

## A REVISION OF THE ATOMIC WEIGHT OF GERMANIUM.\*

### I. THE ANALYSIS OF GERMANIUM TETRACHLORIDE.

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#### Introduction

The atomic weight of germanium has been determined by two investigators. Winkler,<sup>1</sup> the discoverer of germanium, analyzed the tetrachloride and obtained the value 72.5. Quite recently, in a very concordant series of experiments, Müller<sup>2</sup> converted weighed amounts of potassium fluorogermanate into potassium chloride, and found in this way the atomic weight of germanium to be 72.42.

Because germanium has recently become available in moderate quantities and because the tetrachloride may be readily prepared and purified by fractional distillation, by methods perfected in this laboratory for handling other volatile mineral halides, notably the chlorides and bromides of silicon,<sup>3</sup> titanium,<sup>4</sup> and boron,<sup>5</sup> we have undertaken the analysis of germanium tetrachloride. The value which we have obtained is not at all in agreement with that of Müller and is considerably higher even than that of Winkler.

#### Purification of Materials

##### Reagents

*Water.* Ordinary distilled water was twice redistilled, once from alkaline permanganate, and once from very dilute sulfuric acid. The condensers were block tin tubes, fitted to Pyrex flasks with constricted necks which served as stills. The connection was made by a water seal, no cork or rubber being used. The water was collected in Pyrex flasks, generally just previous to use.

*Nitric Acid.* Concentrated C. P. nitric acid was distilled through a quartz condenser, the first two-thirds, as well as the last tenth being rejected. if necessary, the fractional distillation was continued until the product was free from chloride.

*Silver.* This substance was prepared by standard methods. These consisted in brief of the following processes: double precipitation as chloride, followed by reduction with alkaline sugar solution, fusion of the metal on charcoal, solution in nitric acid and repeated crystallization of silver nitrate, precipitation with ammonium formate, fusion on pure lime, electrolytic transport, fusion on pure lime in hydrogen, etching, drying in a vacuum at 500°.

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<sup>1</sup> Winkler: J. prakt. Chem., (2), **34**, 177 (1886).

<sup>2</sup> Müller: J. Am. Chem. Soc., **43**, 1085 (1921).

<sup>3</sup> Baxter, Weatherill and Scripture: Proc. Am. Acad., **58**, 245 (1923).

<sup>4</sup> Baxter and Fertig: J. Am. Chem. Soc., **45**, 1228 (1923).

<sup>5</sup> Baxter and Scott: Science, (2) **54**, 424 (1921); Proc. Am. Acad., **59**, 21 (1923).

Details of these processes may be found in earlier papers from the Harvard Chemical Laboratories.<sup>1</sup> Recent work by Baxter and Parsons<sup>2</sup> and Baxter<sup>3</sup> as well as earlier investigations have shown that these processes yield a product of adequate purity.

*Sodium Hydroxide.* This substance was prepared by metathesis from barium hydroxide and sodium carbonate, both of which had been recrystallized until practically free from chloride. The solution was freed from precipitate by centrifugal settling and after evaporation in platinum dishes was allowed to crystallize. Since the product was found to contain a small amount of chloride it was recrystallized several times in platinum dishes until the chloride had been completely removed.

*Nitrogen.* Nitrogen was prepared by the Wanklyn process. Air was charged with ammonia and passed over hot copper catalyst. The excess of ammonia was removed in wash bottles containing dilute sulfuric acid, and the gas was further purified and dried by passing through towers filled with beads moistened with silver nitrate, potassium hydroxide and concentrated sulfuric acid and through a tube containing resublimed phosphorus pentoxide. The hydrogen formed by decomposition of part of the excess of ammonia was not removed. The apparatus was constructed wholly of glass, with either fused or ground connections, the latter being lubricated with concentrated sulfuric acid.

*Chlorine.* This gas was drawn in part from a tank of liquid material, in part it was prepared from concentrated hydrochloric acid and manganese dioxide. The chlorine was scrubbed with water and dried with concentrated sulfuric acid and finally phosphorus pentoxide, in an apparatus constructed wholly of glass.

#### Extraction of Germanium from Zinc Oxide Residues

We are very greatly indebted to the New Jersey Zinc Company for the generous gift of one hundred and twenty-five pounds of germaniferous zinc oxide, containing approximately 0.25 per cent of germanium dioxide. In extracting the germanium we followed essentially the procedure described by Dennis and Papish<sup>4</sup> by which the germanium and arsenic are first separated together. At the time the improved method of Dennis and Johnson<sup>5</sup> had not been described. On the other hand the final separation of the germanium from the arsenic was effected by fractional distillation of the chlorides in vacuum, instead of by distillation from hydrochloric acid solution in a current of chlorine, as practised by Dennis and his collaborators. Because of the relatively large difference in boiling points, 43°, this separation is comparatively rapid.

<sup>1</sup> See especially Richards and Wells: Pub. Carnegie Inst., No. 28, 16 (1905).

<sup>2</sup> Baxter and Parsons: J. Am. Chem. Soc., **44**, 577 (1922).

<sup>3</sup> Baxter: J. Am. Chem. Soc., **44**, 591 (1922).

<sup>4</sup> Dennis and Papish: J. Am. Chem. Soc., **43**, 2131 (1921). See also Buchanan: J. Ind. Eng. Chem., **8**, 585, (1916); **9**, 661 (1917).

<sup>5</sup> Dennis and Johnson: J. Am. Chem. Soc., **45**, 1380 (1923).

The crude zinc oxide was dissolved in a large flask in a considerable excess of hydrochloric acid, and the solution was distilled until the volumes of the distillate was about twice the volume of the residue. After the acidity of the distillates had been brought to 6 normal by the addition of sulfuric acid, they were saturated with hydrogen sulfide. The precipitated sulfides of arsenic and germanium were washed until nearly free from chloride, with 5 normal sulfuric acid which had been saturated with hydrogen sulfide. Drying at  $110^{\circ}$  followed.

A large portion of the arsenic was next removed by roasting the sulfides in a current of air at about  $500^{\circ}$ . Dennis and Papish<sup>1</sup> state that about 90 per cent of the arsenic is eliminated in this way. In the earlier experiments the sulfides were contained in a copper boat placed inside a glass tube which could be heated electrically. During the roasting a fairly rapid current of dry air was passed through the tube. Owing to extensive contamination of the product by copper oxide, the copper boat was later replaced by one of nickel steel.

The crude germanium dioxide was next finely powdered and subjected to a second roasting in a current of dry air at about  $650^{\circ}$ , while contained in an alundum boat inside a quartz tube. Material evaporating during this treatment and the following one was collected in traps connected with the outlet of the silica tube. After the roasting the air was replaced by a current of pure dry electrolytic hydrogen and the temperature, after being maintained at redness for some time, was ultimately raised to approximately  $1000^{\circ}$ . Most of the reduced material melted and coalesced at this temperature and at the same time a very considerable black sublimate consisting chiefly of arsenic was formed. About one hundred and thirty grams of crude germanium metal were thus secured.

#### Preparation and Distillation of Germanium Tetrachloride

Germanium tetrachloride was next prepared by heating the metal in a current of chlorine, purified and dried as described on page 1050. The chlorine train was connected through a ground joint with a hard glass tube in which the metal was loosely packed between asbestos plugs. This tube was also connected with a supply of dry atmospheric nitrogen prepared as described. The tube containing the germanium was inclined downward and connected at its lower end by means of a ground joint with two condensing bulbs in series, one cooled with ice and salt, the second with alcohol-carbon dioxide mixture.

The nitrogen train and germanium tube were swept out with nitrogen for many hours. At the same time the chlorine train was swept out through a side tube. Chlorine was then admitted to the reaction tube and the germanium was heated electrically by means of a sleeve wound with resistance wire. After a considerable quantity of the chloride had been formed, the apparatus became choked so badly that the experiment was discontinued. The contents

<sup>1</sup> Dennis and Papish: J. Am. Chem. Soc., **43**, 2139 (1921).

of the hard glass tube were washed with water, dried and ignited in hydrogen and the experiment was repeated with similar apparatus. In all about one hundred cubic centimeters of chloride were prepared.

The chloride at this point contained free chlorine. It also was turbid owing in part at any rate to suspended copper salts, for the original metal was contaminated with copper as stated on page 1051. It presumably contained hydrogen chloride and either germanic acid or oxychloride owing to some contact with the moisture of the air. Subsequent examination showed it to contain arsenic trichloride in considerable proportions, and traces of tin and antimony. Silicon might have been introduced in the reaction with chlorine in the hard glass tube but we were unable to discover this impurity. In the formation of boron halides<sup>1</sup> this is a serious difficulty. The boiling points of the chlorides mentioned above and some others are given in the following table together with the effect on the observed atomic weight of germanium of a proportion of 0.1 per cent of each substance alone.

TABLE I  
Boiling Points of Inorganic Chlorides

	Boiling point degrees	Effect of 0.1% on atomic weight of Ge
HCl	-83	-0.070
CCl <sub>4</sub>	76.5	-0.061
SiCl <sub>4</sub>	58	-0.045
TiCl <sub>4</sub>	136	-0.025
GeCl <sub>4</sub>	86.5	
SnCl <sub>4</sub>	114	+0.048
VCl <sub>4</sub>	154	-0.021
PCl <sub>3</sub>	76	-0.032
AsCl <sub>3</sub>	130	+0.028
SbCl <sub>3</sub>	223	+0.049

The germanium tetrachloride was now purified by fractional distillation in a fashion very similar to that used in purifying the halides of silicon, titanium and boron in this laboratory.<sup>2</sup> The two lots of germanium tetrachloride were combined in a single glass bulb (A, Figure 1) in which a few cubic centimeters of mercury had been placed. The bulb was connected with a side tube *a* for exhausting and with a special joint *b* by means of which the bulb could be connected later with additional systems, without breaking the vacuum. In the vertical view of the special joint<sup>3</sup> the sealed-in capillary *m* is closed at the end and is scratched with a file at several points to facilitate breaking. To break the joint the closed tube of glass weighted with mercury *n* is allowed to strike the capillary with some force. The bulb was exhausted

<sup>1</sup> Wöhler and Deville: Ann. chim. phys., (7) 6, 296 (1895).

<sup>2</sup> Loc. cit., page 1049.

<sup>3</sup> Baxter, Weatherill and Scripture: Proc. Am. Acad. 58, 250 (1923).

by means of an efficient water pump through a tube containing sodium hydroxide, while at the same time it was cooled with ice and water to lower the vapor pressure of the germanium tetrachloride. Even under these conditions the tetrachloride boiled gently, thus flushing out the air in the bulbs, together with a part of the chlorine and the hydrochloric acid formed by contact with moisture in the air. After the boiling had proceeded for a short time the tube *a* leading to the pump was sealed off. In order to remove the remainder of the chlorine the tetrachloride and the mercury were emulsified by shaking, and allowed to stand for some time.

Next the bulb A, containing the tetrachloride, was connected through the special joint with another bulb B attached through a vertical tube to a

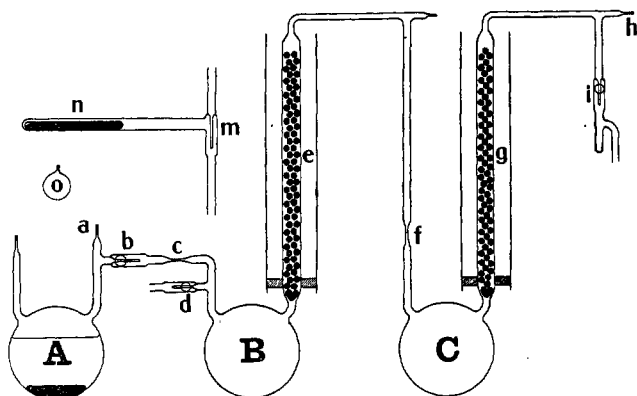


FIG. 1

fractionating column *e* filled with glass pearls and jacketed with a large glass tube. Beyond the fractionating column were another similar bulb C and fractionating column *g* terminating in a special joint *i*. The bulbs B and C and the fractionating columns were exhausted by a Gaede mercury pump through the capillary *h* which was sealed while the pump was operating. Communication between A and B was now made by breaking the special joint *b* and the tetrachloride was largely distilled from A and B by chilling B with salt and ice. After three-quarters of the liquid had distilled the volatility of the remainder became so much less that only by surrounding A with hot water could the distillation be continued. As subsequently found this was due to the concentration of the less volatile arsenic trichloride. The bulb A containing a small amount of liquid together with a residue of mercury and mercurous chloride was detached by sealing the capillary *c*. In the next distillation from B to C the fractionating column *e* was first chilled with ice water. The still B was then surrounded with warm water and the bulb C was chilled with salt and ice. Under these conditions a very efficient fractionation took place with refluxing throughout the fractionating column but without choking. When the residue in B had been reduced to about ten cubic centimeters the volatility was obviously so much less than that of the main portion that the apparatus was divided by sealing the capillary *f*.

The less volatile residue in B was now fractionated into five exhausted bulbs attached through the special joint *d*. These fractions, 40, 41, 42, 43, 44, (Figure 3) were hydrolyzed and found by treatment with hydrogen sulfide to consist largely of arsenic. Spectroscopic examination of the sulfide fractions on graphite electrodes with a Féry quartz spectrograph indicated also the presence of traces of tin and antimony.

In the next distillation from C to a similar system attached through the special joint *i*, difficulty was experienced in condensing a light fraction in a small bulb even with the use of alcohol-carbon dioxide mixture, owing apparently to the presence of non-condensable gas. Therefore, a one-liter exhausted globe was inserted between two special joints, and, the bulb containing the tetrachloride having been warmed and the globe chilled with salt and ice, connection was made between the two and the globe was sealed off. Before the seal could be made several cubic centimeters of the tetrachloride

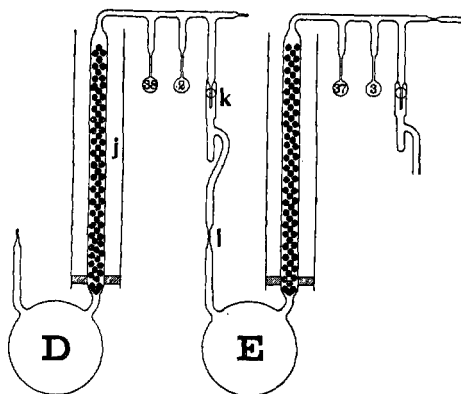


FIG. 2

distilled into the globe, carrying with it the bulk of the troublesome gas. This most volatile fraction, 1 (Figure 3), was hydrolyzed and the solid hydrolytic product when tested spectroscopically, except for a trace of arsenic seemed to contain nothing but germanium.

In all twenty fractional distillations with Hempel columns were carried out in apparatus of the general type shown in Figure 2. The tetrachloride being in the exhausted bulb D and the fractionating column *j* being chilled with ice and water, a less volatile fraction was condensed in the small bulb 2 by means of alcohol and carbon dioxide and was sealed off at the capillary. The special joint *k* was then broken and the main bulk of the liquid was condensed in E with great care to have the fractionating column operating with greatest efficiency. When the residue in the still had been reduced to a few cubic centimeters the capillary *l* was sealed. The residue in D was finally condensed in bulb 38 by chilling with alcohol-carbon dioxide, the rest of the apparatus being warmed at the same time.

### Purity of Germanium Tetrachloride

In this way all the tetrachloride was separated into fractions without accident, so that the material was not exposed to the air at any time after the introduction into the distilling apparatus. This fractional distillation is shown diagrammatically in Figure 3, in which the fractions are numbered in the order of decreasing volatility. The light and heavy fractions from the early distillations were tested for impurities as follows. The least volatile fractions from the first seven distillations were hydrolyzed with a considerable amount of water and treated with hydrogen sulfide. These showed rapidly diminishing proportions of arsenic. In fact, Fraction 34 seemed to be practically free from this impurity. The heavy residue from the eighth distillation, Fraction 33, was hydrolyzed with ammonia and the solution evaporated to dryness. This residue was tested spectrographically as described above and no evidence whatever of the presence of arsenic, tin or antimony could be detected. Dennis and Johnson<sup>1</sup> were able to detect 0.0005 per cent of arsenic in germanium by photographing the arc spectrum. We have no reason to believe that our spectroscopic procedure was any less sensitive.

Although in our experiments seven distillations were thus required for removing arsenic there is no question that, if a somewhat larger residue had been rejected in each distillation, fewer steps would have been necessary. Our somewhat limited quantity of material led us to proceed in a more cautious fashion. Although we have assumed that the arsenic was completely removed at this point, the residue of the eleventh distillation, Fraction 29, as well as Fractions 18 and 19 was tested spectrographically. No impurities of any sort could be detected.

Since the germanium tetrachloride was synthesized in a glass tube the possibility of the formation and presence of silicon tetrachloride existed. The boiling point of this substance, 58°, is so far below that of the germanium compound that rapid separation, but in the more volatile fractions, might reasonably be expected. Only one test for silicon was made. The contents of the

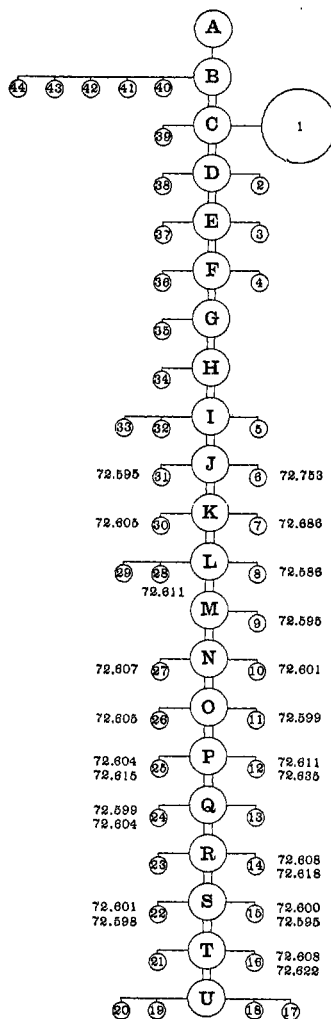


FIG. 3

germanium compound that might reasonably be expected. Only one test for silicon was made. The contents of the

<sup>1</sup> J. Am. Chem. Soc., 45, 1380 (1923).

bulb containing the most volatile fraction from the sixteenth distillation, Fraction 13, were added to a small amount of water in a clean platinum crucible and the crucible was nearly filled with constant boiling hydrochloric acid which had been distilled through a quartz condenser. Evaporation on an electric hot plate followed. Twice more in succession the crucible was filled with constant boiling hydrochloric acid and this acid was eliminated by evaporation. During these three evaporations the germanium was vaporized as chloride, while any silicon tetrachloride must have been hydrolyzed to silicic acid. The crucible was next ignited and carefully weighed by substitution. There was no evidence of any residue in the crucible except a small amount of platinum which had been dissolved by the acid. In order to expel any silica the crucible was next filled with hydrofluoric acid which had been freshly distilled through a platinum condenser, and after evaporation of the acid and ignition, the crucible was reweighed. The observed loss in weight 0.03 mg., is insignificant, and is as likely to be due to experimental error as to the presence of silicon tetrachloride. Even if this really represents silica impurity in the germanium tetrachloride, the corresponding amount of silicon tetrachloride, 0.09 mg., in a fraction weighing approximately five grams would lower the apparent atomic weight of germanium by only 0.001 unit.

### The Analysis of Germanium Tetrachloride

The analysis of germanium tetrachloride followed closely the procedure used in the analysis of silicon tetrachloride.<sup>1</sup> After being weighed the bulb containing germanium tetrachloride was broken under an excess of sodium hydroxide and the glass was collected and weighed. The solution was diluted to considerable volume and made acid with nitric acid, and then was precipitated with a solution of a weighed, very nearly equivalent amount of pure silver. The point of exact equivalence between chloride and silver was then found with the assistance of a nephelometer. In several experiments the silver chloride was collected and weighed.

The bulb containing the material for analysis was first scrubbed with soap solution and then was allowed to stand for some time in sulfuric acid—dichromate solution. After thorough rinsing it was soaked for at least twenty-four hours in the purest water. From this point the bulb was not touched with the fingers. Next the bulb was placed in a basket of platinum wire which had already been weighed under water with an accuracy of one milligram, and the bulb and basket together were weighed under water of known temperature. Rinsing with pure water and draining were followed by drying, first over sulfuric acid, finally over potassium hydroxide which had been fused with permanganate to destroy organic matter. The bulb was then weighed by substitution and the density of the air in the balance case at the time of weighing was found by weighing a sealed standardized glass globe.<sup>2</sup>

<sup>1</sup> Baxter, Weatherill and Scripture: *Proc. Am. Acad.*, **58**, 245 (1923).

<sup>2</sup> Baxter: *J. Am. Chem. Soc.*, **43**, 1317 (1921).



In order to hydrolyze the germanium tetrachloride without forming a semipermanent precipitate of germanium hydroxide, it was found advisable to dissolve the liquid in a solution of at least one hundred per cent excess of the sodium hydroxide necessary to form sodium chloride and sodium germanate. Furthermore, if the solution of sodium hydroxide was less concentrated than 4 normal at the time the reaction occurred germanium hydroxide was precipitated, although subsequent dilution of the solution did not result in precipitation.

A 4 normal solution of the sodium hydroxide was prepared in a heavy walled, two-liter Erlenmeyer Pyrex flask provided with a carefully ground glass stopper, the weight of glass in the bulb containing the tetrachloride being estimated in computing the amount of sodium hydroxide necessary. In the later analyses the sodium hydroxide solution was first filtered through a platinum sponge crucible. The weighed bulb was carefully introduced, and, before the stopper was inserted the flask was warmed gently so that ultimately the pressure should be slightly inward. After cooling the flask with tap water the inner walls of the flask were wetted with sodium hydroxide solution by inclining the flask and rotating, and then the bulb was broken by shaking the flask. A dense fog immediately appeared in the flask. Again the flask was cooled and although the fog disappeared in the course of fifteen minutes the flask was allowed to stand for three hours longer. In the first analysis a 2.5 normal solution of only fifty per cent excess of sodium hydroxide was used in the initial decomposition of the tetrachloride, and the precipitated germanium hydroxide could be dissolved only by long standing after adding more sodium hydroxide. In the third analysis the capillary of the bulb was first broken off and the precipitate which was formed by slow hydrolysis through the opening could be only imperfectly dissolved even by adding a large additional quantity of sodium hydroxide and long standing. In the sixth analysis although one hundred per cent excess of sodium hydroxide was used, the solution was only 2.5 normal when the bulb was broken. In this experiment also germanium hydroxide was precipitated and the precipitate could be ultimately dissolved only by the addition of more sodium hydroxide. In all the other analyses no difficulties of this sort were experienced.

The fragments of the glass bulb were collected on a weighed, platinum-sponge crucible. The solution was filtered directly into the glass-stoppered precipitating bottle or Erlenmeyer flask, and the glass was washed by decantation ten or twelve times with about one hundred cubic centimeters of boiling hot water and once with cold water before being transferred to the crucible. Drying at 300° for eighteen hours in an electrically heated porcelain air bath preceded the weighing of the crucible both empty and with the glass. In order to make sure that no germanium hydroxide was retained by the crucible and glass, the two were further treated with hot 4 normal nitric acid by slowly pouring from 400 to 800 cc. through the crucible. This treatment usually produced a slight loss in weight of a few hundredths of a milligram, but a

second similar treatment produced no further change of appreciable magnitude.

Since it seemed likely, that during the treatment of the glass with sodium hydroxide and with acid solution would occur to some extent, experiments were carried out to test this point. A solution was prepared by dissolving germanium tetrachloride in sodium hydroxide solution as in an analysis, and was filtered through platinum sponge. The glass fragments of several bulbs were weighed in a platinum sponge crucible and then were allowed to stand in the above solution for some time. The glass was collected in the crucible in which it had been initially weighed and then was washed thoroughly with hot water and finally with hot 4 normal nitric acid. Drying at  $300^{\circ}$  followed. After being weighed a second time the glass was washed with hot nitric acid, dried and weighed until the weight was constant. In the first four experiments the glass consisted of a mixture of fragments of different sizes and shapes. In Experiment 5 coarse fragments, in Experiment 6 fine fragments were used. The weights given in the table represent differences between the crucibles and counterpoises.

The slight gain in Experiment 2 is apparently due to an undetected accident. In the other five experiments the losses are consistent with the conditions and indicate an average loss in weight of 0.007 mg. per gram of glass per hour of treatment with the alkaline germanate solution, combined with the nitric acid treatment. A correction of this magnitude was therefore applied to the weight of glass obtained in each analysis. Except in Analyses 1, 3 and 6 (Table IV) this correction did not exceed 0.03 mg.

From the observations with the bulb before breaking and the weight of glass corrected as above and for the buoyant effect of the air, the weight of germanium tetrachloride was found. The weight of silver necessary to precipitate the chloride was computed, and was weighed out, chiefly in the form of a very few large buttons, the final adjustment being made with small electrolytic crystals. After careful solution of the silver in chloride-free nitric acid and elimination of nitrous acid by heating the solution, in a flask provided with a spray trap in the form of a column of bulbs ground into the neck of the flask, fifty cubic centimeters additional of concentrated nitric acid were added, together with sufficient water to make the solution nearly normal in silver. The acid solution was then added slowly with continual agitation to the germanium solution which had been diluted to less than normal concentration during the washing of the glass and also had been made acid by adding 4 normal nitric acid through a funnel tube extending to the bottom of the solution. The mixture was allowed to stand for several days with occasional shaking, and the solution was tested for excess of chloride or silver in a nephelometer. If an excess of either was found, the deficiency of the other was made up by adding hundredth normal silver nitrate or potassium chloride until the end-point had been reached. In the earlier analyses it was necessary to add a considerable amount of chloride in this way because the atomic weight of germanium assumed at the beginning was considerably lower than that actual-

TABLE II  
Solution of Glass by Alkaline Sodium Germanate

Experiment	Wt. of glass gm.	Crucible + glass before treatment with alkali gm.	After treatment with alkali gm.	After treatment with $\text{HNO}_3$ gm.	After treatment with $\text{HNO}_3$ gm.	Glass dissolved gm.	Period of treatment with alkali hours	Glass dissolved per hour per gram
1	2.212	0.25764	0.25659	0.25644	0.25648	0.00120	69	0.000008
2	3.888	0.52810	0.52844	0.52827	0.52826		5	
3	2.212	0.25648	0.25639	0.25637		0.00011	7	0.000007
4	2.206	0.82372	0.82344	0.82350		0.00028	16	0.000008
5	3.616	4.61864	4.61836	4.61834		0.00030	20	0.000004
6	3.839	4.13618	4.13588	4.13585		0.00033	6	0.000010

ly found. In the later analyses the correction to produce equivalence amounted to only a few tenths of a milligram of silver. Even after the apparent endpoint had been reached the solutions were allowed to stand for some weeks longer with occasional shaking in order to allow included or occluded material to be extracted from the precipitate of silver chloride. Although at the beginning of a comparison of this sort the endpoint is likely to alter somewhat with time after two or three weeks have elapsed only slight changes are likely to be produced.

The manipulations of precipitation and testing of the solutions were always carried out in ruby light. In using the nephelometer all the precautions noted by Richards and Wells<sup>1</sup> were observed, such as preparing the comparison tubes under as nearly as possible identical conditions of temperature, concentration and time, allowing the tubes to come to constant ratio by standing for an hour or more, and taking the average of several readings of each ratio.

In the last seven analyses the silver chloride was collected on a platinum sponge crucible and weighed. First the solubility of the silver chloride was reduced by adding an excess of silver nitrate and cooling to 0° for twenty hours with occasional shaking. In Analyses 19-22 one-half gram of silver nitrate was added, in Analyses 23-25 one gram. This relatively large excess of silver nitrate seemed advisable because of the comparatively large amount of nitric acid and sodium nitrate in the solution which increase the solubility of the silver chloride materially. Filtration of the supernatant liquid through a large weighed platinum sponge crucible was followed by thorough washing of the precipitate by decantation with a chilled solution of silver nitrate containing 0.05 gram per liter. The precipitate was transferred to the crucible with chilled water, and after being dried in an electrically heated porcelain oven for about eighteen hours at 300° it was weighed. Moisture retained by the precipitate was determined by fusing the main bulk and finding the loss in weight. In the first two experiments, Analyses 19 and 20, faulty technique may have occasioned too large a loss in weight. The later experiments show a water content of the precipitate more nearly in accord with other experiments of the same sort.

No correction is applied for silver chloride dissolved in the mother liquor. The solubility of silver chloride in the chilled silver nitrate washings was assumed to be 0.03 mg. per liter. This correction was never larger than 0.05 mg. The precipitating flask was rinsed with ammonia and the rinsings were added to the aqueous washings. The resulting solution was diluted to a

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<sup>1</sup> Richards: *Am. Chem. J.*, **31**, 235 (1904); **35**, 510 (1906)

definite volume, either 500 cc. or 1000 cc., and its chloride content was found by comparison with standard chloride solutions in a nephelometer after adding nitric acid and silver nitrate.

In the tables the original weight of silver chloride has been corrected for chloride introduced in the comparison of the germanium chloride with silver. The results of all the analyses undertaken are given.

Weighings were made on a No. 10 Troemner balance, sensitive to 0.02 mg. with a load of fifty grams. A 5 milligram rider was used to determine quantities less than this and more than 0.05 mg. Interpolation from zero points was employed only for amounts less than 0.05 mg.

The weights were of gold plated brass, except the fractional weights which were of platinum, and were compared by the Richards substitution method.<sup>1</sup>

All weighings were by substitution. In the case of the bulb and silver, the weights were substituted for the object weighed. In the case of the glass and the silver chloride the crucibles were substituted for similar counterpoises. A small quantity of impure radium bromide was kept in the balance case to prevent electrostatic effects.

Vacuum corrections were applied as follows:

TABLE III

## Vacuum Corrections

Weights	Density 8.3 0.001293 at 0° and 760 mm.	Vacuum correction per gram
Air		
Glass	2.5	+0.000335
Silver	10.49	-0.000031
Silver chloride	5.56	+0.000071

## Discussion of Results

In the following table the results are arranged in the order of decreasing volatility of the fractions analyzed.

<sup>1</sup> Richards: Jour. Chem. Soc., 22, 144, (1900).

Results  
TABLE IV  
The Atomic Weight of Germanium

Ag = 107.880			GeCl <sub>4</sub> :4 Ag			Cl = 35.458		
Number of analysis	Fraction of GeCl <sub>4</sub>	Weight of GeCl <sub>4</sub> in vacuum gm.	Weight of Ag in vacuum gm.	Weight of Ag added or subtracted in solution gm.	Corrected weight of Ag in vacuum gm.	Ratio GeCl <sub>4</sub> : 4 Ag	Atomic weight of germanium	
1	6	4.32030	8.69804	-0.01010	8.68794	(0.497276)	(72.753)	
2	31	4.86658	9.80158	-0.00790	9.79368	0.496910	72.595	
3	7	5.16272	10.38923	-0.00400	10.38523	(0.497121)	(72.686)	
4	30	3.85268	7.75236	+0.00055	7.75291	0.496933	72.605	
5	8	4.67090	9.39916	+0.00110	9.40026	0.496891	72.586	
6	28	4.27610	8.60360	+0.00110	8.60470	0.496949	72.611	
7	9	5.96671	12.00707	+0.00050	12.00757	0.496912	72.595	
8	10	4.53734	9.13063	+0.00020	9.13083	0.496925	72.601	
9	27	3.11571	6.26925	+0.00055	6.26980	0.496939	72.607	
10	11	3.97498	7.99912	+0.00010	7.99922	0.496921	72.599	
11	26	5.07110	10.20445	+0.00030	10.20475	0.496935	72.605	
12	12	4.91397	9.88796	+0.00035	9.88831	0.496947	72.611	
13	25	6.05244	12.17973	-0.00010	12.17963	0.496931	72.604	
14	24	5.21384	10.49237	-0.00005	10.49232	0.496920	72.599	
15	14	5.20164	10.46750	-0.00020	10.46730	0.496942	72.608	
16	15	4.34510	8.74401	0.00000	8.74401	0.496923	72.600	
17	22	4.18788	8.42750	+0.00010	8.42760	0.496924	72.601	
18	16	4.24281	9.53775	+0.00010	9.53785	0.496941	72.608	
Average omitting Analyses 1 and 3						0.496928	72.602	



TABLE VI  
Atomic Weight of Germanium

Fraction	Atomic weight GeCl <sub>4</sub> :4 Ag	Atomic weight GeCl <sub>4</sub> :4 AgCl
6	72.753	
7	72.686	
8	72.586	
9	72.595	
10	72.601	
11	72.599	
12	72.611	72.635
14	72.608	72.618
15	72.600	72.595
16	72.608	72.622
22	72.601	72.598
24	72.599	72.604
25	72.604	72.615
26	72.605	
27	72.607	
28	72.611	
30	72.605	
31	72.595	

Aside from the first two fractions, no systematic trend is apparent, and in view of the uniformity of the material over a wide range of fractions, the conclusion may reasonably be drawn that the purification of the germanium tetrachloride had been carried as far as it is possible to carry it by the method of fractional distillation. Furthermore, direct evidence of the absence of arsenic and silicon in the fractions analyzed was secured. So far as hydrogen chloride is concerned, the uniformity of the material is the only evidence which can be adduced that this substance had been eliminated. However, aside from the possibility of the existence of a constant boiling distillate of germanium tetrachloride and hydrogen chloride, the wide difference in boiling points of the two substances would lead to the expectation of rapid separation at the start.

The high results of the analyses of Fractions 6 and 7 cannot be ascribed to the presence of arsenic since these fractions were the *most* volatile of those analyzed. These two analyses were the first and third undertaken and as explained on page 1057 considerable difficulty was experienced in the hydrolysis of these fractions. Since it seems unlikely in view of the uniformity of the rest of the material that these fractions were really different from the rest, the more complicated and protracted manipulation and technical inexperience with the method seem to us more probable reasons for the divergence.

Aston<sup>1</sup> has recently found by means of the mass spectrograph that germanium consists of at least three isotopes of masses 74, 72, and 70, the relative

<sup>1</sup> Aston: *Nature*, 111, 771 (1923).



abundance being that of the order listed. He also states that the atomic weight 72.5 is not incompatible with the apparent proportions of the three isotopes. A difference in observed atomic weight of 0.1 unit is not likely to introduce inconsistency in this situation. With two isotopes of chlorine, there are evidently possible fifteen tetrachlorides of germanium with molecular weights ranging, with intervals of two units, from 210 to 222. The unlikelihood of appreciable separation of such isotopic molecules during fractional distillation has already been emphasized in the case of silicon and boron halides. Furthermore, as pointed out in the case of the boron halides, experimental evidence that isotopic separation is inappreciable is furnished by the ratios between the silver used in a comparison with the germanium chloride and the silver chloride obtained in the second step in the same analysis, since separation of the chlorine isotopes is as probable as that of the germanium isotopes. In the following table these ratios are given.

TABLE VII

Analyses	Fraction of $\text{GeCl}_4$	Ratio $\text{Ag} : \text{AgCl}$
12 and 19	12	0.752711
15	22	0.752659
16	23	0.752609
18	25	0.752677
17	24	0.752617
14	21	0.752645
13	20	0.752664
	Average	0.752655
Average, excluding		
Fractions 12 and 14		0.752642
Richards and Wells found		0.752627

As explained on page 1060 the silver chloride determinations in Analyses 19 and 20 are subject to some uncertainty in the estimation of the moisture. Furthermore it is certain that silver chloride cannot be made wholly insoluble by the addition of silver nitrate in excess. In fact we found that by adding more silver nitrate to the filtrate of Analysis 22 a very slight but unmistakable opalescence was produced. Winkler<sup>1</sup> found that silver chloride precipitated in the presence of germanium carried down germanium hydroxide. Although the results of our chloride determinations show little indication of such an effect, the silver chloride from Analyses 24 and 25 was tested for germanium spectrographically on graphite electrodes. In both cases a trace of germanium was present, for the line  $\lambda$  2651 was faintly visible in both cases, although the two lines  $\lambda$  3039 and  $\lambda$  3270 could not be seen in the photographs. From previous experience with other elements we estimate the proportion of germanium in the silver chloride as less than 0.001 per cent. This proportion would affect the atomic weight of germanium by 0.002 unit.

<sup>1</sup> J. prakt. Chem., (2) 34, 177 (1886).

There is no reason to believe that this slight contamination of the silver chloride is unique in the case of germanium. It is a question whether it is possible by a single precipitation to prepare absolutely pure silver chloride, owing to the phenomena of inclusion and occlusion. Furthermore, experience in the past has been that in this type of analysis the results of a comparison with silver is in general slightly higher than that of a silver halide determination, a fact which is in accord with the idea that slight contamination of the silver halide invariably occurs.

Because of these two uncertainties, solubility and contamination, a silver chloride determination is sure to be somewhat less reliable than a comparison with silver.

It is difficult to reconcile the result of this investigation with that of Müller, 72.418. From the standpoint of simplicity in the formula of the substance analyzed, however, much can be said in favor of the tetrachloride over the potassium fluorgermanate. Further investigation is obviously necessary and we propose to prepare and analyze the tetrabromide of germanium as the next step.

### Summary

1. A method for the purification of germanium tetrachloride from arsenic trichloride by fractional distillation in exhausted vessels is described.

2. The atomic weight of germanium has been found to be 72.60 by analysis of germanium tetrachloride.

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*Cambridge, Mass.*