetra-iodide, a deposit of light yellow crystals that were found to be germanous iodide, GeI<sub>2</sub>. The crystals were of the hexagonal system with external angles of 120°. The compound will be fully described in a later article.

**Analysis.**—Portions of the red product were weighed in porcelain crucibles and were moistened with water. Conc. nitric acid was added, and the contents of each crucible was evaporated to dryness on a steam cup. A few drops of conc. sulfuric acid were added, the acid was carefully fumed off, and the crucible was then heated to about 900°. The residual germanium dioxide was then weighed.

For the determination of iodine, samples were dissolved in water, 0.1 *N* solution of silver nitrate was slowly added and the liquid was vigorously shaken until the yellow precipitate collected and the supernatant liquid became clear. About 3 cc. of conc. nitric acid and a few cc. of a solution of ammonium ferric alum were then added, and the excess of silver was titrated with potassium thiocyanate solution.

Wt. of GeI <sub>4</sub> G.	Wt. of Ge		Wt. of I	
	Calc. G.	Found G.	Calc. G.	Found G.
0.1975	0.02468	0.0243	....	....
1.0856	0.13565	0.1357	....	....
0.1790	0.02237	0.0225	....	....
0.1329	0.0166	0.0165	....	....
0.2015	.....	....	0.1763	0.1761
0.2067	.....	....	0.1809	0.1807

**Melting Point.**—The measurements were made with a "Tycos" Precision Thermometer, nitrogen filled, range 100° to 155°. The apparatus was that described by Dennis,<sup>4</sup> which was filled with conc. sulfuric acid. The sample was placed in a small melting-point tube that was

<sup>3</sup> Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, 1903, vol. I.

<sup>4</sup> Dennis, *J. Ind. Eng. Chem.*, **12**, 366 (1920).

attached to the thermometer, and the sulfuric acid was then heated at such rate as to cause a rise of  $1^\circ$  per minute. The yellow, powdered, germanium tetra-iodide assumed an orange tint as the temperature rose, and at  $132^\circ$  it became deep red in color. It melted sharply to a ruby-colored liquid at  $144^\circ$ . Repetition of the experiment gave the same result as did a third determination in which was employed an Anschutz thermometer that had been corrected by the Bureau of Standards.

**Crystal Form.**—A crystallographic examination of the substance was kindly made for us by Professor A. C. Gill of the Department of Mineralogy. The crystals were prepared by slow and careful sublimation in a current of dry, warm air. They were found to be regular octahedrons; the plane angles were  $60^\circ$ , indicating that they belong to the regular system. The crystals showed no double refraction.

**Specific Gravity.**—In searching for a liquid medium in which the specific gravity of germanium tetra-iodide might be determined, its behavior toward more than 20 inorganic or organic liquids was investigated. In every case the substance was dissolved or decomposed by the liquid. (See Chemical Properties.)

Since the tetrachloride and tetrabromide of germanium had been found to be unaffected by conc. sulfuric acid at room temperature,<sup>5</sup> the behavior of the tetra-iodide toward this acid was examined, and it was found that at room temperature no visible change could be observed in the substance after submersion in the acid for 24 hours. Consequently, conc. sulfuric acid was used in the determination of the specific gravity of the compound. Pure germanium tetra-iodide was prepared in the form of pellets by spreading the powdered substance along the inside of a long tube of Jena glass and melting it in a partial vacuum. The temperature was kept below  $150^\circ$ . When the compound melted, it coalesced into small globules about 3 mm. in diameter. A pycnometer of 5 cc. capacity was weighed, was then half filled with the pellets of the tetra-iodide, and was again weighed. Conc. sulfuric acid was now run in until the sample was completely covered, and the air occluded in the pycnometer was then removed by placing the bottle in a vacuum desiccator and exhausting the air. The pycnometer was then filled with sulfuric acid and was again weighed. The specific gravity of the sulfuric acid at the same temperature was determined with the same pycnometer. Two determinations at  $26^\circ$  gave 4.322 and 4.321. Hence  $d_{26}^{26} = 4.3215$ .

**Color of Germanium Tetra-iodide.**—At room temperature, fused germanium tetra-iodide in lump form is of the color of coral, the precise shade being "O. R. Normal."<sup>6</sup> When powdered, it has an orange color "O. Y. Normal."

<sup>5</sup> See Dennis and Hance, *THIS JOURNAL*, **44**, 299 (1922).

<sup>6</sup> Mulliken's Color Standards. Ref. 3.

The compound in lump form shows at various temperatures the colors listed below.

Temp.	Color	Mulliken	Temp.	Color	Mulliken
- 185°	Canary-yellow	Y.	+ 50°	Brick-red	R.O.
- 50°	Buff	O.Y.	+ 90°	Red	O.R.
- 10°	Orange	Y.O.	+ 144°	Ruby-red	R.
+ 35°	Salmon	O.			

**Sublimation of Germanium Tetra-iodide.**—About 5 g. of the substance was placed in a test-tube; in the neck of the tube was inserted a cork that carried a thermometer and inlet and outlet tubes of glass. The test-tube was immersed in an oil-bath, and a slow current of dry air was passed through the tube. The oil was slowly heated. At 110° a yellow vapor appeared in the upper portion of the tube, and as the temperature rose beyond this point a finely crystalline, yellow powder collected on the tube wall. When the tetra-iodide had reached a temperature slightly above its melting point (144°), sublimation was rapid. The heating was then stopped, and the tube was allowed to cool slowly. At the conclusion of the experiment a mass of quite large, orange-colored crystals had collected on the stem of the thermometer and the unsublimed residue in the tube was of ruby-red color. It is thus apparent that when germanium tetra-iodide is carefully heated in a current of air to a temperature but slightly above its melting point it sublimes without decomposition.

Nilson and Pettersson have stated<sup>7</sup> that the compound "exists undecomposed in the gaseous condition at 440° but dissociates at higher temperature." They base this statement upon the result of a determination of the vapor density of the compound when it was volatilized at 440° (vapor of sulfur). They obtained a vapor density of 20.46, the theoretical vapor density being 20.0. Our observations during the preparation of germanium tetra-iodide seemed, however, to indicate that the compound is dissociated when heated to temperatures appreciably above its melting point. To gain definite information upon this question glass tubes 1 m. long and 10 mm. wide were sealed at the lower end and were inserted in vertical position into an electric heating furnace to a distance of 20 cm. The tubes were then heated to a temperature of 445°, and a small open tube containing germanium tetra-iodide was dropped into each. In a few minutes a reddish brown vapor appeared in the long tubes just above the top of the electric furnace, and shortly thereafter dark-colored crystals were deposited on the inner walls of the tube at a distance of about 8 cm. above the top of the furnace. The heating was continued for some time at a temperature between 442° and 448°, and the tubes were then cooled and removed from the furnace. The crystalline deposit 8 cm. above

<sup>7</sup> Nilson and Pettersson, *Z. physik. Chem.*, **1**, 36 (1887).

the furnace was identified as free iodine. Just at the top of the furnace there was a deposit of yellow crystals which proved to be germanium tetra-iodide. Midway between the bottom of the tube and the top of the furnace there was a deposit of canary-yellow crystalline plates of germanium di-iodide.

A small quantity of germanium tetra-iodide was placed in a tube of Jena glass which was then sealed and was gradually heated in an electric combustion furnace to a temperature of  $440^{\circ}$ . Dissociation resulted and iodine amounting to over 5% of the weight of the tetra-iodide was set free.

From these experiments it would appear that the result of the vapor-density determination at  $440^{\circ}$  made by Nilson and Pettersson showed agreement with the theoretical vapor density not because germanium tetra-iodide does not dissociate at that temperature, but rather because the vapor consists of a mixture of undissociated tetra-iodide and of vapor of iodine which results from the dissociation of the tetra-iodide and which at  $440^{\circ}$  is diatomic.<sup>8</sup>  $\text{GeI}_4 \rightleftharpoons \text{GeI}_2 + \text{I}_2$ .

Before leaving the point, however, two determinations were made of the vapor density of germanium tetra-iodide with a modified Victor Meyer apparatus.<sup>9</sup> The tube was heated in an electric resistance furnace which made possible the regulation of the temperature within narrow limits,  $442$ – $446^{\circ}$ . Taking the temperature as  $445^{\circ}$ , 0.2827 and 0.6209 g. of substance gave 10.5 and 24.5 cc. of displaced gas at  $0^{\circ}$  and 760 mm., equivalent to vapor density of 20.87 and 19.67, respectively.

These results show the same agreement with the calculated vapor density, 20.01, as was obtained by Nilson and Pettersson, but crystals of free iodine were found in the inner tube at the close of each determination which proves that germanium tetra-iodide undergoes partial dissociation under these experimental conditions.

**Chemical Properties.**—Winkler<sup>2</sup> stated that germanium tetra-iodide is highly hygroscopic and that it deliquesces when exposed to the air. He found that it first gained in weight (50% in 1 day), and then lost weight during the next 18 days, the residue then weighing only about  $\frac{1}{4}$  as much as the original sample.

Several different samples of the substance that we have prepared have shown identical properties which are widely different from those that Winkler has described. Germanium tetra-iodide neither gained nor lost appreciably in weight when exposed to the air for 2 days. A sample that weighed 0.5622 g. was allowed to lie on a watch glass exposed to the air of the Laboratory for 5 months. At the end of that period its weight had decreased 6.5 mg., and a slight, white incrustation had formed around

<sup>8</sup> Meyer, *Ber.*, **13**, 394, 401 (1880).

<sup>9</sup> Weiser, *J. Phys. Chem.*, **20**, 532 (1916).

the sample on the watch glass, but the appearance of the sample was unchanged.

When germanium tetra-iodide is immersed in a small amount of water, it is slowly decomposed with the separation of germanium dioxide, which dissolves when more water is added and forms a clear, colorless solution of acid reaction.

A sample of the compound, placed under conc. sulfuric acid of room temperature, apparently suffered no change in 24 hours, for at the end of that period the acid gave no test for either germanium, or iodine, or for hydriodic acid. When the acid was warmed to 80°, iodine was slowly liberated.

When placed in a 1:4 solution of potassium hydroxide, germanium tetra-iodide is slowly dissolved. Under conc. nitric acid it turns black and nitrogen dioxide is evolved. After standing under the acid for 4 months, the residue still retained its black color.

Conc. hydrochloric acid of room temperature slowly dissolves germanium tetra-iodide, solution being complete after some weeks. When dropped into conc. ammonium hydroxide, the compound is at once decomposed and decolorized, a white solid being formed. When exposed to dry ammonia gas, the substance is slowly converted into a white powder that is soluble in water.

**Solubility.**—Germanium tetra-iodide dissolves without apparent decomposition in the liquids listed below, the solution in each case undergoing no visible change for 4 months.

Solvent	Color of solution	Solvent	Color of solution
Benzene	Red-orange	Monochlorobenzene	Red-orange
Carbon disulfide	Red-orange	Carbon tetrachloride	Light orange
Methyl alcohol	Deep orange	Ethylene glycol	Very light yellow
Ethylene chloride	Light orange	Ethylene chlorohydrin	Very light yellow

The following solvents dissolved the substance at once, but decomposition slowly took place.

Solvent	Color of solution	After standing for 4 months
Hexane	Orange-red	Pink (free iodine)
Amyl alcohol	Deep orange	Yellow ppt., brown solution
Chloroform	Pale yellow	Reddish yellow solution
Nitrobenzene	Red-orange	White ppt., dark brown solution
Petroleum ether	Pink	Decomposition, black ppt.
Butanol	Orange	Dark brown solution
Glacial acetic acid	Pale yellow	Dark brown solution

The following liquids decomposed the substance at once.

Acetone	Light brown ppt.
Ether	Ruby-red solution, yellow ppt.
Turpentine	2 liquid layers formed, the upper one a light red, the lower a deep orange; solid residue, dark brown in color

Oil of lavender	Light yellow ppt. changing to black
Absolute alcohol	Yellow solution, white ppt.
Iso-propyl alcohol	Orange solution, white ppt.
Pyridine	Light yellow solution, white ppt.
Amyl alcohol	Brown solution, white ppt.

### Summary

This article deals with the preparation of germanium tetra-iodide, its analysis, the determination of its melting point, crystal form and specific gravity, its color at various temperatures, the sublimation and dissociation of the compound, and some of its chemical properties.

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[CONTRIBUTION FROM THE BIOPHYSICAL LABORATORIES OF THE CANCER COMMISSION OF HARVARD UNIVERSITY]

## THE POTENTIAL DIFFERENCE BETWEEN GLASS AND ELECTROLYTES IN CONTACT WITH THE GLASS

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Haber and Klemensiewicz<sup>2</sup> found that the potential difference between electrolytes in contact with the 2 sides of a thin glass wall is determined in part by the hydrogen-ion concentration of the electrolytes. Haber's apparatus was arranged as in Fig. 1.

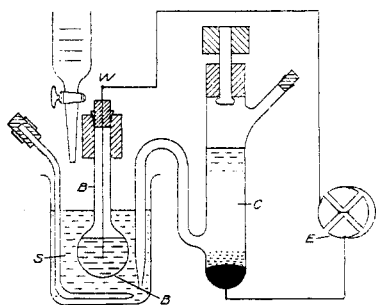


Fig. 1.

S is the solution whose composition is to be varied; B is a glass bulb with walls 0.06 mm. thick, filled with potassium chloride solution; W is a platinum wire dipping into the potassium chloride solution; E is a quadrant electrometer; C is a mercury-calomel-potassium-chloride electrode.

The potential difference between the quadrants of the electrometer was measured by observing the deflection of the electrometer mirror. This potential difference is the algebraic sum of several potential differences at different points in the system, of which the following are the most important: (1) that between the interior of the glass composing the bulb and the solution (S) outside the bulb; (2) that between the solution S and the potassium chloride of the calomel electrode. When the composition of the solution S is changed, these potential differences are obviously the only ones in the system which vary.

The change in the diffusion potential at the potassium chloride liquid junction is known to be small (about 10–20 millivolts) under the condi-

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<sup>2</sup> Klemensiewicz, *Z. Physik. Chem.*, **67**, 385–431 (1909).