HYDROGEN TELLURIDE AND THE ATOMIC WEIGHT OF TELLURIUM.

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1. Introduction.

The position of tellurium in the Mendeléeff arrangement of the elements is, in respect to the atomic weight of the element, strikingly anomalous, and has given rise to ingenious speculations and many experimental investigations that have had as their object the explanation or the removal of this anomaly. Contributions that have been made to the chemical literature upon this subject up to the year 1911 have been summarized by Dudley and Jones.[1] Since that time a further article by Flint[2] has appeared, in which the author states that no variation in the atomic weight of tellurium was obtained when his method of hydrolytic precipitation was used on crude material. Pellini[3] tested the method of Browning and Flint,[4] and as a result of numerous analyses concludes that this method offers no evidence of a decomposition of tellurium. The same conclusion concerning the method of Browning and Flint has been reached by Morgan.[5] In this connection it is interesting to note that while so many investigators have been endeavoring experimentally to demonstrate the complexity of tellurium, and thus to furnish an explanation of its high atomic weight, Kusnezow[6] suggests that the atomic weight now assigned to the element may, after all, not be abnormal even though it is higher than that of iodine.[7] He bases this idea upon certain variations in the atomic weights in the elements of the uneven series, but the data that he cites do not appear strongly to support the validity of his suggestion.

If the high atomic weight of tellurium is due to the presence of a small amount of an element that is analogous to the members of the primary group of Group 6 of the Mendeléeff table, it seems reasonable to suppose that this substance might be separated from what is now termed tellurium by some process of fractionation, a method that has yielded such excellent results in the separation of other markedly similar elements and compounds. Mendeléeff predicted[8] the existence of such an element, giving it provisionally the name dvi-tellurium and assigning to it an atomic weight of 212. If, however, such an element exists, its atomic weight is probably some-

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[1] This Journal, 34, 995 (1912).

[2] *Ibid.*, 34, 1325 (1912).

[3] *Atti R. Accad. Lincei,* [5] 21, I, 218 (1912).

[4] *Am. J. Sci.,* [4] 28, 347 (1909).

[5] This Journal, 34, 1669 (1912).

[6] *Iswestja des Donschen Polytechn. Inst. zu Nowotscherkäsk,* 1, II, 380 (1912): *Chem. Zentralb.,* 84, I, 772 (1913).

[7] See also Werner, *Ber.,* 38, 914 (1905).

[8] *J. Chem. Soc.,* 55, 649 (1889).

what greater than this value. The elements in the odd series of Groups 4 and 5 of the Periodic Table show the following differences in their atomic weights:

Series.	Group 4. At. wts.	Differences.	Group 5. At. wts.	Differences.
3...............	Si 28.3		P 31.04	
		44.2		43.92
5...............	Ge 72.5		As 74.96	
		46.5		45.24
7...............	Sn 119.0		Sb 120.2	
		88.1		87.8
11...............	Pb 207.1		Bi 208.0	

It is seen that in each group the difference between the atomic weight of the element in the 7th series and that of the element in the 11th series is very nearly twice (1.99 times) as great as the difference between the atomic weights of the elements in the 3rd and 5th series in that group. If this holds true for the 6th group as well, the atomic weight of dvi-tellurium would be equal to twice the difference between the atomic weights of selenium and sulfur, or 2 × 47.13 = 94.26, plus the atomic weight of tellurium. If the atomic weight of tellurium is 127.5, the present value, the atomic weight of dvi-tellurium would be about $127.5 + 94.3 = 221.8$. If the atomic weight of tellurium is less than that of iodine, say 126.5, dvi-tellurium would then have an atomic weight of about $126.5 + 94.3 = 220.8$. In this latter case, what is now known as tellurium would consist of 98.94% of true tellurium and 1.06% of dvi-tellurium.

If this dvi-tellurium is really the cause of the high atomic weight, it seems reasonable to suppose that, even though it is present in comparatively small amount, it should, by reason of its much higher atomic weight, be rather easily separable from tellurium. The failure of so many able investigators to resolve tellurium into two or more components would appear to support the view that the high atomic weight of the substance is, as has been suggested by others, due rather to the presence of a comparatively large amount of a body that resembles tellurium very closely and that possesses an atomic weight but slightly above that of tellurium. If this were the case, the lack of success in the attempts to separate the two substances might readily be understood, for the history of the separation of the chemical elements furnishes more than one illustration of such a case. For example, the composite nature of didymium was suggested by Marignac as long ago as 1853, and the same idea was later advanced by Delafontaine and by Brauner. Nevertheless many investigations and many methods of extended fractionation failed to yield any distinct components of didymium until Auer von Welsbach, by the use of a method that had been suggested by Mendeléeff, succeeded, in 1885, in splitting didymium into praseodymium and neodymium. He accomplished this result because he employed a method of fractionation that was practically new, and also because he started with a large amount of material which he subjected to many hundred fractional crystallizations.

If tellurium is really of composite nature, and if it consists of two elements of closely similar properties, the work that already has been done upon this subject would seem to demonstrate that the fractional separation of these components will be successful only (*a*) if the procedure that is used yields quite rapid and complete separation of the two substances, or (*b*) if a very large number of fractional separations is made with large amounts of material.

The methods of fractionation that have thus far been employed in the attempt to split tellurium into components are:

1. The distillation of tellurium.[1]
2. The distillation of tellurium dioxide.[2]
3. The distillation of tellurium tetrachloride.[3]
4. The sublimation of tellurium tetrabromide in a vacuum.[4]
5. The crystallization of hydrated telluric acid, $H_2TeO_4.2H_2O$.[5]
6. The crystallization of potassium tellurium bromide, K_2TeBr_6.[6]
7. Crystallization of barium tellurate.[3]
8. The precipitation of tellurium from a solution of tellurium in potassium cyanide by a current of air.[4]
9. Precipitation of sodium thiotellurate.[7]
10. Hydrolysis of a hydrochloric acid solution of tellurium tetrachloride.[8]
11. Precipitation of tellurium from a solution of tellurium tetrachloride by hydrazine hydrochloride.[9]
12. Electrolysis of tellurium tetrabromide and tetrachloride.[3]
13. Decomposition of hydrogen telluride.[3]

The results of most of these methods of fractionation have been such as to lead to the conclusion that tellurium is homogeneous and that the anomalously high atomic weight of the element must be regarded as cor-

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[1] Baker and Bennett, *J. Chem. Soc.*, **91**, 1849 (1907).

[2] Baker and Bennett, *J. Chem. Soc.*, **91**, 1849 (1907); Marckwald, *Ber. d. chem. Ges.*, **40**, 4730 (1907); Norris, THIS JOURNAL, **28**, 1675 (1906).

[3] Baker and Bennett, *Loc. cit.*

[4] Brauner, *J. Chem. Soc.*, **55**, 382 (1889).

[5] Staudenmaier, *Z. anorg. Chem.*, **10**, 189 (1895); Baker and Bennett, *J. Chem. Soc.*, **91**, 1849 (1907); Marckwald, *Ber. d. chem. Ges.*, **40**, 4730 (1907).

[6] Norris, Fay and Edgerly, *Am. Chem. J.*, **23**, 105 (1900).

[7] Brauner, *J. Chem. Soc.*, **67**, 549 (1895); *Chem. News*, **71**, 196 (1895).

[8] Brauner, *J. Chem. Soc.*, **55**, 382 (1889); Baker and Bennett, *Loc. cit.*; Browning and Flint, *Am. J. Sci.*, [4] **28**, 347 (1909); Flint, *Ibid.*, [4] **30**, 209 (1910); Harcourt and Baker, *J. Chem. Soc.*, **99**, 1311 (1911); Flint, THIS JOURNAL, **34**, 1325 (1912); Pellini, *Atti R. Accad. Lincei, Roma*, [5] **21**, I, 218 (1912); Morgan, THIS JOURNAL, **34**, 1669 (1912).

[9] Dudley and Jones, THIS JOURNAL, **34**, 995 (1912).

rect. It has seemed, however, to the authors of this paper that, before such a conclusion is accepted as final, further attempts should be made to decompose tellurium; for it is still possible that, as has been pointed out above, a new method of fractionation may give positive results although the methods heretofore in use have failed to do so. In choosing a procedure, it seemed to us that the fractional distillation of a gaseous compound of tellurium offered the best promise of success, and of such compounds hydrogen telluride was selected.

Both Metzner[1] and Baker and Bennett[2] have determined the atomic weight of tellurium that was prepared by the decomposition of hydrogen telluride, but the systematic fractional distillation of hydrogen telluride does not appear to have previously been attempted.

Hydrogen telluride dissociates at a much lower temperature, 0°, than either of its analogues, hydrogen sulfide and hydrogen selenide. It may logically be inferred, therefore, that the hydride of a higher member of the group, such as the hypothetical dvi-tellurium, would break down at a temperature considerably below 0°, and that, if a mixture of the hydrides of tellurium and dvi-tellurium in solid form were prepared with the aid of liquid air and were then allowed gradually to rise in temperature, there might result not only the decomposition of tellurium through the fractional distillation of its hydride, but also the segregation, in the distilling flask, of dvi-tellurium because of the breaking down of its hydride before the boiling point of hydrogen telluride, 0°, was reached.

2. Purification of Material.

The material that was used in this investigation comprised 500 g. of "pure" tellurium from C. A. F. Kahlbaum, Berlin, and about 1400 g. of tellurium of a purity of approximately 85% from the American Smelting and Refining Company.

In the purification of this material the method of Staudenmaier[3] was rather closely followed. The tellurium was dissolved in a slight excess of nitric acid (1 : 1) and there was then added a slightly greater amount of chromium trioxide than was needed to oxidize all of the tellurium to the hexavalent state. The resulting solution was concentrated by evaporation on a water bath until the greater part of the telluric acid was precipitated. This telluric acid, still moist with adhering nitric acid, was placed in a funnel and washed with alcohol. The alcohol reduces the chromium trioxide to chromic oxide which then forms chromic nitrate with the nitric acid that is present and this is removed by the alcohol. Washing with alcohol was continued until the alcohol took on no color, and the telluric acid was then further purified by repeatedly dissolving it

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[1] *Ann. chim. phys.*, [7] **15**, 203 (1898).

[2] *J. Chem. Soc.*, **91**, 1849 (1907).

[3] *Z. anorg. Chem.*, **10**, 189 (1895).

in hot water and precipitating it with concentrated nitric acid. The pure white telluric acid thus obtained was placed in a Büchner funnel, and was washed with absolute alcohol to remove the nitric acid. In this manner about three kilograms of telluric acid that gave no test for either sulfur or selenium was prepared.

This purified telluric acid was then reduced by hydrazine hydrochloride,[1] by adding a concentrated solution of the latter, in small amounts at a time, to a boiling, concentrated solution of the telluric acid. Reduction takes place readily, the reaction being chiefly that expressed in the equation:

$$2H_2TeO_4 \cdot 2H_2O + 3N_2H_4 \cdot 2HCl = 6HCl + 12H_2O + 2Te + 3N_2$$

The resulting tellurium was collected on a filter, and was washed, first with hot water to free it from hydrochloric acid, and then with alcohol to remove the water. It was then dried at a temperature of 105–110°. Tellurium prepared in this manner varies in color from light gray to black, the tint depending upon the conditions pertaining during the reduction.

The filtrate from the reduction of telluric acid by hydrazine chloride, which contains some of the latter compound together with some tellurium tetrachloride, was utilized for the reduction of further amounts of telluric acid; hydrazine chloride and telluric acid were added to the successive filtrates until the concentration of the hydrochloric acid became so great as seriously to interfere with the further precipitation of tellurium. The tellurium was recovered from this solution of its tetrachloride by evaporating the liquid nearly to dryness to expel the hydrochloric acid, treating the residue with water which hydrolyzes the tellurium tetrachloride, and then reducing the suspended tellurium dioxide by hydrazine chloride.

3. Preparation of Metallic Tellurides.

Since it seemed probable that the most convenient means of preparing large quantities of hydrogen telluride would be afforded by the decomposition of a metallic telluride by water or by an acid, tellurides of certain elements were prepared and the yield of hydrogen telluride from each of them was studied.

In the preliminary experiments the telluride was made by heating

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[1] The hydrazine hydrochloride was prepared in large quantities from hydrazine sulfate (Raschig) in the following manner: Hydrazine sulfate was dissolved in hot water and the equivalent amount of barium chloride in solution was added. The liquid was thoroughly stirred by a current of air, and was then allowed to stand until the greater part of the barium sulfate had separated out. A sample of the supernatant liquid was then drawn off and filtered, and this filtrate was tested for barium and for sulfate. A small amount of barium chloride or hydrazine sulfate was added until the final solution contained a very slight excess of barium chloride. The barium sulfate was then allowed to settle out, the supernatant liquid drawn off, filtered, and then evaporated to such point that the hydrazine chloride would crystallize. Recrystallization of this product gave a hydrazine chloride that was free from sulfate and that contained but a very slight trace of barium chloride.

proper amounts of tellurium and the metal in question in an atmosphere free from oxygen. The reaction was carried out in a flask that was made by blowing a small bulb on the end of a piece of combustion tubing that was about 25 centimeters long. This flask was supported in a vertical position, and the air in it was displaced by a current of nitrogen that was introduced through a tube reaching nearly to the bottom of the flask. Either all of the mixture of tellurium and the metal that was to be heated was placed in the flask, or, in those cases where the combination of the elements took place with considerable violence, portions of the mixture were dropped into the heated flask from time to time. The flask was heated by the flame of a Bunsen burner to the temperature at which the union of the two elements readily resulted.

The approximate yield of hydrogen telluride from each sample of metallic telluride prepared in the above manner was determined by decomposing the telluride in the flask in which it had been made. The flask was fitted with a three-hole stopper that carried an inlet tube for the admission of nitrogen, an outlet tube, and a separatory funnel through which the decomposing liquid was introduced. The outlet tube was joined to a chain of apparatus that comprised a test tube containing water, U-tubes containing calcium chloride and phosphorus pentoxide, and finally a test tube containing a solution of cadmium chloride. The telluride was decomposed either by water or by dilute hydrochloric acid. To avoid, so far as possible, the decomposition of the hydrogen telluride during the evaluation of the sample, the water in the test tube next to the flask was first boiled to free it from dissolved oxygen and was cooled by ice and salt during the run; the decomposing liquid, either water or dilute hydrochloric acid, was boiled to free it from dissolved oxygen, and was cooled nearly to 0° before being placed in the separatory funnel; the flask containing the sample of telluride was immersed in a solution of salt that was kept at a temperature of about —10° by surrounding it by a freezing mixture, and the air was completely removed from the apparatus by passing through it a current of nitrogen. After the air in the chain had been displaced, the decomposition of the sample was effected by slowly dropping water, or dilute hydrochloric acid, from the separatory funnel upon the metallic telluride in the flask. The gas that was evolved, which consisted chiefly of hydrogen and hydrogen telluride, passed through the chain of apparatus, was freed from hydrogen chloride by the water in the test tube, was freed from moisture by the calcium chloride and phosphorus pentoxide, and the hydrogen telluride then reacted with the cadmium chloride to form a precipitate of cadmium telluride. The gas was washed and dried before passing it through the solution of cadmium chloride because these operations would be necessary in any subsequent method for the preparation of pure hydrogen telluride, and it was consequently desirable in these preliminary experiments to determine the yield of gas under the conditions that would later pertain. It was noted that the hydrogen telluride was decomposed by the water in the test tube to an extent sufficient to cause the separation of a black, flaky deposit of tellurium. Moreover, the calcium chloride and the phosphorus pentoxide, as well as the walls of the U-tubes that contained these substances, became blackened by tellurium that was set free by the spontaneous decomposition of the gas. It is evident, therefore, that the washing and drying of the hydrogen telluride in the manner above described materially decrease the yield of the gas.

Zinc Telluride.—When a mixture of powdered zinc and powdered tellurium, in equi-atomic proportions, was heated in the flask to dull redness, combination of the two elements took place quietly, the resulting product had a brownish red color, was stable in dry air, and was slowly decomposed by moist air or by dilute hydrochloric acid with the evolution of a mixture of hydrogen and hydrogen telluride in which hydrogen predominated.

Antimony Telluride.—Mixtures of powdered antimony and powdered tellurium in varying proportions melted quietly when the flask was heated, but gave no visible indication of chemical action. When the two substances, in the proportion called for by the formula Sb_2Te_3, were heated together, the product was tin-white in color, stable in the air, and not affected by cold, dilute hydrochloric acid.

Iron Telluride.—When a mixture of powdered iron and powdered tellurium, in equi-atomic proportions, was heated, the reaction took place quietly and a black product, that was not attacked by cold, dilute hydrochloric acid, resulted.

Magnesium Telluride.—Powdered magnesium and powdered tellurium, in equi-atomic proportions, combine vigorously when heat is applied to the mixture, and for this reason this telluride was prepared by successively dropping small amounts of the mixture into the flask. When neither constituent is present in excess, the product is pure white in color. This magnesium telluride is decomposed by moist air with the formation of hydrogen telluride; this, in turn, is acted upon by the oxygen of the air with the liberation of tellurium which forms a black deposit on the surface of the telluride. The compound is rapidly decomposed by water or by dilute hydrochloric acid with the evolution of hydrogen and hydrogen telluride.

Aluminum Telluride.—When a mixture of powdered aluminum and powdered tellurium in the proportion called for by the formula Al_2Te_3 was placed in the flask and the reaction was started by heating the flask to dull redness, the union of the two elements proceeded with almost explosive violence. The product was of a brownish color and was decomposed by moist air more rapidly than was magnesium telluride. When water or dilute hydrochloric acid was brought into contact with the aluminum telluride, there resulted vigorous reaction which was accompanied by the evolution of a large amount of heat and the production of hydrogen and hydrogen telluride.

Of these five metallic tellurides, aluminum telluride gave the highest yield of hydrogen telluride. Calculating the yield on the basis of the tellurium obtained as hydrogen telluride compared to the amount of tellurium employed in the preparation of the metallic telluride, the yield from the aluminum telluride was 10%, a value slightly higher than that obtained for magnesium telluride. In no case did the yield from the latter substance approximate what would be expected from a statement by Berthelot and Fabre[1] to the effect that pure magnesium telluride yields, on decomposition, a gas that is entirely absorbed by potassium hydroxide.

4. Preparation of Hydrogen Telluride from Aluminum Telluride.

The preparation of hydrogen telluride from somewhat larger amounts of aluminum telluride was next taken up. The small flask used in the preliminary experiments was replaced by a Kjeldahl flask of Jena glass of 250 cc. capacity. This was placed upright in a clamp, a current of nitrogen was passed into the flask to displace the air, and the bottom of the flask was heated to dull redness by means of a Bunsen flame. The mixture of powdered aluminum and tellurium was then dropped into the flask in small amounts at a time, the successive additions to the mixture being made only after the union of the elements in the preceding portion was complete. After a few grams of the telluride had formed, the mass became sufficiently hot to cause subsequent portions of the mixture to react without the application of external heat. When the flask became filled with the product it was carefully stoppered to prevent the entrance of moisture. The operation was then repeated in other flasks until about two kilograms of the aluminum telluride had been prepared. The violence of the reaction between aluminum and tellurium, and consequently the amount of the mixture that can be dropped into the flask at a time, depend upon the physical condition of the tellurium, and this varies with the manner of its preparation.

The tellurium and aluminum were first used in the proportion of 3Te : 2Al, but later it was found that a better yield of hydrogen telluride is obtained when a proportionately larger amount of aluminum is used in the preparation of the aluminum telluride. Consequently in the later experiments an excess of about 30% of aluminum above the amount called for in the ratio 3Te : 2Al was employed.

The reaction between aluminum and tellurium is so violent as to cause the expulsion of fine particles of the telluride from the mouth of the flask into the air. These particles readily decompose and form some hydrogen telluride. It is therefore important that the apparatus be placed in

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[1] *Ann. chim. phys.*, [6] 14, 103 (1888).

a hood with strong draft to protect the operator from the possibility of inhalation of hydrogen telluride.[1]

Hydrogen telluride was next prepared by decomposing aluminum telluride with dilute hydrochloric acid. The decomposition of large amounts of aluminum telluride by the addition of water or dilute hydrochloric acid to the entire mass gives a very unsatisfactory yield of hydrogen telluride, for the reason that it is difficult to prevent a marked rise in temperature because of the appreciable heat of reaction between aluminum telluride and water. The apparatus that was finally devised to overcome this difficulty is shown in Fig. 1. With its use it is possible to rapidly bring about the interaction of successive small amounts of aluminum telluride and dilute hydrochloric acid in a small, cooled chamber without allowing air to enter the apparatus, or hydrogen telluride to escape into the room.

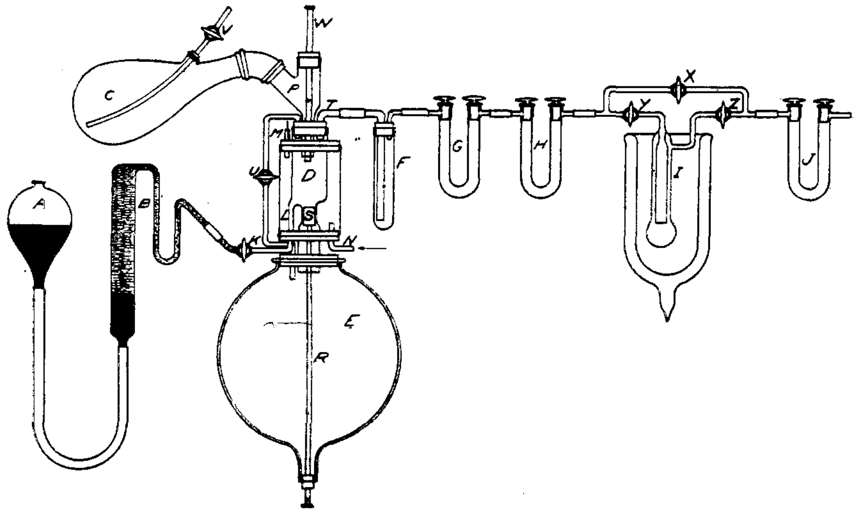

Fig. 1.

The aluminum telluride is placed in the flask C. It is brought into contact with dilute hydrochloric acid in the chamber D, and there decomposed. The slime that is formed in the reaction is drawn off into the flask E. The decomposing liquid, dilute hydrochloric acid, is contained in the tube B and is driven over into the apparatus by the mercury in the level-bulb A. The pear-shaped container C is joined with a hopper, P, by means of a piece of rubber tubing of large diameter and of a length of about 5 cm. The decomposition chamber D is closed at the top by a rubber stopper,

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[1] The inhalation of a small amount of hydrogen telluride causes an inflammation of the throat and nasal passages, and when a larger amount of the gas is inhaled it causes the sensation of an acute inflammation of the lungs.

through which are inserted the lower end of the hopper *P*, the exit tube *T*; and another tube which joins *D* to *E*. The lower opening of *D* may be closed by a rubber stopper, *S*, which is fastened to the glass rod *R*. When *S* is in the position shown in the figure, it closes the lower end of *D* and supports the aluminum telluride during the decomposition. By drawing the glass rod downward through the rubber stopper in the lower end of *D*, *D* is brought into communication with *E*, and any material that has collected in *D* may be washed down into *E*. The chamber *D* is surrounded by a water jacket with inlet and outlet tubes *MN*. The tube *L* serves as an inlet for the decomposing liquid from *B*, and connection between *L* and *B* is made with a short piece of rubber tubing.

The gases that are evolved in the reaction pass through a chain of apparatus that comprises: a test tube, *F*, that contains water free from dissolved oxygen, which absorbs any hydrogen chloride that may be carried over from *D*; a U-tube, *G*, that contains calcium chloride and a U-tube, *H*, that contains phosphorus pentoxide, these two tubes serving to dry the gas mixture; a tube, *I*, in which the hydrogen telluride is condensed; and a U-tube, *J*, that contains calcium chloride which serves to prevent the entrance of moisture into the exit tube of *I*. There is also connected to the outlet tube of *J* a wash bottle that contains either nitric acid or a concentrated solution of potassium hydroxide, and which thus serves to prevent the escape of any hydrogen telluride into the room.

The evolution of hydrogen telluride with the aid of the apparatus was carried on as follows: From 300 to 500 g. of aluminum telluride were placed in the flask *C*, and the air in the entire apparatus was displaced by passing nitrogen gas in at *V*, allowing the gas to escape first through the end of the tail stopcock *K*, then through the lower opening of *E*, and finally out of the exit tube of *J*. The tube *B* was filled with dilute hydrochloric acid that had previously been boiled to free it from air. *B* was then connected to *L* and the air in *B* was driven out through the side arm of the tail stopcock *K*. The rod *R* was then pushed up until the stopper *S* closed the lower opening of *D*.

A few grams of aluminum telluride were now introduced into *D* through the side arm of *P* by raising the container *C*. The dilute hydrochloric acid in *D* was then slowly run into *C* through the stopcock *K*, the liquid in *B* being kept under a pressure somewhat above that of the atmosphere by raising the level-bulb *A* which is filled with mercury. Gas was rapidly evolved in *D* and passed from it through the chain of apparatus. After the decomposition of this portion of aluminum telluride was complete, the rod *R* was lowered, and the contents of *D*, consisting of aluminum hydroxide, aluminum chloride and tellurium, was washed down into *E* by means of more of the acid from *B*. The stopper *S* was then again pushed up into place and the operation was repeated until all of the aluminum telluride in *C* had been decomposed. Throughout these several operations the reaction chamber *D* was surrounded by a cold, circulating salt solution to lessen, so far as possible, the decomposition of hydrogen telluride by the heat produced in the reaction. Pieces of aluminum telluride stuck at times in the inlet tube below *P* and the glass rod plunger *W* served to displace these and push them down into the decomposition chamber. There was a slow evolution of gas, chiefly hydrogen, from the material that had been washed down into *E*, and the gas pressure that was thus caused was relieved, from time to time, by opening the stopcock *U* when the lower opening of *D* was closed by the plug *S*. The exit tube *T* was of rather large diameter to prevent its being clogged by the tellurium and aluminum hydroxide that are carried over by the foaming of the material during the reaction.

The hydrogen telluride that was formed in this manner was condensed in the tube *I* which was immersed in liquid air during the decomposition of the aluminum telluride.

The yield of hydrogen telluride from the decomposition of from 300 to 500 g. of aluminum telluride in this apparatus was found to vary from 2 to 5%, which is much lower than the yield that was obtained with small portions of the material. Moreover, it was found that the gas evolved from the aluminum telluride did not consist entirely of hydrogen and hydrogen telluride. In some of the early experiments white fumes were seen to issue from the exit tube of the decomposition flask (see Part 5). It seemed possible that these fumes might be due to the formation of silicon dioxide from the decomposition of silicon hydride in the gas mixture. To ascertain whether this supposition was correct, about one-fifth of the hydrogen telluride from one of the runs was distilled off, and passed into a dilute solution of potassium hydroxide, which would react with any silicon hydride that might be present to form potassium silicate. The potassium telluride that was formed in the absorbing liquid was decomposed by blowing air through the solution which was then filtered, acidified with hydrochloric acid, and refiltered to remove the small amount of tellurium that separated. The filtrate was then evaporated to dryness. The residue was treated with water to remove potassium chloride, and the silica was collected on an ashless filter, and was dried, ignited, and weighed. A blank determination was also made by acidifying a solution containing the same amount of potassium hydroxide as was used above, and evaporating to dryness. The results were as follows:

	Experiment.	Blank.
Weight crucible + silica	12.1297	12.0837
Weight crucible	12.0997	12.0712
Weight silica	0.0300	0.0125

Weight silica from SiH_4 = 0.0300 — 0.0125 = 0.0175 gram.

It is apparent, therefore, that when the gas is prepared in the manner here described an appreciable amount of silicon hydride is present in the hydrogen telluride. This, probably, is due to the presence of aluminum silicide, the silicon either being present in the aluminum, or being extracted from the glass of the decomposition flask when the telluride is prepared. In the determinations that were made after the presence of silicon hydride in the evolved gas had been detected, the hydrogen telluride was freed, so far as possible, from silicon hydride by passing a current of nitrogen over the liquefied gases at a temperature slightly below the boiling point of hydrogen telluride.

5. Fractional Distillation of Hydrogen Telluride Prepared from Aluminum Telluride.

The hydrogen telluride that had been collected in *I*, Fig. 1, was decomposed by passing it through small flasks of the form shown in Fig 2, these flasks being made from Jena glass tubing of a diameter approximately 1.8 cm. The inlet tube is also of Jena glass, and is ground into the neck of the flask. The flasks were heated in small electric resistance furnaces to 500°. At this temperature the decomposition of hydrogen telluride into tellurium and hydrogen seems to take place most readily,[1] and the resulting tellurium melts and flows together in a globule in which form it may conveniently be weighed.

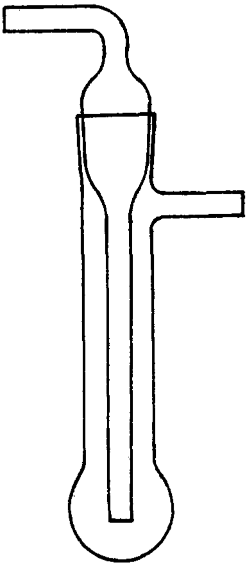

Fig. 2.

The decomposition of the hydrogen telluride was carried out in the following manner: The stopcocks *Y* and *Z* of the tube *I* were closed and the tube was disconnected from the chain of apparatus. One end of *I* was then joined directly to the inlet tube of one of the decomposition flasks by means of a small piece of rubber tubing, the ends of the glass tubes being brought into contact within the rubber. A current of dry nitrogen was then passed into the other end of *I* and through the upper tube *X*, the stopcock of which was open. While the air in the flask was being displaced by the nitrogen, the electric furnace was brought up into position around the flask, and the flask heated to 500° When all air had been removed from the apparatus, the stopcocks *Y* and *Z* were opened, *X* was closed, and nitrogen was slowly passed over the frozen hydrogen telluride and through the flask.

The Dewar tube containing the liquid air was then lowered to such a distance as to cause the hydrogen telluride in *I* to melt and slowly vapor-

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[1] Ditte, *Annales Scientifiques de l'École Normale*, [2] I, 293 (1872).

ize. After tellurium sufficient in amount for one fraction had been collected in the flask, the stopcock *Z* was closed and the liquid air under *I* was raised at such speed that the increase of pressure due to the inflowing nitrogen was counterbalanced by the decrease of pressure caused by the cooling of the apparatus. When the bulb of the flask had been entirely immersed in liquid air and the pressure on the inside of the flask had begun to rise, the stopcock *Y* was closed, the stopcock *X* opened, and nitrogen was again allowed to pass through the flask. Any hydrogen telluride still remaining in the connecting tubes was thus quickly driven over into the flask and decomposed, whereupon the furnace was removed and the flask containing the globule of tellurium was allowed to cool to room temperature. While this was taking place, the current of nitrogen was maintained at a speed sufficient to prevent air from being drawn back into the flask as the latter cooled. When the flask had reached room temperature it was replaced by a second flask, and the operation was repeated until all of the hydrogen telluride that had been collected in *I* had been decomposed. It was possible in this manner to decompose successive portions of hydrogen telluride, and to collect the globules of metallic tellurium without allowing air at any time to come in contact either with the gas or with the tellurium while the latter was hot enough to cause it to unite with the oxygen of the air.

6. The Atomic Weight of Tellurium Prepared from Aluminum Telluride.

The atomic weight of the tellurium comprising the several fractions that were made in the manner just described was determined by dissolving the globule of tellurium in nitric acid, evaporating the solution to dryness and heating the residue until all nitric acid had been driven off and any basic nitrate present had been decomposed. The atomic weight of the sample was then calculated from the ratio of tellurium to tellurium dioxide.

All of the operations—the solution of the tellurium, evaporation and subsequent heating of the residue—were performed in a single flask, Fig. 3, without the removal of the material. The flask was blown from Jena combustion tubing and the float *A* was also made of Jena glass. The relative sizes of the float and the opening of the constriction in the flask are shown in the figure. Two protuberances were blown out just above the constriction to allow space for the float when that occupied a horizontal position.

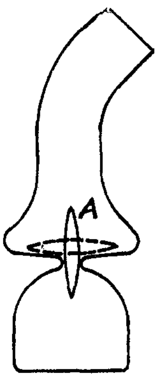

Fig. 3.

The flask and the float were first carefully cleaned, dried and weighed. A globule of tellurium was then placed in the flask, the piece being of such size that it would drop through the constriction. The apparatus was weighed once more to obtain the weight of the tellurium. Nitric acid of 1.25 specific gravity was then poured into the flask until the lower bulb was half filled, and by gently shaking the flask, the float *A* was brought into a vertical position in the constriction and about 3 cm. of distilled water were then poured into the flask. The reaction between the tellurium and the nitric acid is in the beginning so slow as to allow ample time to adjust the float and add the distilled water before any spattering occurs. All of the nitric oxide that is evolved must bubble through the water in the upper compartment, and this serves effectually to prevent mechanical loss of tellurium dioxide during solution. When the tellurium had completely dissolved, the flask and its contents were cooled, whereupon the water flowed into the lower compartment. The float was then brought into horizontal position by gently shaking the flask, and the contents of the apparatus were evaporated to dryness in one of the electric furnaces previously mentioned. The float was then again brought into vertical position to prevent mechanical loss of tellurium dioxide during the next operation, and the temperature of the furnace was raised to 650° at a rate of about 100° per hour. At this higher temperature any basic tellurium nitrate is decomposed into the dioxide and the tellurium dioxide is fused. For convenience in regulating the temperatures during these operations the electric furnaces were first calibrated, amperes being plotted against temperatures.

At the end of the heating, the flask was cooled, and was then weighed, the increase in weight being equal to the weight of the oxygen that had combined with the tellurium. All weighings were made by the method of vibrations with calibrated weights, and the flasks were allowed to stand in the balance case for several hours before weighing.

Several runs were made with the apparatus described under Part 4. The resulting hydrogen telluride was fractionally decomposed, and the atomic weight of the tellurium in each of the several fractions was determined. Forty-five determinations, representing the total number of fractions from the decomposition of the hydrogen telluride obtained in eleven runs, were made. Of these determinations thirty-one gave values between 127.3 and 127.8, the average being 127.6. Sixteen of the determinations gave values between 127.5 and 127.7 with an average of 127.61 for the atomic weight of tellurium. It is clear, therefore, that the method does not give closely agreeing results. This lack of accuracy appears to be due, first, to the large size of the flask and the consequent variation in the amounts of moisture that would condense on its surface and affect the weighings, and, second, to the unsatisfactory character of the ratio Te : TeO_2 for the determination of the atomic weight of tellurium. The difference between the weight of the tellurium that was used and of the tellurium dioxide that was formed from it is relatively so small as to necessitate the employment of large samples if accurate results are to be obtained. In the determinations that were here made, the globules of tellurium ranged from 0.4 to 0.8 g. in weight. With a sample weighing 0.6 g., an error of one-tenth of a milligram in its weight would cause an error of eight-hundredths of a unit in the atomic weight of tellurium. Globules of greater size could not be used without increasing the size of the flask, and this, for the reasons given above, would not have enhanced the accuracy of the determinations. It seems evident, therefore, that this method for the determination of the atomic weight of tellurium does not, under the conditions above described, yield accurate results. The yield of hydrogen telluride from aluminum telluride was, moreover, so small as to necessitate the development of a more satisfactory method for the preparation of hydrogen telluride if the fractional distillation of the gas were to be carried out on a scale sufficiently large to yield conclusive results.

7. Preparation of Hydrogen Telluride by Electrolysis.

Ernyei[1] discovered that hydrogen telluride is formed when dilute sulfuric acid is electrolyzed with a tellurium cathode. This method was examined to ascertain whether it might not be utilized in the preparation of large quantities of the pure gas. It seemed advisable, however, to use an electrolyte other than sulfuric acid because of the possibility of the formation of volatile compounds of sulfur, the analogue of tellurium.

Preliminary experiments with an apparatus similar to that of Hofmann for the electrolysis of hydrochloric acid showed that hydrogen telluride that is free from volatile compounds of phosphorus is formed when the electrolysis is carried on with a tellurium cathode, a platinum anode, and a 50% solution of orthophosphoric acid as the electrolyte. It was also ascertained that the best yield resulted when the temperature of the electrolyte was kept at 0°. At higher temperatures some of the hydrogen telluride would be decomposed; a lower temperature than 0° would be of no advantage because the hydrogen telluride would be liquefied, and would remain in the apparatus until the temperature was allowed to rise above 0°. The run at 0° gave the following efficiencies:

$$\frac{100\ \mathrm{H}}{\mathrm{T}} = 22\%, \quad \frac{100\ \mathrm{L}}{\mathrm{T}} = 27\%, \text{ and } \frac{100\ \mathrm{H}}{\mathrm{L}} = 82\%$$

in which H represents the weight of the tellurium in the hydrogen telluride that was formed; T, the theoretical cathode loss, figured from the amperage and the duration of the run; and L, the actual cathode loss, ascertained from the weight of the cathode before and after the run. The weight of hydrogen telluride that was formed was determined by passing the gas into a solution of cadmium chloride, and weighing the resulting cadmium telluride. The preliminary experiments also show

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[1] *Z. anorg. Chem.*, **25**, 313 (1900).

that for the continuous production of hydrogen telluride over a period of several hours, the following factors are of importance:

(*a*) Minimum distance between the electrodes. The resistance of the electrolyte, and consequently the heating effect of the current, is lessened by decreasing the distance between the electrodes.

(*b*) Minimum space above the electrolyte in the cathode compartments. Small free space above the electrolyte shortens the time between the evolution of the gas and its condensation, and thus decreases the loss of hydrogen telluride by spontaneous decomposition.

It further is advantageous to lessen the diffusion of oxygen from the anode into the cathode compartment so far as possible, and to employ low current density because that favors high reduction efficiency.

With these points in mind, the cell for the production of hydrogen telluride was constructed as shown in Fig. 4.

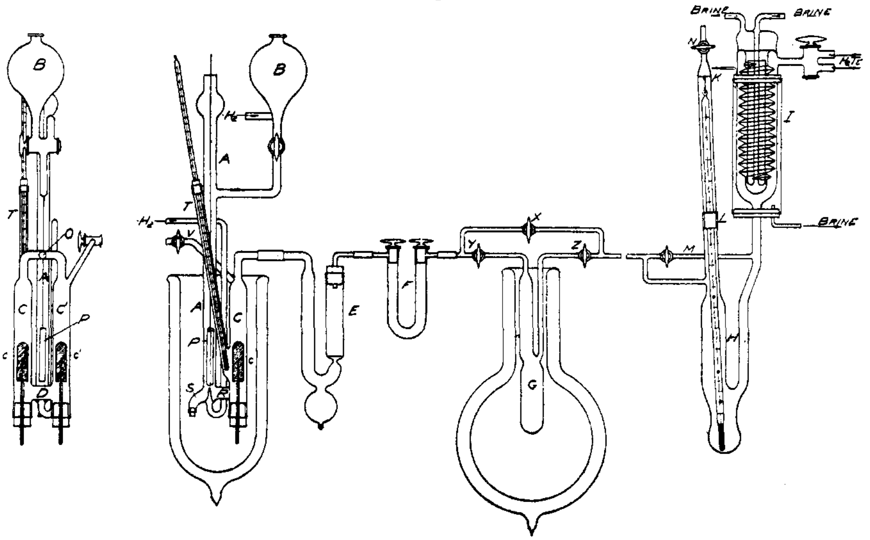

Fig. 4.

Description of Apparatus.—Two views, one from the front and one from the side, of the apparatus in which the electrolysis was carried on, are shown in the figure. The two cathode tubes *C* and *C'* were about 2 cm. in diameter, and were joined together at the top. They had a common outlet *O* through which the hydrogen telluride passed on into the tube *E*. They were furthermore joined together near the bottom by the tube *D* which was 2.5 cm. long. The anode tube *A* was connected to *D* by a short tube, *R*. The tellurium cathodes *c* and *c'* weighed about 50 g. each and were about 1.3 cm. in diameter. They were prepared by fusing tellurium in hard glass tubes that were sealed at one end, inserting a platinum rod in the molten tellurium and holding it in place until the metal solidified. The glass tube was then carefully broken off with a hammer. These tellurium cathodes were held in upright position by forcing the ends of the platinum rods into holes drilled in brass rods, the rods being inserted in one-hole rubber stoppers. In the drawing, the brass rods are represented by the heavy black lines. Those portions of the platinum rods between the tellurium and the brass were encased in glass tubes which were slipped over the platinum rods before the latter were inserted into the brass holders. These protecting glass tubes were pushed into the opening in the rubber stoppers for a short distance. The cathodes were adjusted at such height as to bring their lower ends just above the opening into the anode tube, so as to keep the distance from anode to cathode as small as possible. The stoppers supporting the cathodes reached nearly to the lower side of the tube *D*. This served to prevent the pocketing above each stopper of some of the electrolyte which might be frozen on the application of external refrigerant and thus damage the apparatus.

At the proper height on one of the cathode tubes (*C* in the figure) was attached a side arm, *T*, through which a thermometer was inserted, the bulb of the thermometer being brought nearly in contact with the electrode. This arrangement permitted of accurate control of the temperature within the cell, and it was preferable to the insertion of the thermometer from directly above the electrode through the upper end of one of the cathode tubes: first, because the space above the electrolyte in the cathode tube could thus be made smaller than if the tube were large enough to accommodate the thermometer bulb and the electrode side by side,[1] and, second, it avoided the decomposing action upon the hydrogen telluride of the stopper that must have been used to hold the thermometer in place. If the thermometer had been placed entirely within the apparatus it would have been impossible to read it because the hydrogen telluride was found to decompose and to deposit a mirror-like layer of tellurium on the inner walls of the tube. The zero point on the toluene thermometer that was used was near the upper end of the thermometer, and was consequently above the rubber stopper that held the thermometer in place.

The anode *P* consisted of a small roll of sheet platinum, and was suspended by a platinum wire in the anode tube at such height that its lower end was but slightly above the opening in the side arm. The glass tip, shown in the figure just at the left of *R*, served as the inlet of a current of hydrogen, which was caused to bubble up through the liquid in the anode tube during electrolysis to prevent, so far as possible, solution of the oxygen that is evolved in the electrolyte. The side arm *S*, which could be closed with a small cork, served to draw off the electrolyte when the apparatus was cleaned, or when the electrolyte was to be renewed.

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[1] The measurement of temperature would not have been accurate if the thermometer had been placed above the electrode.

The side arm, attached to the upper part of the anode tube *A*, carried a two-way stopcock and the bulb *B*. By turning the stopcock into suitable position, the electrolyte could be introduced into the apparatus from *B*, and by turning the stopcock through 180°, hydrogen could be passed through it into the apparatus to free the latter from air. A side arm, *V*, attached to the cathode tube *C'*, served as an inlet for hydrogen when that gas was passed through the chain of apparatus, after a run, to drive the hydrogen telluride over into the condensing tube.

Manipulation of Apparatus.—With the apparatus set up as shown in Fig. 4, with the exception that the anode was not yet inserted, the preparation of hydrogen telluride was carried on as follows:

A current of hydrogen was admitted through the side arm of the stopcock below *B* and was passed through the chain of apparatus until the air was completely displaced. While this was being done a cork was inserted in the top of the anode tube *A* to prevent the escape of hydrogen in that direction. When all air had been removed, the stopcock below *B* was turned, and the 50% solution of orthophosphoric acid, that had been boiled to free it from dissolved oxygen, was run in until the liquid stood about 1 cm. above the top of the tellurium cathodes. The cork in the upper end of the anode tube was then removed and the platinum anode was placed in position. The anode and the two cathodes were then connected to the source of current. There was then brought up around the apparatus a large Dewar tube that was filled with a mixture of solid carbon dioxide and alcohol. When the temperature in the apparatus had fallen to 0° a direct current at 110 volts was turned on. The temperature in the cell was kept near 0° by the addition, from time to time, of solid carbon dioxide. It was found that, with no external resistance in the circuit, a current of about five amperes flowed through the cell, and this was found to be too high to permit of thorough cooling by the refrigerant. The current was consequently cut down to about four amperes and maintained at that value. Under these conditions the temperature of the cell could easily be maintained at 0° by the addition of suitable amounts of carbon dioxide. A current of hydrogen was bubbled through the anode liquid throughout the electrolysis.

The gases from the cathode, hydrogen and hydrogen telluride, rose in the cathode tubes *C* and *C'* and passed over into the U-tube *E* which served to catch any phosphoric acid or tellurium that might be carried over by the foaming of the electrolyte. The further arm of the tube *E* was filled with calcium chloride, which served to free the gases from some of the moisture that they contained. An opening in the lower bulb of *E*, which was kept closed during the run by a stopper, made it possible to draw off from the U-tube, between the runs, any liquid material that had collected in the tube. The U-tube *F* was charged with phosphorus pentoxide, which served to complete the drying of the gases. The hydrogen telluride was condensed in the receptacle *G*. The exit tube beyond the stopcock *Z* was connected to two U-tubes that are not shown in the figure, one of these tubes containing calcium chloride to prevent the back diffusion of moisture into *G*, and the second tube containing nitric acid, which would decompose any hydrogen telluride that might pass over from *G*, and thus prevent the escape of that gas into the room. The condensation of the hydrogen telluride in *G* was effected by bringing up around *G* a Dewar bulb containing liquid air.

The apparatus was run continuously for three to six hours at a time. At the end of each run hydrogen was passed in at *V* until the hydrogen telluride had been completely driven over into *G* and there condensed. The stopcocks on *F* and *G* were then closed and the cell and the U-tube *E* were detached, cleaned, and then reconnected to the apparatus for the next run. The manipulation above described was then repeated; but *Y* and *Z* were not opened at the beginning of a run until the air in the apparatus had been driven out through the tube *X* and the electrolysis had been started.

The hydrogen telluride produced during each electrolysis was condensed in *G* until there had collected in all about 40 g. of the substance. The duration of the electrolysis was 35 hours; the average current was four amperes. The efficiencies of the entire run were as follows:

$$\frac{100\text{ H}}{\text{T}} = 12\%, \frac{100\text{ L}}{\text{T}} = 28\%, \text{ and } \frac{100\text{ H}}{\text{L}} = 43\%$$

That this run gave a lower yield than the 82% that was obtained in one of the preliminary experiments is probably due to the difficulty in keeping the electrolyte free from oxygen. The ratio of actual to theoretical cathode loss is nearly the same in both cases.

The production of so large an amount of hydrogen telluride as 40 g., by means of successive electrolyses, rendered it necessary to keep the compound constantly frozen in *G* during several days and nights. It was found that, by inserting some wool in the mouth of the Dewar flask, which had a capacity of three liters, a temperature of —110° C. was obtained in the neck of the flask, and this was sufficiently low to effect the condensation and retention of the hydrogen telluride. The Dewar flask itself stood in a felt holder, and two liters of liquid air were found sufficient to maintain the hydrogen telluride in *G* in a frozen condition for two days, or even longer. Hydrogen telluride always condensed in the upper portion of the inlet arm of *G* during a run and thus clogged the tube. When this occurred the Dewar flask was lowered, whereupon the solid hydrogen telluride melted and flowed downward into the cylindrical container at the bottom of the tube.[1]

[1] It may be proper to add that the preparation of hydrogen telluride by the method

8. Fractional Distillation and Decomposition of Hydrogen Telluride.

The hydrogen telluride that had been prepared and condensed in the tube *G*, in the manner above described, was then subjected to fractional distillation with the aid of the apparatus shown in the right-hand portion of Fig. 4. This consisted of a tube, H, similar in form to *G*, which was provided with a thermometer for the determination of the melting and boiling points of the gas; and of a condenser, *I*, for the fractional distillation of the liquid hydrogen telluride. A Friedrichs spiral condenser was adapted to the purpose in hand by attaching a two-way stopcock to the exit tube, and fitting the condenser with a jacket to permit of external cooling. The thermometer was held in place without the aid of a rubber stopper, by suspending it by means of a platinum wire from a thread of glass, *K*, fused across a glass tube and connecting this enclosing tube to the upper end of *H* by a ground glass joint, *L*. A stopcock, *N*, attached to the upper end of the tube, served for the admission of hydrogen.

The tube *M*, connecting the inlet and outlet tubes of *H*, served as a safety device in distilling the hydrogen telluride from *G* into *H*, in case the inlet tube of *H* became clogged by the frozen gas. Before beginning the distillation of the hydrogen telluride the stopcocks *X*, *Y* and *Z* were closed, the apparatus to the left of *Y* was detached and the exit tube beyond *Z* was fused to the inlet tube of *H*. After this had been done, a current of hydrogen was passed through *X* until the air in *H* and *I* had been driven out. In the meantime, a current of brine, cooled to —5° by a mixture of calcium chloride and ice, was passed through the inner and outer condensers of *I*, and the two branches of the exit stopcock at the top of *I* were connected with Kjeldahl flasks that contained redistilled nitric acid of 1.25 specific gravity. This was prepared by diluting redistilled nitric acid with redistilled water. The exit tube of each flask was joined to another Kjeldahl flask containing nitric acid, which served to retain any hydrogen telluride that might pass through the acid in the first flask.

Stopcock *Z* was now opened, *X* was closed and the hydrogen telluride was distilled over into *H*, by lowering the Dewar bulb from around *G* and immersing *H* in a mixture of solid carbon dioxide and alcohol. After the distillation was finished, determinations were made in *H* of the melting and boiling points of hydrogen telluride. The results of these determinations are given on a later page. The refrigerant around *H* was then removed and the liquid was allowed to vaporize slowly. The gas that escaped condensation in *I* passed over through one of the exit tubes of the stopcock into nitric acid, and was there oxidized to tellurium dioxide.

here described was completed in January, 1911, some time before the appearance of the article by Hempel and Weber [*Z. anorg. Chem.*, 77, 48 (1912)], in which a modification of Ernyei's procedure was described.

When sufficient of this substance had collected in the first flask, the stopcock was turned through 180°, and the gas was passed into the flask attached to the other arm, the first flask being in the meantime replaced by a third flask. This process was continued until the entire quantity of hydrogen telluride had been fractionally distilled and decomposed. The solutions of tellurium dioxide and nitric acid that were thus obtained were evaporated to dryness in the Kjeldahl flasks and the residues, which consisted of tellurium dioxide and basic tellurium nitrate, were transferred to porcelain crucibles and were fused therein to effect the complete removal of nitric acid.

9. Determination of the Atomic Weight of Tellurium.

Lenher[1] determined the atomic weight of tellurium by decomposing weighed amounts of the double salt K_2TeBr_6 by means of chlorine and hydrogen chloride, and weighing the potassium chloride that was formed. The apparent simplicity of this method and the close agreement of the results that were obtained by Lenher through its use led the authors to attempt to employ it. It was found, however, to be impossible completely to free the potassium tellurium bromide from water without causing decomposition of the salt. Lenher states that he removed the last traces of moisture and hydrogen bromide from the compound by letting it stand over soda lime for eight months. Attempts were made to dehydrate the double salt and remove the hydrogen bromide by placing potassium tellurium bromide, that had been carefully recrystallized and centrifuged after each crystallization, in a vacuum desiccator over phosphorus pentoxide and fused potassium hydroxide. In some experiments the salt was allowed to stand at the temperature of the room, and in others it was raised to different temperatures (from 80° to 150°) by means of an electric "hot-plate" within the desiccator, but in no case was it found possible to completely dry the salt without decomposing it to some extent.

Inasmuch as accurate *comparative* determinations of the atomic weight of tellurium in the several fractions would serve the object of the present research quite as well as absolute determinations of the atomic weight of the element, the volumetric method suggested by Brauner[2] and modified by Gooch and Danner[3] was examined and was finally adopted. It was carried out by the authors in the following manner: Weighed amounts (usually about 0.5 g.) of tellurium dioxide were dissolved in an approximately 10% solution of potassium hydroxide and about 25 cc. of sulfuric acid (1 : 1) were added. The solution was heated to about 60°, and an excess of a standardized $N/20$ solution of potassium permanganate slowly added. The oxidation of the tellurium dioxide does not take place

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[1] THIS JOURNAL, 31, 20 (1909).

[2] *Chem. News*, 63, 136 (1891).

[3] *Am. J. Sci.*, 144, 301 (1892). See also Morgan, *Loc. cit.*

very rapidly, and it is accompanied by precipitation of some manganese dioxide. An excess of a standardized solution of ammonium oxalate, of about the same strength as the potassium permanganate, was now added, and the solution was reheated to 60° and was kept at that temperature until the precipitate disappeared. The titration was then completed with the solution of potassium permanganate. The computation of results is based upon the reaction expressed by the equation

$$5TeO_2 + 2KMnO_4 + 3H_2SO_4 = 5TeO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O.$$

To ascertain whether the method would yield concordant results, preliminary experiments were made on fused tellurium dioxide that was obtained by heating purified telluric acid prepared as described in Part 2. Five determinations on different portions of the same material gave results for the atomic weight of tellurium that agreed within 0.12 of a unit. The method was then employed for the determination of the atomic weight of the tellurium in the various fractions prepared as already described, and the results that were obtained are set forth in Table I.

TABLE I.

Fraction.		Atomic weight.	
1		127.52	127.41
2		127.49	127.41
3		127.46	127.45
4		127.43	127.52
5		127.36	127.46
6		127.50	127.51
7		127.59	127.51
8		127.57	127.57
9		127.76	..
10		127.40	127.42
11		127.74	..
12		127.45	127.41
13		127.38	127.43
14		127.41	127.40
15		127.56	127.47
16		127.52	127.54
17		127.44	127.47
Average		127.50	127.47
a	129.35	129.05	127.69
b	129.85	129.08	127.62
c	128.24	127.81	127.48
y	128.06	..	127.52
z	127.72	..	..

Fractions 9 and 11.—The first two determinations on Fraction 9, and on Fraction 11 also, gave low results, about 127.0 for each. The tellurium in each of the solutions that remained after the titrations of these fractions was then recovered and purified. Sulfuric acid was first removed by the addition of an excess of barium chloride, the supernatant liquid decanted and evaporated to a volume of about 150 cc., and the tellurium was precipitated therefrom by an excess of hydrazine chloride. This tellurium was washed until free from chlorides, dissolved in hydrochloric acid, to which a little nitric acid was added, and the resulting tellurium tetrachloride was hydrolyzed with water, complete precipitation of the dioxide being effected by adding ammonium hydroxide to slight alkaline reaction, and then acetic acid to slight acid reaction. This material (TeO_2) was washed by decantation, dissolved in hydrochloric acid, and again precipitated as above. After a repetition of this process, the tellurium dioxide was finally dried and fused. Each fraction was then again titrated with potassium permanganate, and the results that were obtained are those given in the table.

Fraction a.—Some hydrogen telluride escaped condensation during the preparation of the hydrogen telluride, and it was caught in a wash-bottle containing nitric acid. A further amount of hydrogen telluride passed over into this wash bottle whenever the solidified hydrogen telluride was melted to clear the inlet tube of *G*, Fig. 4. The first determination of the atomic weight of the tellurium that collected in this wash bottle yielded a result of 129.35. The tellurium dioxide was then dissolved in nitric acid, the solution filtered, evaporated to dryness, and the product was fused. A result of 129.05 was then obtained. This material was then purified by the method outlined under "Fractions 9 and 11," and a result of 127.69 was obtained.

Fraction b.—On distilling the hydrogen telluride from tube *G* into the tube *H*, a small amount escaped condensation and passed over into nitric acid by which it was decomposed. The first titration of this material gave an atomic weight of 129.85. It was then hydrolyzed twice in the manner described under "Fractions 9 and 11," and the redetermination of the atomic weight gave 129.08. The tellurium was next recovered from all of the various titrations of Fraction *a* and was purified by the process used on Fractions 9 and 11. The resulting material gave 127.62.

Fraction c.—During the determinations of the melting and boiling points of the hydrogen telluride, some of the gas escaped and was decomposed by nitric acid. The value that was obtained from this material was 128.24. Continued fusion of this material brought the result to 127.81. After recovery and purification (see Fractions 9 and 11), 127.48 was obtained as the atomic weight.

Fraction y.—Some tellurium remained in the apparatus after the hydrogen telluride had been completely decomposed. This material showed an atomic weight of tellurium of 128.13 and 127.98, an average of 128.06. After purification similar to that used for Fractions 9 and 11, it showed an atomic weight of 127.52.

Fraction z.—The tellurium which became detached from the cathode during the electrolysis, but which was not converted into hydrogen telluride, was removed from the electrolyte by filtration, purified by the Staudenmaier method and converted into tellurium dioxide. This material gave an atomic weight for tellurium of 127.72.

Discussion of Results.—If the high atomic weight of tellurium is due to the presence of a group analogue of still higher atomic weight, that substance should form a hydrogen compound similar to hydrogen telluride. The hydride of the hypothetical element might be expected, under the experimental conditions herein described, to cause a gradation in the atomic weights of the various fractions, because this substance would probably have a higher boiling point than that of hydrogen telluride, and would consequently tend to concentrate in the later fractions. The earlier fractions would then yield low atomic weights and the later fractions would give higher results. Moreover, low atomic weights would also be obtained with the material from Fractions *a*, *b* and *c*, since these comprise the most volatile portion of the liquefied hydrogen telluride. Fraction *y* would presumably show a high atomic weight because hydrogen telluride would probably be more stable than the hydrogen compound of the hypothetical analogue of tellurium.

If, however, it is assumed that the hydride of the higher analogue of tellurium is not formed under the conditions that pertain in the experiments that have here been described, there would be no gradation in the values for the atomic weights of the various fractions, but the results should be uniformly lower than the atomic weight now accepted for tellurium. The hypothetical analogue would be concentrated in Fraction *z*, and that material should therefore give a higher atomic weight than any of the other fractions.

The results that are given in Table I do not appear to support either of these hypotheses. Fractions 1 to 17 show no gradation in values, nor is the atomic weight of the tellurium in those fractions lower than that obtained with pure tellurium dioxide from other sources. Fractions *a*, *b* and *c* did not yield low results, and the high values that were first obtained were reduced to the now accepted value by purification of the material. Fraction *z* showed an atomic weight that was not materially higher than that obtained with the other fractions, while Fraction *y*, which first showed a high atomic weight, gave a normal value after purification. The high results that were first obtained with Fractions *a*, *b*, *c*, and *y* must be ascribed to the presence of impurities, but the amount of foreign substance in the several samples that were titrated was in each case so small as to practically preclude the possibility of its identification. It is obvious that, since the purification of the material in these several fractions affected all of them alike, it cannot be claimed that the high results first obtained support either of the hypotheses that have been suggested.

It might be urged that the high results first yielded by Fractions *a*, *b*, and *c*, 129.85 to 128.24, indicate that the fractional distillation of hydrogen telluride does actually segregate in certain fractions an element of higher atomic weight than that of tellurium, and that the high values for these fractions are brought down to the now accepted atomic weight because the process of purification of the fractions serves to separate this new substance from the "old" tellurium. To this it may be replied that the methods that were used in the purification of the fractions are not new, and that if they here serve to separate tellurium from an element of higher atomic weight, they would have done so in the hands of other investigators.

The results that are here presented appear, therefore, strongly to indicate that the hypothetical element, dvi-tellurium, does not exist. If this be true, it follows either that the substance now termed tellurium is an element of anomalously high atomic weight, or that which we now term tellurium is a mixture of a "true" tellurium of normal atomic weight with another substance, or perhaps other substances, of slightly higher atomic weight, and of closely similar chemical and physical properties. Yet this suggestion is open to the criticism that if such were the case the element of higher atomic weight must then be placed beyond iodine in the Periodic Table, and would thus be forced into a group of elements that it does not at all resemble. It is true that the Periodic Table contains pairs of elements, such as nickel and cobalt, praseodymium and neodymium, that differ but little in atomic weight, and closely resemble each other in their properties and in the properties of their compounds. Yet the elements in these pairs are adjacent to each other; they are not separated by elements of distinctly different characteristics.

If the high atomic weight of tellurium is not to be explained by the presence either of a group analogue, dvi-tellurium, of much higher atomic weight, or of an element of but slightly higher atomic weight and of closely similar properties, the inevitable conclusion would seem to be that suggested by Kusnezow and by Werner, who hold that tellurium is not complex and that the atomic weight now assigned to tellurium, 127.5, although abnormal, and greater than that of iodine, is nevertheless the correct value.

10. Properties of Hydrogen Telluride.

(*a*) *The Solvent Action of Hydrogen Telluride upon Tellurium.*—When solidified hydrogen telluride, that has been prepared in an atmosphere free from oxygen, is liquefied by allowing the temperature to rise very gradually to the melting point of the compound, there is obtained a liquid that is either colorless or of a very faint straw-yellow tint. If the temperature is allowed to rise above the melting point, or if a trace of oxygen is admitted to the apparatus, the liquid gradually takes on a deep red color and finally becomes opaque. Observations that were made during the distillation of hydrogen telluride (see Part 8) appear to afford an explanation of these changes in color. At the beginning of the distillation the hydrogen telluride in *G* (Fig. 4) was of a pale yellow color. During the progress of the distillation this color gradually increased in depth, and when the distillation was about half completed, the hydrogen telluride in the tube appeared as a dark red, transparent liquid. At this point, clogging of the inlet tube of *H* by solid hydrogen telluride necessitated the stopping of the distillation, which was done by immersing *G* in liquid air. The entrance of outside air into the apparatus during this operation was prevented in the manner described in Part 5. The inlet tube of *H* was then cleared by lowering the refrigerating mixture, alcohol and carbon dioxide, in which the tube was immersed, and allowing the tube to rise in temperature until the solid hydrogen telluride had melted. When the distillation was resumed, it was noticed that the hydrogen telluride in *G* had become black and opaque, and after the completion of the distillation, a thin layer of black, finely divided tellurium was found upon the inner walls of the lower part of the condensing tube *G*. When the hydrogen telluride that had been condensed in *H* was first melted, it possessed a very pale yellow color that was about the same as that of the liquefied hydrogen telluride in *G* at the beginning of the distillation.

Freshly distilled hydrogen telluride is much lighter in color than the liquefied gas that has stood for some time. When liquefied hydrogen telluride is brought under conditions that favor its decomposition, the depth of its color increases. When liquefied hydrogen telluride of pronounced color is frozen, free tellurium is deposited. These observations would seem to indicate that the color of liquefied hydrogen telluride is due to the solution in the liquid of tellurium that has resulted from the decomposition of the compound. When the conditions are such as would tend to prevent the breaking down of hydrogen telluride, the liquefied gas is almost free from color. It is, therefore, probable that pure liquefied hydrogen telluride is colorless.

(*b*) *Melting Point and Boiling Point of Hydrogen Telluride.*—The melting point and the boiling point of hydrogen telluride have been determined by earlier investigators, but since the redetermination of these values could easily be made in connection with the distillation of the compound, it seemed desirable to repeat the measurements. In many determinations of the melting point of hydrogen telluride, it was found that, although the compound uniformly began to melt at —57°, the temperature did not remain constant throughout the melting of the entire mass, but gradually rose. Liquefied hydrogen telluride was found to begin to boil at 0°, but the temperature soon rose to +0.5° where it remained for some time, and then gradually rose toward the end of the distillation. If hydrogen telluride is allowed to diffuse into the tube *K* that surrounds the thermometer, tellurium will be deposited upon the thermometer and the inner wall of *K*, and will render it impossible to read the thermometer. This is prevented by passing a current of hydrogen in at *N*. These determinations were made with a toluene thermometer, and absolute accuracy is not claimed for them. The gradual changes of temperature during the melting and the boiling of the hydrogen telluride are possibly due to the fact that there was no means of stirring the liquid.

Ernyei[1] gives —54° as the melting point of hydrogen telluride and states that the boiling point of the compound lies above 0°. A melting point of —48° and a boiling point of 0° are given by de Forcrand and Fonzes-Diacon,[2] but they do not state how the measurements were made.

(*c*) *The Action of Light upon Hydrogen Telluride.*—De Forcrand and Fonzes-Diacon[3] state that the decomposition of hydrogen telluride is accelerated by the action of light. The same statement appears in an article by Hempel and Weber.[4] In the hope that the gas might prove stable at ordinary temperatures in the absence of light, and thus permit of the determination of its density in light-tight containers, an examination of the extent to which the decomposition of the gas is retarded by the exclusion of light was made.

A small amount of hydrogen telluride was prepared by the electrolytic method already described. The gas was dried and condensed in the usual manner, and was then distilled through a series of bulbs that were sealed to the outlet tube of the condensation tube. The row of bulbs was placed in an inclined position to facilitate the displacement of the hydrogen in the bulbs by the heavier hydrogen telluride. The bulbs, filled in this manner with pure, dry hydrogen telluride, were sealed off with a very small blast flame applied to the constrictions in the tubes that connected the bulbs. The preparation of the gas and the sealing of the samples were carried on in faint red light. Two of the bulbs were placed in diffused daylight, and two were kept in the dark. All of the four bulbs were examined in red light at the end of half an hour and again at the end of ten hours. It was observed that at the end of half an hour there had occurred in all four of the bulbs an amount of decomposition of hydrogen telluride sufficient to give a visible deposit of tellurium upon the walls of the bulbs. At the end of ten hours the walls of all the bulbs were covered almost completely with a mirror-like deposit of tellurium. So far as the eye could judge, the deposit of tellurium in the bulbs that had

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[1] *Z. anorg. Chem.*, **25**, 313 (1900).

[2] *Annales chim. phys.*, [7] **26**, 258 (1902).

[3] *Loc. cit.*

[4] *Z. anorg. Chem.*, **77**, 48 (1912).

been kept in the dark was quite as heavy as in those that had been exposed to the light.

Summary.

1. Magnesium telluride and aluminum telluride were prepared, and the production of hydrogen telluride from aluminum telluride was studied.

2. Hydrogen telluride that was prepared from aluminum telluride was fractionally distilled, and the atomic weight of the tellurium in the fractions was determined by use of the ratio $Te : TeO_2$.

3. A new form of apparatus for the electrolytic preparation of hydrogen telluride was devised, and about forty grams of the gas were prepared.

4. Hydrogen telluride prepared by electrolysis was fractionally distilled, the fractions were decomposed by passing the gas into nitric acid, and the atomic weight of the tellurium in the several fractions was determined by titration of tellurium dioxide with potassium permanganate.

5. Solidified hydrogen telluride is a white crystalline substance that melts to a liquid of a very pale yellow color. Tellurium dissolves in liquefied hydrogen telluride, and the color of the liquefied gas seems to be due to the presence of this dissolved tellurium.

6. Determination of the melting point of hydrogen telluride gave a result of —57°; the boiling point was found to be 0°.

7. Hydrogen telluride in sealed tubes slowly dissociates. This decomposition of the gas is not materially retarded by the exclusion of light.

8. The results of the investigation indicate that the hypothetical element, dvi-tellurium, does not exist.

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SOME ERRORS IN THE DETERMINATION OF THE RARE EARTHS AS HYDROXIDES.

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The writers have observed that, when the rare earths are precipitated as the hydroxides and ignited to oxides, the results are higher than when they are precipitated as oxalates and ignited. Moreover, the former method gives results which are not concordant with varying amounts of the precipitant. Since this method has been often recommended for quantitative determinations it seemed desirable that a careful investigation should be carried out.

As a basis for determining the source of error it was thought advisable to compare the following precipitants: oxalic acid, ammonium oxalate, sodium hydroxide and ammonium hydroxide. If the cause of error were due to the formation of a basic salt, lanthanum being the most