

value 138.8 calculated by Clarke.¹ Nearly all the earlier determinations depend upon the results of methods in which lanthanum oxide plays an important rôle. The recognized difficulty of preparing rare-earth oxides free from traces of the compounds from which they are made by ignition is probably a chief cause of the wide variation among earlier determinations.

It is to be noted that the presence of the usual companions of lanthanum, namely, cerium, praseodymium and neodymium would raise the apparent atomic weight of lanthanum so that the value obtained in this investigation unquestionably represents a maximum.

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ATOMIC WEIGHT OF GERMANIUM.

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It is recognized that the atomic weight of germanium is not accurately known, the accepted value being entirely dependent upon the investigations of its discoverer.² Aside from the lack of confirmation of this constant on the part of other workers it should be noted that Winkler's determinations were made very shortly after his discovery of the element, so that the time interval between the announcement of the existence of the new element and the determination of its atomic weight could not have permitted the determination of special means of purification to which germanium compounds may now be subjected.

The purpose of this investigation was to develop a more thorough means of purification of germanium compounds, especially in connection with the elimination of tin, arsenic and silica with which germanium is always associated, and to use the purified product for a redetermination of this much neglected constant.

Winkler decomposed the tetrachloride by sodium carbonate, added an excess of standardized silver solution and titrated back the excess of the latter with ammonium thiocyanate solution. Four determinations were recorded. Winkler's reasons for the use of the Volhard method are interesting, namely, that the silver chloride which he precipitated after decomposition of the tetrachloride could not be determined gravimetrically on account of occlusion of germanic acid in the precipitated silver chloride. His effort to oxidize the disulfide with nitric acid and to precipitate the equivalent of sulfuric acid as barium sulfate also met with failure for the same reason.

¹ Smithsonian Misc. Coll., "Constants of Nature," Part V. *A Recalculation of the Atomic Weights*, 493, 1910.

² *J. prakt. Chem.*, [2] 34, 177 (1886).

Thus it is not possible to determine halogen or sulfuric acid accurately in a solution containing germanic acid by the usual gravimetric procedure.

This behavior on the part of aqueous solutions of germanic oxide is analogous to the occlusion of stannic acid when the corresponding tetrachloride and sulfide of tin are treated in the same manner.

The brevity of the literature of germanium at this date is doubtless due to the great rarity of the element which until 1915-16 was not known to exist in other than a few scarce minerals, argyrodite, in which it was first found, and certain canfieldite-argyrodite mixtures.

Urbain states that Winkler's original source of germanium was not really argyrodite but mixed minerals containing much less than the theoretical 7% of germanium present in the pure mineral.¹ Hillebrand and Scherrer in their work on gallium in spelter, mention the existence of germanium in a number of blends, as shown spectroscopically by K. Burns of the U. S. Bureau of Standards.²

The same element has been reported in euxenite to the extent of 0.1%^{3,4} and has been reported and also denied to be present in tantalite, samarskite, fergusonite and some other allied minerals.

The writer has examined large quantities of Swedish samarskite, euxenite, aeschinite and gadolinite and failed to find any germanium in these with the exception of a single sample of euxenite which contained 0.03%. All of these minerals were decomposed by alkali carbonate fusion, the melts converted to chlorides, and these subjected to the hydrochloric acid and chlorine distillation method for germanium.

Argyrodite is very scarce and since its discovery in Freiberg ore in 1885 has been reported in only a few localities, notably in the silver ores of Oruro, Bolivia. Hence the recent discovery of workable quantities of germanium in the zinc oxide residues of the spelter industry, is most interesting and important. Certain of these residues contain as much as 0.25% of germanium dioxide.⁵

Through the courtesy of the New Jersey Zinc Company a quantity of this crude zinc oxide was procured, from which nearly all the germanium compounds used in this investigation were prepared.

The oxide-to-metal ratio for the atomic weight of germanium was tried by Winkler but was abandoned as unsatisfactory. Aside from difficulty in preventing enclosure of oxide in the reduced metal Winkler did not mention specific reasons for his failure to obtain good results. An attempt was made to redetermine this ratio using specially constructed quartz apparatus so arranged as to prevent loss of metal by volatilization.

¹ *Compt. rend.*, **150**, 1758 (1910).

² Hillebrand and Scherrer, *J. Ind. Eng. Chem.*, **8**, 225 (1916).

³ Krüss, *Ber.*, **21**, 131 (1888).

⁴ *Ibid.*, **20**, 1665 (1887).

⁵ Buchanan, *J. Ind. Eng. Chem.*, **9**, 661 (1917).

Results were very unsatisfactory for two reasons. First, the purity of the oxide was questionable for traces of sulfur were contained in it (when prepared from the sulfide) and small amounts of chlorine (when prepared from the tetrachloride) were not eliminated. Second, the hydrogen stream carried away small quantities of metal as hydride. This was proved by washing the waste hydrogen in a solution of silver salt, when a small black deposit was slowly formed which contained silver germanide and metallic silver.

It was noted however, that the reduction to metal proceeded to completion at 700° , *i. e.*, 200° lower than the melting point of the metal. Every reheating in hydrogen at this temperature, however, caused further loss in weight.

The chief difficulties in determining the chlorine in the tetrachloride, or halogen in the other halides, are twofold: the occlusion of germanic acid in the precipitated halide previously mentioned, and the instability of the halide of germanium in air and the elaborate method required for the preparation and preservation of this group of salts.

The writer examined the properties of potassium fluogermanate and found that the stability and definite character of this salt strongly recommend it in what appears to be a simple and satisfactory ratio, namely, the conversion of this compound to potassium chloride in hydrogen chloride. The ratio of potassium fluogermanate to potassium chloride offers certain important advantages. The complex salt contains no water of crystallization, and the dried product is remarkably non-hygroscopic. It is sufficiently stable and non-volatile to withstand the action of heat at 400° to 500° without loss of weight.

The fluogermanate melts at about 730° to a clear liquid, and at about 835° rapidly vaporizes without change. The salt is slightly volatile in an air current below its melting point—as might be expected, but as a much lower temperature could be used for its conversion to chloride no difficulty was encountered in this direction.

The decomposition of the double fluoride in hydrochloric acid was shown by preliminary experiments to be complete at a temperature well below 400° and in the presence of water was completed at about 100° . That is to say, tests for germanium and fluorine in the residual chloride gave entirely negative results in these cases. Concerning the final product, potassium chloride, the work of Richards on the atomic weight of potassium¹ has already shown that this salt may be weighed with great accuracy. Finally the method outlined was free from complicated manipulation and required no transference of material after placing the original sample of fluogermanate within the weighed platinum bulb.

¹ Richards and Staehler, *THIS JOURNAL*, 29, 623 (1907).

Preparation of Material.

Twenty-nine kg. of germanium-bearing zinc oxide was slowly sifted into conc. commercial "c. p." hydrochloric acid (sp. gr. 1.18). Solution was nearly complete, and on cooling large masses of lead chloride crystallized out, yielding in all 3 kg. The filtrate (which measured about 65 liters) was placed in 5-gallon carboys and saturated with hydrogen sulfide under pressure. The calculated excess of hydrochloric acid present was such that the precipitate contained little else than the crude sulfides of arsenic and germanium. Siphon filters were used to remove most of the filtrate and the sulfides were collected in large Büchner funnels upon which they were washed and sucked as dry as possible. The sulfides were then dissolved in a very slight excess of dil. ammonium hydroxide. The thio salts obtained were strongly acidified with hydrochloric acid and the sulfides were reprecipitated with hydrogen sulfide, after which they were washed and dried, roasted in air in quartz vessels, and digested, with frequent addition of pure nitric acid. Ignition gave a snow-white voluminous residue of crude germanium dioxide which weighed approximately 50 g.

This oxide was introduced into a large distilling bulb, together with 20% hydrochloric acid, a quartz condenser was attached, and the whole system was filled with chlorine to saturation in the cold. Distillation was then carried out in a stream of chlorine and the distillate caught in a receiver containing cold water. The distillation was repeated four times. The final distillate was then saturated with hydrogen sulfide prepared from selected pure antimony trisulfide. The snow-white germanium sulfide thus obtained was treated in quartz dishes with pure freshly-distilled nitric acid, gradually brought to dryness, and ignited. Treatment with nitric acid and subsequent ignition was repeated many times. The strongly ignited residue of oxide finally obtained weighed approximately 46 g.

The oxide was then placed in freshly distilled water contained in 3-liter Erlenmeyer flasks of well-seasoned resistance glass, the mixture stirred by a current of washed air until most of the oxide had dissolved. Warming was avoided on account of possible reaction with the glass surface. Twelve liters of aqueous solution and a residue of undissolved oxide were obtained. The perfectly clear supernatant liquid was removed through a siphon filter and the residual oxide, amounting to about 3.5 g., discarded.

Later examination of this residue showed that it was nearly completely soluble in water. Several milligrams of a white insoluble powder remained, however, which required alkali-carbonate fusion for decomposition. Indistinct tests for sulfur and silica were obtained, but lack of sufficient material prevented an exact determination of its nature.

The large volume of aqueous solution was evaporated in quartz vessels enclosed in bell jars. The dishes rested upon steam-heated copper coils, and a current of washed warm air was drawn through the system to remove water vapor. The first deposit of hydrated germanic oxide (3.4 g.) was removed by filtration and set aside. Evaporation was then continued until most of the oxide had crystallized. Slightly over a liter of the mother liquor was set aside, and the middle portions of hydrated oxide deposited were filtered out, washed with a little cold water, and finally strongly ignited in platinum. 37.1 g. was obtained. The fluogermanate of potassium was now prepared from this fraction of oxide.

Potassium Fluogermanate.—The purest obtainable commercial potassium nitrate was recrystallized in platinum 5 times with centrifugal draining, then fractionally precipitated as chloride in quartz vessels by a stream of hydrogen chloride. The chloride was reprecipitated three times by hydrogen chloride and the resulting chloride then converted to the acid tartrate, using tartaric acid which had been recrystallized until no weighable residue remained upon ignition of a 5-g. sample. The bitartrate after

three reprecipitations was centrifuged in platinum cones and finally ignited to the carbonate in a platinum dish. Cesium, rubidium and sodium could not be detected spectroscopically in this potassium carbonate.

Hydrofluoric acid was prepared, starting with the best commercial "C. P." acid. The common impurities in this acid are silica, lead, iron, chlorine and organic matter. Precipitation to eliminate any of these possibly present was carried out as follows. Potassium carbonate, prepared as described above, was added to the hydrofluoric acid, but no visible trace of any precipitate was found. The acid was then filtered through paper which had been thoroughly washed with a portion of the acid, and potassium fluoride was then added, the acid distilled from a platinum retort and condenser, and redistilled first in presence of a little permanganate and then over a little pure silver fluoride, formed by adding a little silver carbonate to the acid. The resulting purified acid was then again distilled alone, and tested for non-volatile matter, but gave no weighable residue.

The pure germanium dioxide described above was warmed in a platinum dish with an excess of this acid until solution took place. Very slightly more than the calculated amount of purified potassium carbonate was added to the hot, perfectly clear, acid solution of the fluoride. Precipitation of the double fluoride which began in the hot solution was made as complete as possible by chilling. The precipitate was filtered out upon platinum cones and centrifuged, washed with a little cold water, fractionated by crystallization from hot water slightly acidified with hydrofluoric acid, recrystallized four times from hot water containing a little free acid, and finally again from water alone. Each fractionation was accompanied by thorough centrifuging of the crystals and because of the marked difference in solubility of the salt in hot and cold water, all filtrates were set aside without further concentration.

The pure white glistening crystals thus obtained were preserved in a platinum vessel over sulfuric acid in a desiccator whose inner surface was protected from the action of traces of hydrogen fluoride by a coat of Canada balsam.

Reagents.

Water.—Ordinary distilled water was redistilled from alkaline permanganate solution, then from acid permanganate, and then alone. A block-tin condenser was employed, and the distillate was received in well-seasoned Jena glass flasks. Ground glass surfaces were avoided, the receiving flasks being provided with caps ground on the outside of their necks. Spray from the still was eliminated by use of a bead-filled splash trap. The first third portions of distillates were not used.

Small quantities of specially pure water were required from time to time, to be added to the weighing bulb wherein evaporation to dryness was effected. For this purpose water prepared as described above was again distilled from an all-platinum still and condenser, collected in a receiver of the same material, and used immediately.

Hydrogen chloride was prepared by the Hare method, using arsenic and iron-free conc. hydrochloric and sulfuric acids. The gas was washed and dried in 4 sulfuric acid towers filled with beads and glass wool. The generator connection was a ground glass joint and all other connections were sealed by fusion.

Nitrogen was required only for fusion of the potassium chloride previous to the estimation of that salt. The gas was purified by passing it through sulfuric acid, over fused potassium hydroxide sticks, finely divided hot copper, again over fused caustic potash and finally through phosphorus pentoxide. Fused glass connections were used throughout.

Air.—An air current produced by a water blast was purified by passing through a silver salt solution, alkaline permanganate solution, over caustic potash, through sulfuric acid towers, over fused caustic potash and soda lime and finally through 2 towers

containing phosphorus pentoxide. As in the case of the nitrogen and hydrogen chloride systems all connections were of sealed glass.

Nitric acid was prepared from a commercially obtained *c. p.* potassium nitrate. The acid was redistilled thrice from an all-quartz apparatus; 10 cc. of the final distillate was free from non-volatile residue, and gave a negative test for chlorine and iron.

The Apparatus.—For obvious reasons the conversion of potassium fluo-germanate to potassium chloride had to be effected in an all-platinum vessel, illustrated in Fig. 1. With slight modifications the weighing bulb and counterpoise were identical with those used by Smith and Van Haagen in their recent determination of the atomic weights of boron and fluorine, in this laboratory.

The capacity of the long-necked platinum weighing bulb was 30 cc. The neck was 1.5 cm. wide and the total volume of the flask about 40 cc.

The inner tube A permitted the passage of the current of gas to the bulb and contents and was furnished with two perforated disks C. The disks were about 5 cm. apart and almost touched the walls of the neck of the flask. Their principal function was, of course, to prevent mechanical loss but they also served to guide the inner tube into correct alignment for the adjustment of the platinum stopper, an important advantage because of the delicate nature of a ground platinum connection.

The bulb was supported upon two stout arms or lugs near the top of the flask and diametrically opposite each other. These rested upon the platinum-covered prongs of a fork projecting from a stand (not shown).

B shows the platinum elbow-tube, the end of which was ground to fit the entrance to the inner tube. A small platinum stopper ground to the same size (*b*) served to

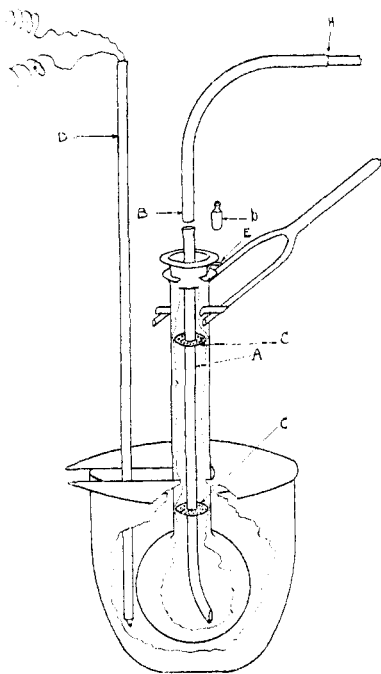


Fig. 1.

close the inner tube during weighing.

A large platinum crucible and perforated cover prevented direct contact of the bulb and flame; and as the temperature during each determination had to be controlled, a platinum-iridium thermo-couple, D, was introduced through the crucible cover, the end of the couple being on a level with the bottom of the weighing bulb.

The waste hydrogen chloride bearing the decomposition products, germanium tetrachloride and hydrogen fluoride, was taken off through a pure gold cap and tube G (shown in Fig. 2) and drawn through large wash-bottles containing water and caustic soda solution. The cap fitted loosely over the entire top of the flask during the use of the hydrogen chloride but was not required while the nitrogen and air were in use. These latter gases were simply allowed to escape into the air around the stopper, which was slightly raised from its seat by means of a small piece of platinum foil inserted at E, Fig. 2. Thus the neutral gases were thrown away, but excess of acid gas was disposed of and its germanium content recovered without complicating the apparatus further by adding a side arm and stopper.

The generators and entire systems for washing and drying of air, nitrogen and hydrogen chloride were constructed wholly of glass, all connections between washing

bottles being fused together, and ground connections were only used between generator flasks and the anterior ends of the washing trains. These three gases passed to a 3-way stopcock from which any one gas could be taken off through a single supply tube leading to the platinum connection H. The connection between glass and platinum at H was a carefully ground joint and a very tight connection was effected at this point by first grinding the glass and platinum to accurate fitting, heating the platinum and then slipping it while hot on to the cooler glass. Upon cooling and contracting, the softer platinum took fast hold and the joint remained gas-tight throughout all determinations.

The apparatus proper (excepting only the gas generators and washing systems), was enclosed in a large glass-sided cabinet furnished with a tight sliding door and a small opening at the top for the escape of hot air. This precaution was important on account of the many hours of exposure of the bulb for a single determination and served admirably to exclude dust and laboratory fumes from the vicinity of the weighing bulb.

Manipulation of the bulb and counterpoise adjustment of platinum connections, etc., were facilitated by the use of 4 thoroughly washed and lint-free linen finger covers. These allowed a much firmer hold of the flask and more accurate adjustment of stoppers than the usual use of tongs or handkerchief. They were kept ready for use and free from dust in a compartment of the desiccator used for the bulb and counterpoise.

Balance and Weighing.—Weighings were made on a Troemner balance No. 10, which is easily sensitive to 0.02 mg. The weights were carefully calibrated by Richards' substitution method. The larger weights were of gold-plated brass and the fractions of platinum. The counterpoise was a platinum flask of nearly the same weight and surface as the weighing bulb. Both bulb and counterpoise were allowed to come to the same temperature and surface condition side by side in a large desiccator, and the desiccator was allowed to remain near the balance for some hours before final weighings were taken.

For vacuum corrections, 1.995 was taken as the accepted density of potassium chloride.¹ The density of potassium fluogermanate had to be determined. For this purpose pure toluene distilled over sodium and redistilled alone was used. The mean of three determinations at 22° was 3.244. The corrections were of quite appreciable magnitude, amounting to +0.00045 per gram of chloride and +0.00024 per gram of fluogermanate.

The atomic weights used in calculating the atomic weight of germanium were chlorine, 35.46; potassium, 39.10; and fluorine, 19.00.

The Dehydration of Potassium Fluogermanate.

It is known that the removal of water from a number of double fluorides is accompanied by partial decomposition, small amounts of oxygen being introduced into the salt with the elimination of some hydrofluoric acid. As such decomposition would introduce serious error into exact determina-

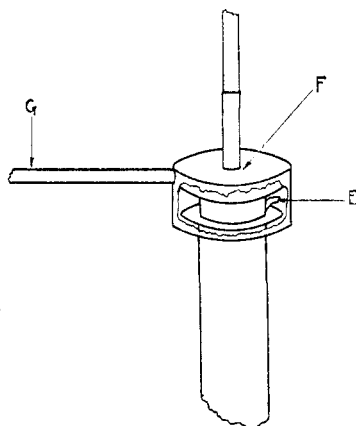


Fig. 2.

¹ THIS JOURNAL, 29, 632 (1907).

tions the proper conditions for dehydration of the fluogermanate were studied in preliminary experiments.

A 15-g. sample of the moist centrifuged purest potassium fluogermanate was allowed to dry in dust-free air at room temperature. 4.50071 g. of this air-dried sample was then exposed to a slow current of perfectly dry air for 6 hours at 70° to 80°. The loss in weight was 0.00035 g. When further exposed to dry air at 450° the weight became constant after a loss of 0.00810 g. Reheating for 14 hours at the same temperature afforded no further loss. The salt then weighed 4.49128 g.

Another portion of the original air-dried salt was exposed *in vacuo* over sulfuric acid for nearly a week, when the moisture content was only slightly changed. It was then evident that the small quantity of water in the salt was enclosed within the crystals and could not be removed except at a temperature at or near the melting point. As mentioned before the melting point of the salt is over 700° but at that temperature it is appreciably volatile. At 450° no volatility could be detected. It seemed advisable therefore not to use a temperature higher than 450°; but as the long-necked flask and its perforated disks acted as a condenser it was possible after a preliminary drying at 400° to 450° to stop the air current and raise the bottom of the flask to a higher temperature for a few moments without loss. The salt then sintered together but did not lose more weight. Accordingly the conclusion was drawn that a temperature of 450° and a slow current of air will completely dry the salt if time enough be allowed. At higher temperatures it is evident that the condensation of sublimed salt upon the obstructions well up in the neck of the flask would have introduced a greater error than the possible trace of moisture that might have been left in the salt dried at 450°.

A much higher temperature was used, of course, to melt the residual potassium chloride, but this operation was not necessary until all of the germanium and fluorine had been removed in hydrogen chloride.

Final Determinations.

The general procedure in the dehydration of the potassium fluogermanate was the same in all determinations and may be outlined as follows.

The empty bulb, protected by the platinum crucible air-bath, was ignited at 800° for about 20 minutes, and a current of dry air was allowed to pass through the bulb during the application of heat. It was reweighed to constant weight ± 0.02 mg., approximately. The sample of fluogermanate was then introduced through a platinum funnel, the stem of which projected well down into the neck of the flask. The bulb was then connected with the air supply and a slow current of dry air was passed through at 60° to 70° for 3 hours, then at 150° for 2 hours; and then the temperature was raised slowly to 400° to 450° and so main-

tained for 4 to 6 hours. More than three reheatings at 400° were seldom required to give a weight constant to 0.02 or 0.03 mg.

The weighing bulb was then connected with the supply of hydrogen chloride, and this gas was allowed to act on the dry salt, at 100° to 150° for 3 hours during which time the major portion of the germanium passed off. Several cubic centimeters of water was now introduced into the bulb (except in the first determination) and the aqueous mass was then carefully heated to 70° or 80° in the same gas until practically all of the water was removed. The initial partial drying took about 6 hours. The temperature was then elevated slowly to about 500° for a short period and finally to the melting point of the residual chloride. The bulb was allowed to cool, water was again introduced and the process outlined above was repeated. A third introduction of water and repetition of the drying process was carried out in the last four determinations. The residual chloride was then raised to 600° in the presence of hydrogen chloride, and most of the latter gas was removed in a current of nitrogen at that temperature. The passage of nitrogen was continued for some time, and the chloride was finally brought to fusion. The temperature was then lowered and the nitrogen swept out of the bulb by passing in a slow current of air for several hours. This gave the first weighing of the chloride.⁴ The entire operation described above was then repeated and carried out to obtain a constant weight of the chloride. The long time required for the complete expulsion of all of the hydrogen chloride made it advisable to prolong the first treatment with this gas far in excess of the actual time required for the conversion of the fluoride to chloride. In Determination No. 1 the operation was made entirely in the dry way. Five reheatings in hydrogen chloride were needed to arrive at constant weight within the limit of 0.04 mg. Hence the other determinations were all carried out with the use of the acid gas in the presence of water and the length of time of exposure to the acid was greatly increased to bring about the removal of the added water before high temperature was applied. It need hardly be mentioned that after the introduction of water into the bulb, evaporation was carried to nearly complete dryness at a temperature below 100° .

One determination was lost because of the introduction of water into the bulb before the most of the germanium had been expelled in dry hydrogen chloride, the trouble being then caused by the sudden elimination of germanium along with water vapor. A deposit of germanium oxychloride was thus produced which collected upon the upper portions of the neck of the flask and the stopper. As this part of the flask could not be properly heated and was in contact with air at all times, this determination was not carried further.

In the other six determinations the dry fluogermanate was treated with dry hydrogen fluoride at 100° to 150° for some hours before any water

was used to decompose the residual chloride and fluoride mixture. The water was added in just about sufficient quantity to dissolve the entire residue in the cold.

Results of the seven determinations are given in the table below.

Determination.	Weight of potassium fluogermanate in <i>Vacuo.</i> G.	Weight of potassium chloride in <i>Vacuo.</i> G.	Atomic weight of germanium. K = 39.10. Cl = 35.46. F = 19.00.
I.....	1.94831	1.09814	72.37
II.....	3.09380	1.74350	72.41
III.....	2.10784	1.18774	72.44
IV.....	2.36113	1.33044	72.44
V.....	4.38070	2.46863	72.42
VI.....	1.52575	0.85970	72.45
VII.....	4.00100	2.25483	72.40
			Mean 72.418

Summary.

The results and conclusions derived from the preceding investigations may be summarized as follows.

1. The processes of purification of the germanium salt used for the determination of the atomic weight of this element embodied a more thorough treatment for the elimination of the known impurities of germanium than previously reported.

2. The chlorine-hydrochloric-acid distillation process, though adequate for the removal of silica and tin can hardly be accepted as a means of eliminating the last traces of arsenic from germanium compounds. Four redistillations of the chloride from hydrochloric acid solution in a stream of chlorine failed to remove the last of the arsenic.

3. The treatment of the nearly pure germanic oxide with sufficient water to dissolve nearly all of it, and the fractional crystallization of the hydrated oxide from this solution served a twofold purpose, to remove the much more soluble arsenic oxide at one end, and to remove any remaining traces of tin and silica in the less soluble fractions at the other. It should be noted that the formation of the potassium fluogermanate was not carried out until the absence of the isomorphous fluostannate and fluosilicate was insured by complete removal of tin and silica from the original oxide.

4. The stability of the final product, potassium fluogermanate, and the anhydrous nonhygroscopic nature of this salt, together with its complete decomposition in hydrochloric acid seemed to indicate that it was the most favorable compound of germanium for accurate analysis. The complete conversion of the salt to potassium chloride was in every case established by negative tests for both germanium and fluorine.

5. The mean of seven determinations of the ratio of potassium fluogermanate to the potassium chloride equivalent gave 72.418 for the atomic

weight of germanium, calculations being based on the assumption that chlorine is 35.46, fluorine, 19.00, and potassium, 39.10.

In conclusion, the above investigation suggests that an examination of other double halides of germanium and the alkalis might give desirable compounds for accurate analysis by a similar volatilization of the germanium content, and thus furnish a check upon the results obtained in this work.

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CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF PARIS.]

A NEW METHOD OF MEASURING ELECTROLYTIC CONDUCTANCE.

BY CHARLES MARIE AND W. ALBERT NOYES, JR.

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Since the original researches by Kohlrausch,¹ the alternating current Wheatstone bridge has been universally accepted as the basis for measurement of electrolytic conductance. This method has been improved by various investigators, until Washburn² claims that this method, with the precautions proposed by him, is limited only by the ability to keep the temperature constant.

The present work was undertaken, therefore, to compare conductivities as measured by the ordinary Kohlrausch method with those measured under exactly similar circumstances on the same bridge by a direct-current method. Newbery³ has done some work on direct-current conductivities by a direct-current method, using two calomel electrodes to determine the potential drop along an electrolytic conductor. He finds slight differences from values obtained by Kohlrausch's method, but offers no satisfactory explanation of the differences.

Since the work described in the present paper was completed, Eastman⁴ has published an article on "Conductivity and Frequency" in which he discusses the form of the conductivity-frequency curve. His results with direct current show variations but slightly greater than the experimental error from values obtained with alternating currents, but are smaller, as would be expected.

The present work is a continuation of research started before the war by the senior author.⁵ The principle of the apparatus is not complicated. Two hydrogen electrodes of exactly equal potential are placed in the solution in question and an ordinary direct-current Wheatstone bridge is used to determine the resistance.

¹ Kohlrausch and Holborn, "Leitvermögen der Elektrolyte."

² Washburn, *THIS JOURNAL*, **35**, 177 (1913); **38**, 2431 (1916); **39**, 235 (1917).

³ Newbery, *J. Chem. Soc.*, **113**, 701 (1918).

⁴ Eastman, *THIS JOURNAL*, **42**, 1648 (1920).

⁵ C. Marie, *Soc. chim. phys.*, July 1910; cf. *J. chim. phys.*, **8**, 699 (1910).