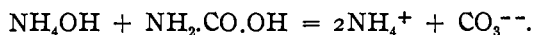


The results of Fenton for the molal concentrations 0.277, 0.185, 0.138, 0.111, are respectively 74.87, 79.62, 84.47, 91.56 per cent carbonate. These agree with ours only in the order of magnitude.

If the reaction be written $\text{NH}_2\text{CO.ONH}_4 + \text{H}_2\text{O} = (\text{NH}_4)_2\text{CO}_3$, then in dilute solution the ratio of carbamate to carbonate might be expected to remain constant. But this equation takes no account of ionization and hydrolysis. We have no information regarding the strength of carbamic acid. If, as might be presumed, it is a very weak acid, then its ammonium salt would be almost completely hydrolyzed; that is, would consist essentially of free ammonium hydroxide and carbonic acid. The ammonium hydroxide from this source would, to a large extent, prevent the hydrolysis of the ammonium carbonate and the reaction would best be written in the form



In other words, we should expect, if these assumptions be correct, the square of the carbamate concentration to be roughly proportional to the cube of the carbonate concentration. This is approximately the case, for if we assume this law and calculate from the percentage of carbonate in 0.2 molal, the percentage in 0.05 molal solution, the result is 88.5%, while the observed was 90.1%.

At present data are lacking for a more careful consideration of this problem. We hope, especially through the study of the conductivity of freshly prepared ammonium carbamate solution, to obtain more definite evidence concerning the strength of carbamic acid.

A SPECTROGRAPHIC STUDY OF TELLURIUM.

BY WM. L. DUDLEY AND E. V. JONES.

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Historical.

In 1869, Mendeléeff,¹ in announcing the Periodic Law, pointed out that the atomic weight of an element can sometimes be corrected as soon as its properties are known, and he said that the atomic weight of tellurium must be not 128, as it was then given, but 123 to 126. This statement at once suggested a problem which challenged the attention of a number of chemists, and has since been the subject of many researches. Various theories have been advanced to explain the anomalous position of tellurium in the periodic system. Tellurium, from a consideration of its general properties, falls into group 6, Series 7, of the periodic table. Its atomic weight, however, now given as 127.5, is higher than that of iodine, which is found in group 7, series 7, with an atomic weight of 126.92, which fact is out of harmony with the principles upon which the periodic table was

¹ *Ber.*, 13, 1799.

constructed. With few exceptions,¹ the solution of this problem has been sought in the direction indicated by Mendeléeff, *viz*, the lowering of the atomic weight of tellurium.

After an investigation extending over a period of six years, Brauner² first reported his conclusions in 1889. He held that tellurium is undoubtedly a complex substance, probably a mixture of three elements, as was the case with the gadolinium of that time. The same year that Brauner's report appeared, a theory was advanced by Grünwald,³ who argued that the coincidence in certain lines in the ultraviolet spectra of tellurium, copper and antimony pointed to a common impurity in these three elements. This impurity he thought to be an unknown element of the tellurium group, with an atomic weight of about 212. This view was strengthened by Mendeléeff,⁴ who in 1899, in illustrating the prediction of new elements through the periodic law, outlined briefly the properties of an unknown element which he called divitellurium. He assigned to it an atomic weight of 212 and placed it in the tellurium group. In 1895 Brauner,⁵ who had continued the work previously cited, using larger amounts of tellurium and better methods of purification, said: "I conclude that it is very improbable that the abnormally high atomic weight of tellurium is due to an admixture of the higher homolog of tellurium having the atomic weight of 214." He suggested as a more probable theory that the ordinary tellurium, like didymium, consisted of "equal parts (atoms) of true tellurium and tetrargon, for $\frac{125.4 + 130}{2} = 127.7$." He pointed out as a significant fact that a contemporary (Lecoq de Boisbaudran⁶) had arrived at identically the same conclusion from an entirely different view point by a process of reasoning based on certain laws of harmony of spectral lines. Staudenmeier⁷ reported during the same year (1895) that fractional crystallization of telluric acid gave no evidence of breaking down the tellurium. A similar conclusion was reached by Norris, Fay and Edgerly⁸ in 1899 through fractional crystallization of potassium bromtellurate. Later and more extensive work by Norris⁹ confirmed this conclusion.

Köthner¹⁰ in 1901 departed somewhat from the ordinary methods of

¹ *Z. anorg. Chem.*, 12, 98.

² *J. Chem. Soc.*, 55, 382.

³ *Monatsh.*, 10, 829; *Abs. J. Chem. Soc.*, 58, 434.

⁴ *J. Chem. Soc.*, 55, 649.

⁵ *Ibid.*, 67, 549.

⁶ *Compt. rend.*, 120, 361.

⁷ *Z. anorg. Chem.*, 10, 189.

⁸ *Am. Chem. J.*, 23, 105.

⁹ *THIS JOURNAL*, 28, 1675.

¹⁰ *Ann.*, 319, 1.

procedure in applying the spectrograph as a test of the purity of the tellurium compounds prepared by the methods previously used, and declared that probably no investigator had yet succeeded in getting absolutely pure tellurium. He found characteristic lines in the spectra of the preparations by Brauner's¹ and Staudenmeier's¹ methods, indicating traces of copper, antimony, silver, arsenic and gold. In a like manner the preparations by Norris, Fay and Edgerly's¹ method showed traces of silver and copper even after numerous recrystallizations. Köthner succeeded in separating all traces of known elements from tellurium and recommended as a very satisfactory process the redistillation under 9 to 12 mm. pressure of the product obtained by reducing with sulphur dioxide the recrystallized basic nitrate of tellurium. This tellurium, however, which was probably of the highest degree of purity yet obtained, he found to exhibit in its ultraviolet spectrum a number of lines coincident with lines in the spectra of copper, antimony, thallium and indium. These coincident lines were shown also by tellurium obtained from Steiner's² diphenyl telluride of constant boiling point, which was free from all known impurities, as shown by the spectrograph. These were not characteristic lines, but they did not change in appearance in the least throughout the various processes of purification. No record is given of their wavelength determinations. Köthner did not agree with Grünwald¹ in attributing these coincident lines to a common impurity in these elements. His conclusions were that these elements must be regarded as having certain properties in common, and that he had obtained tellurium free from all impurities. Gutbier³ in 1905 tried a new method similar to Köthner's, but concluded that no change had been produced in the atomic weight of tellurium. Two years later Baker and Bennett,⁴ after extensive investigations of tellurium covering 13 years, declared in favor of elementary tellurium with an atomic weight of 127.6. In the same year (1907) Marckwald,⁵ by several hundred recrystallizations of telluric acid, obtained 20 fractions which agreed perfectly in properties, thus indicating uniform composition for tellurium. However, his value for the atomic weight 126.85 was lower than that usually given. He repeated his atomic weight determinations by a volumetric method,⁶ which he considered more accurate, and got a mean value of 127.61. Browning and Flint⁷ in 1909, using hydrolysis of a hydrochloric acid solution of tellurium tetrachloride, got some very interesting results. Two fractions were obtained which

¹ *Loc. cit.*

² *Ber.*, 34, 570.

³ *Ann.*, 342, 266.

⁴ *J. Chem. Soc.*, 91, 1849.

⁵ *Ber.*, 40, 4730.

⁶ *Ibid.*, 43, 1710.

⁷ *Am. J. Sci.*, (4) 28, 347.

were designated as alpha (the more easily hydrolyzed part) and beta (the part remaining in the solution). The alpha fraction gave an atomic weight of 126.53, and the beta fraction an atomic weight of 128.97. These results were confirmed by three methods of atomic weight determinations. Viewed in the light of Brauner's conclusions and Mendeléeff's predictions, these results are exceedingly interesting. Flint¹ continued this work, making ten fractions by hydrolysis of the tetrachloride solution, and got fractions of the more easily hydrolyzed tellurium, which exhibited a progressive diminution of the atomic weight. The last fraction, of more than 20 grams, gave by the basic nitrate method, as a mean of seven determinations, an atomic weight of 124.3. The final residue from the less easily hydrolyzed portions was reported as containing a small amount of an unidentified substance very similar to tellurium, though not identical with it in its properties.

The preceding pages give a brief survey of the more important investigations of the abnormalities of tellurium that had been made up to the time of beginning the investigation herein described. Harcourt and Baker² have recently reported on a repetition of Flint's method of fractionation of the tetrachloride. They, however, used the tetrabromide method for determining the atomic weight, and got the usual value 127.54. They discussed Flint's work and attributed his low atomic weight to the presence of tellurium trioxide in his tellurium dioxide, which was used in calculating the atomic weight of the element. The general consensus of opinion favors 127.5 as the accepted figure for the atomic weight of tellurium. However, the work of Marckwald³ in 1907, of Browning and Flint³ in 1909, and especially of Flint³ in 1910 indicates that the question of the homogeneity of tellurium is not as yet finally settled.

Purification of the Tellurium.

The purpose of this investigation was: 1st, to obtain pure tellurium; 2nd, to measure the spectral lines of tellurium; 3rd, to study the effect on the spectrum of tellurium of fractional precipitation by hydrazine hydrochloride; and 4th, to determine the nature of the final residues.

The tellurium which formed the basis of this investigation was obtained as crude tellurium dioxide from the Baltimore Copper Smelting and Refining Company, and purified in this laboratory by one of us, (D) and Mr. P. C. Bowers, in the following manner: The silica present was dehydrated and removed by repeated evaporations to dryness of a hydrochloric acid solution of the crude material and the tellurium dioxide finally dissolved in hydrochloric acid. The selenium was removed by fractional precipitation with sodium sulfite in a cold acid solution. The selenium came

¹ *Am. J. Sci.*, (4) 30, 209.

² *Chem News*, 104, 260.

³ *Loc. cit.*

down first and was filtered off. The tellurium was thrown out of a hot acid solution by adding sodium sulfite until most of the acid had been neutralized and then passing sulfur dioxide into the hot solution. The precipitated tellurium was oxidized with nitric acid and evaporated to dryness twice with hydrochloric acid and taken up in the least possible excess of hydrochloric acid and filtered. Any silver present was left on the filter as the chloride. The tellurium was precipitated again, as above, with sodium sulfite and sulfur dioxide, filtered by reverse filtration using a long stemmed funnel with the large end covered by two layers of a cheese cloth with a filter paper between. The filtrate was sucked into a large bottle by means of a filter pump. The precipitate was digested with hydrochloric acid (1 : 1) and washed thoroughly by reverse filtration with ammonia free water until all of the acid was removed. It was then converted into the basic nitrate by treating it with nitric acid (sp. gr. 1.25) and crystallized out by evaporation at 70°. A portion of the nitrate was recrystallized from nitric acid, but owing to great difficulty in getting it all to dissolve in nitric acid this process was abandoned and the nitrate was heated carefully in a porcelain crucible to convert it into the dioxide. The dioxide was reduced and the tellurium distilled and redistilled by heating to dull redness in a porcelain boat within a silica combustion tube while a current of dry hydrogen was passing through the tube.

Approximately 135 grams of the tellurium, twice distilled in hydrogen, were dissolved in nitric acid and evaporated to dryness twice with concentrated hydrochloric acid to remove the excess of nitric acid. The tellurium tetrachloride which was formed was dissolved in the least possible excess of hydrochloric acid. Twenty fractions of tellurium, approximating 6.25 grams each, were precipitated from this solution by adding hydrazine hydrochloride.

The hydrazine hydrochloride was prepared from hydrazine sulfate by adding a very slight excess of barium chloride and precipitating the excess of barium by carefully adding dilute sulfuric acid. We found, however, that this method was not satisfactory, since the barium sulfate was not completely thrown out, apparently being quite soluble in hydrazine hydrochloride.

The general method of procedure was as follows: A solution of the hydrazine hydrochloride was added to the tellurium tetrachloride solution; and after standing over night at a temperature of about 50° it was heated to boiling to complete the reaction. The precipitated tellurium was collected on a hardened filter paper (which had been previously treated with hydrochloric acid) and washed thoroughly, first with hydrochloric acid (1 : 2) then with ammonia free water, and finally with absolute alcohol followed by concentrated ether. After the ether was removed by

suction, the tellurium was carefully dried in an oven at about 75° . The various fractions were preserved in glass stoppered bottles. The temperature at which the reduction took place was varied somewhat. But so long as it was allowed to finish at boiling temperature it seemed to make no difference whether the hydrazine was added to a cold or hot solution, except that the reduction proceeded more rapidly in a hot solution. There are at least two possible reactions when tellurium tetrachloride is reduced by hydrazine hydrochloride. The equations are: $\text{TeCl}_4 + (\text{NH}_2)_2\text{HCl} \rightarrow \text{Te} + \text{N}_2 + 6\text{HCl}$ and $\text{TeCl}_4 + 4[(\text{NH}_2)_2\text{HCl}] \rightarrow \text{Te} + 2\text{N}_2 + 4\text{NH}_4\text{Cl} + 8\text{HCl}$. The yield of reduced tellurium indicated that the reaction took place almost wholly according to the first equation. This reaction tended to increase the excess of hydrochloric acid present in the solution. But this tendency was overcome by the water introduced with the hydrazine, and in making the fourth reduction several grams of tellurium dioxide, resulting from hydrolysis of the tetrachloride, came down with the metallic tellurium. Each succeeding fraction was likewise accompanied by a

considerable amount of the dioxide. This dioxide was washed into the filtrate with hot hydrochloric acid (1 : 2).

Preparation of Electrodes.

Electrodes were made of the tellurium fractions by a method suggested by one of us (D), as follows: A piece of glass tubing (Fig. 1) about 35 cm. long and 3 mm. internal diameter was plugged with loosely packed asbestos (b) about 5 cm. from one end. The precipitated or powdered tellurium was placed in this tube, and the tube was then clamped in a vertical position and the lower end connected with a hydrogen generator. After the air had been expelled the tellurium was fused by carefully heating the tube up to a temperature just below dull redness. It was found that the tellurium did not stick to the glass tube if the fusion

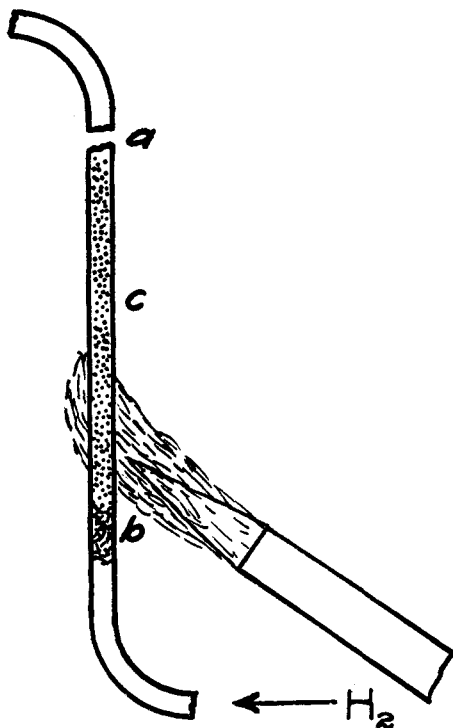


Fig. 1.

began at the bottom. When the tellurium had cooled just below the fusion point, the glass tube was shattered by throwing a fine stream of water on

it so that the glass could be picked off without breaking the tellurium rod. Sometimes the tellurium could be pushed out of the tube without picking the glass to pieces.

Photographing the Spectra.

A large quartz spectrograph, Style C, made by A. Hilger (limited), Optical Works, London, was used in this investigation. It consists of two quartz lenses of 24 inch focus and a dispersion system of one Cornu quartz prism. This gives a spectrum of wave lengths from 8000 to 1900 tenth-meters, which is recorded on a photographic plate 4 by 10 inches, carried in a plate holder which can be shifted by means of a rack and pinion so that one plate may be exposed in a dozen different positions. A quartz sphero-cylindrical condenser is used to focus the light in a sharp line on a vertical slit regulated by a micrometer screw. By modifying the slide for the slit as indicated in (Fig. 2) to that shown in (Fig.3), it

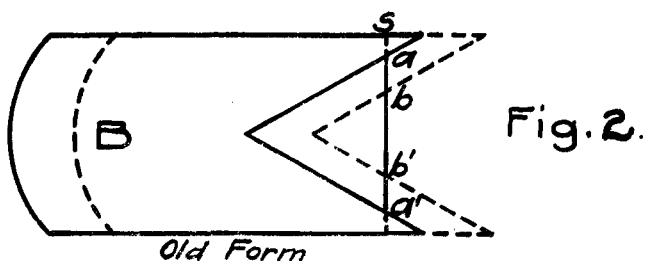


Fig. 2.

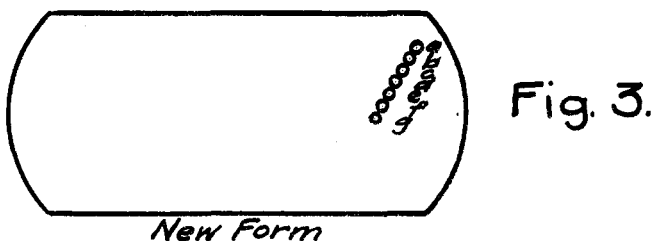


Fig. 3.

was made possible to photograph seven spectra in each position so that as many as 84 spectra may be photographed on a single plate. By using the old form of slide (Fig. 2) only one photograph can be taken in each position of the plate although the length of the slit may be varied. On the other hand, by shifting the new form of slide (Fig. 3) we expose different parts of the slit at openings *a*, *b*, *c*, *d*, *e*, *f* and *g*, and thus make seven photographs, one above the other, without moving the plate. This proved very useful in comparing the spectra of the different elements and of the different fractions of the tellurium, since it made the spectrum so narrow that four could be brought at the same time into the field of the comparator microscope. A Zeiss comparator was used for measuring the positions of the lines.

The photographic plates used were Cramer's Special Spectrum plates, sensitive throughout the entire spectrum, and Cramer's Crown plates, especially sensitive in the ultraviolet region. About 700 photographs of spectra were examined in this investigation.

The spark was furnished by a condenser consisting of four plates prepared especially for this work, using bakelite as the dielectric. The plates are about 40 cm. square and 4.5 mm. thick. The condenser was charged by an induction coil carrying a current of 2.5 amp. under a pressure of about 20 volts supplied by nine storage cells in series.

The principal standard lines were obtained by using copper electrodes, and ammonium nitrate solution with gold electrodes. Solutions of the nitrates of lithium, barium and sodium with gold electrodes were also used for standards in the yellow and red.

The tellurium electrodes were made by the method previously described, from the different fractions and the spectra of them compared. Exceedingly careful comparison of the first, middle and last fractions was made. Two series were chosen, *i. e.*, fractions 1, 11, and 19 in the first series, and 2, 12 and 20 in the second series. Almost perfect photographs of these spectra were obtained, one above the other. There was no difference between these spectra, except that two copper lines (3273.4 and 3246.8) appeared in the last fraction in each series.

Comparison and Measurement of the Spectral Lines.

The spectra of tellurium, copper, antimony and gold were compared by photographing them one above the other. At first the spectrum of the tellurium did not show the presence of either of the other elements mentioned above, but by using heavy voltage on the induction coil and reducing the resistance of the spark circuit to a minimum, a much fatter spark was obtained, which brought out the two copper lines referred to above. These lines were also mentioned by Köthner¹ as being a common impurity in tellurium. In this connection it was noted that Hartley and Adeney² in their measurements of the wave lengths of the tellurium lines, give these lines as tellurium lines with an intensity of 10. *They are not present in the spectrum of pure tellurium.*

In Köthner's¹ report of his spectrographic work he called attention to a "shift" in the extreme ultraviolet lines when the same spectrum was photographed twice in succession, one above the other, on the same plate. This "shift" was investigated and found to be only an apparent "shift" due to moving the plate. We found that no "shift" occurred when our new form of slit cover was used.

¹ *Loc. cit.*

² Watts, "Index of Spectra," p. 136.

The tellurium purified in this laboratory but not fractionally precipitated by hydrazine hydrochloride, though apparently pure by chemical methods, was found to contain traces of copper, iron and silver. Kahlbaum tellurium was also found to contain a trace of copper.

While tellurium can be obtained free from all impurities by fractional precipitation with hydrazine hydrochloride, the evidence of the spectrograph indicates that we have not brought about any breaking down or separation of the tellurium into parts differing in properties. The twenty fractions showed no variations in their spectra except the appearance of the copper lines in the last fractions.

Concerning the apparently coincident lines, mentioned by Köthner¹ and Grünwald,¹ in the ultraviolet spectra of tellurium, copper and antimony, we have noted that there are a few, but we think it probable that wider dispersion would show that the coincidence was only "apparent."

A careful study of the extreme ultraviolet spectrum of tellurium resulted in the discovery of a group of six lines of shorter wave length than any tellurium lines given in Watts' "Index of Spectra," and no record of their previous measurements has been found. They are 2002.6, 2001.8, 2000.4, 1997.6, 1994.8, and 1993.8. It was also found that a number of strong lines given in Hartley and Adeney's¹ measurements as tellurium lines do not appear in the spectrum of our purified tellurium. These lines belong to silver, copper and gold.

We give herewith the following wave length measurements of the lines in the spark spectrum of tellurium as purified by us. We give also in the table the measurements previously recorded by Huggins and by Hartley and Adeney.¹ It is stated above that a number of lines belonging to copper, silver and gold were given by Hartley and Adeney as tellurium lines. The wave lengths, with the symbols of the elements to which they belong, are given opposit the corresponding lines in Hartley and Adeney's table. The intensities range from 1, for lines easily visible, to 10, for the strongest lines in the tellurium spectrum. *O*, is used for lines just visible. *n*, denotes nebulous; *s*, denotes sharp; *b*, denotes broad, the reading of the heaviest part being given; *sn*, denotes a nebulous line which is rather sharply defined. After some of the lines an "A," will be found followed by a ?, indicating that it is possible that this line is an "air" line.

¹ *Loc. cit.*

Huggins ¹ & Hartley & Adeney.		Our measurements;		Other elements present in Hartley & Adeney's Tellurium.		Hartley & Adeney.		Our measurements.		Other elements present in Hartley & Adeney's tellurium.	
Wave length.	Intensity and character.	Wave length.	Intensity and character.	Wave length.	Element.	Wave length.	Intensity and character.	Wave length.	Intensity and character.	Wave length.	Element.
		6690.0	1 n					5062.0	2 n	A?	
6645.0	4	6642.5	2 n			5038.0	4 sd	5038.0	1 n		
		6604.5	1 n					4922.2	1 n		
		6481.6	1 n					4908.1	2 n		
6431.0	10 s	6433.4	4 sn			4895.1 ²	2 nd	4893.8	4 n		
6366.0	1 s	6363.5	2 n					4886.0	2 n		
6347.0	1 n					4866.0	4 nd	4868.0	8 sn		
6290.0	2 s	6289.5	2 n					4842.8	3 n		
6243.0	3 n	6242.4	2 n			4832.0	2 nd	4835.0	5 n		
6228.0	3 s	6227.6	2 n			4785.0	2 nd	4785.5	4 sn		
		6160.4	1 n					4769.0	4 n		
		6084.0	1 n					4737.1	1 n		
6042.0	6 sd	6043.0	2 n					4731.6	4 n		
6010.0	6 sd	6010.0	2 n			4707.5	4 sd	4706.8	4 sn	A?	
5995.0	1 n	5993.6	1 n			4693.0	4 sd	4693.4	5 n		
5970.0	10 sc	5970.4	5 sn			4664.0 ³	1 n	4665.0	3 n		
5934.0	8 sc	5932.0	4 n			4652.0 ³	1 n	4656.2	3 n		
5854.0	4 sc					4602.0	2 sd	4604.2	5 s		
5849.0	4 sd	5850.0	3 n			4599.0 ³	1 n				
5825.1 ²	4 nd	5825.2	2 n					4570.1	3 n		
5805.6 ²	4 nd	5804.4	1 n					4547.4	3 n		
		5761.5	3 s			4544.0 ³	1 b				
5756.0	10 sc	5753.8	6 sn			4487.0	2 sd	4489.4	3 n	A?	
5740.0	2 sd	5742.2	2 n			4480.0	2 sd	4481.8	4 n		
5708.0	10 sc	5710.2	6 s			4436.0	2 sd	4436.2	3 n		
		5666.4	4 sn	A?		4400.0	2 sd	4402.4	3 n		
5646.0	10 sc	5650.5	7 sn					4390.0	2 s		
5618.0	4 sd	5618.8	2 sn			4378.0	2 sd	4377.4	3 s		
5575.0	8 sc	5575.0	6 sn			4364.5	2 sd	4363.8	5 s		
5486.0	6 sd	5486.2	5 sn			4353.0	2 sd	4356.2	5 s		
5476.0	6 sd	5476.0	4 sn			4324.6	4 sd	4326.8	3 s		
5447.0	8 sc	5449.4	6 sn			4301.5	6 sd	4302.6	5 s		
5409.0	4 sd	5410.5	3 sn			4292.7	4 sd	4294.6	3 n		
5366.0	6 sc	5369.5	4 sn			4287.3	4 sd	4289.0	3 n		
5309.0	6 sd	5310.8	3 s			4274.4	6 sd	4276.0	4 sn		
5298.0	2 sd	5299.0	2 s			4259.8	6 sd	4261.8	7 sn		
		5252.4	3 n			4222.1	6 sd	4221.0	5 s		
		5241.5	2 n					4190.2	3 s		
5222.0	8 nc	5220.0	1 n			4180.7	2 sd	4181.4	5 nb		
5172.2 ²	2 sd	5174.5	4 n			4170.3	4 sd	4172.0	2 nb		
5152.2 ²	6 sd	5151.4	1 n					4162.5	3 n		
5134.0	2 nd	5133.6	3 n					4125.5	3 n		

¹ Huggins, *Loc. cit.*
Huggins-Watts' tables.

² The lines are from Thalen-Watts' tables.

³ The lines are from

Hartley & Adeney.		Our measurements.		Other elements present in Hartley & Adeney's Tellurium.		Hartley & Adeney.		Our measurements.		Other elements present in Hartley & Adeney's Tellurium.	
Wave length.	Intensity and Character.	Wave length.	Intensity and character.	Wave length.	Element.	Wave length.	Intensity and character.	Wave length.	Intensity and character.	Wave length.	Element.
4119.7	4 sd	4119.8	3 n	A?		3626.7	4 sd	3627.0	1 n		
4072.7	2 sd	4073.8	7 sn			3617.0	6 sd	3617.4	4 sn		
4061.3	6 sd	4061.5	4 s			3611.0	4 sd	3611.2	2 n		
4054.2	6 sd	4053.4	4 sn			3601.7	4 sd		4 s	3601.1	Au
4048.3	4 sd	4086.6	3 n			3599.6	4 sd				
		4011.6	1 n			3594.5	4 sd	3593.0	3 n		
4006.0	8 sd	4006.5	4 s			3580.4	4 sd				
		3985.2	3 n					3584.0	2 n		
3983.8	6 sd	3982.2	2 n			3551.6	8 sd	3551.8	6 sn		
		3976.8	2 n			3541.8	4 sd		3 s	3541.7	Au
		3970.2	3 n			3533.1	4 sd		5 sd	3533.7	Sb
3968.6	6 sd		5 s	3968.3	Ag			3522.0	4 sn		
3948.0	6 sd	3947.5	3 n			3520.3	8 sd		5 sd	3520.3	Sb
3932.5	2 sd	3932.0	3 n			3510.8	2 sd				
3908.7	2 nd	3907.8	1 n			3496.3	8 sd	3496.8	6 sn		
		3870.0	1 n			3483.7	2 sd	3484.0	3 sn		
3841.3	8 sd	3842.5	6 sn			3480.8	4 sd	3480.0	2 n		
		3805.5	1 n			3474.4	2 sd	3475.0	3 n		
3803.0	4 sd	3801.5	1 n			3465.5	4 sd	3466.0	1 n		
3796.9	2 sd	3797.4	3 n					3457.6	4 n		
3789.0	4 sd	3789.0	2 n			3456.0	8 sd	3456.0	4 n		
3776.0	4 sd	3776.4	2 n			3450.4	2 sd		3 s	3450.4	Cu
3771.0	4 sd		3 s	3771.1	Au			3442.8	5 sn		
3765.0	4 sd	3765.0	2 n			3441.2	8 sd				
3759.0	4 sd		3 s	3759.0	Au			3423.5	0 n		
3754.0	4 sd		3 s	3754.8	Au	3422.2	4 sd				
		3750.0	3 n			3415.3	4 sd		2 sd	3414.7	Sb
		3737.2	4 n			3407.5	8 sd	3407.8	6 nb		
3735.5	8 sd					3382.4	10 sc		10 sc	3382.9	Ag
3726.2	8 sd	3726.0	4 n			3374.1	4 sd	3374.5	3 n		
3716.0	4 sd	3716.7	2 n			3362.4	8 sd	3362.8	6 n		
		3713.5	1 n			3352.1	6 sd	3352.0	3 n		
		3709.6	1 n					3340.8	1 n		
		3708.8	0 n			3329.0	6 sd	3329.1	4 sn		
3698.7	4 sd					3322.7	4 sd	3322.8	2 n		
3683.3	4 sd					3315.8	4 sd	3316.0	2 n		
		3679.0	0 n			3307.1	8 sc	3308.0	2 n		
3676.7	4 sd							3302.2	2 n		
3670.4	4 sd	3671.2	0 n					3295.6	2 n		
3656.4	4 sd					3289.6	2 sc				
		3650.0	3 s					3283.0	5 sn		
3649.2	6 sd	3648.5	3 s					3281.2	5 sn		
3644.3	6 sd	3645.0	3 s			3280.0	10 sc		10 sc	3280.8	Ag
3636.3	4 sd					3273.4	10 sc				

Hartley & Adeney.		Our measurements.		Other elements present in Hartley & Adeney's Tellurium.		Hartley & Adeney.		Our measurements.		Other elements present in Hartley & Adeney's Tellurium.	
Wave length.	Intensity and character.	Wave length.	Intensity and character.	Wave length.	Element.	Wave length.	Intensity and character.	Wave length.	Intensity and character.	Wave length.	Element.
		3278.4	3 n			3004.1	4 sd	3004.2	3 n		
		3269.5	3 n			2996.4	4 sd	2997.0	3 n		
		3266.8	5 n			2988.8	4 sd	2989.0	2 n		
3267.4	2 sd					2976.2	4 sd	2977.4	2 n		
3264.6	2 sd					2975.5	4 sd	2976.0	3 s		
		3261.5	3 n			2973.1	2 sd	2973.8	3 s		
3256.3	8 sd	3257.4	5 sn			2966.1	8 sd	2967.4	6 n		
		3252.4	5 sn			2960.3	2 sc	2960.4	2 n		
3250.8	4 sd					2956.3	2 sd	2957.0	3 n		
3246.8	10 sc		10 s	3247.6	Cu	2950.6	2 sd	2950.8	2 n		
3242.1	4 sd					2948.8	2 sd	2948.8	2 n		
3234.2	4 sd					2945.3	2 sd	2946.0	1 n		
3229.4	2 sd	3232.8	4 nb			2940.8	8 sd	2941.4	6 sn		
3221.8	4 sd	3220.0	3 n			2937.7	4 sd				
3217.6	4 sd					2932.5	4 sd	2932.5	2 n		
3213.3	4 sd	3214.2	3 n			2928.1	2 sd	2929.8	2 n		
3210.4	2 sd	3211.6	3 n			2923.4	4 sd				
3192.2	4 sc					2918.9	2 sd	2919.4	5 n		
3188.1	4 sc	3188.3	3 n			2905.9	2 sd	2906.8	3 s		
		3185.0	4 n			2901.9	4 sd		4 s	2902.0	Ag
3183.7	2 sd					2894.3	8 nd	2895.4	9 sn		
3174.4	4 sc	3175.2	5 s			2893.3	6 sd	2893.8	4 n		
3168.5	4 sd					2877.4	2 sd		7 sc	2877.1	Sb
		3160.4	3 n			2873.6	2 sd		5 s	2873.6	Ag
3158.4	2 sd					2867.7	8 nd	2868.8	8 sn		
3154.1	4 sd	3153.4	2 n			2859.9	6 sd	2860.6	4 n		
3145.7	4 sd					2857.0	8 nd	2857.9	8 sn		
3131.7	2 sd	3132.4	4 s			2844.9	6 sd	2846.4	4 n		
		3129.0	1 n			2840.0	6 sd	2841.0	6 n		
3124.7	2 sd					2836.9	2 sd				
3119.5	4 nd	3119.6	3 n			2834.4	2 sd	2835.0	3 sn		
3107.5	6 sd	3107.8	4 n			2823.2	6 sc				
3098.7	4 sd	3098.2	2 n					2818.8	4 n		
3095.5	4 sd	3096.4	4 n			2815.3	2 sd				
3088.0	4 sd	3090.0	3 n			2813.0	2 sd	2812.0	2 s		
3072.7	6 sd	3073.0	5 n			2799.1	4 sd				
3063.2	2 sd	3063.0	4 n			2795.5	4 sd	2797.0	4 n		
3052.8	2 sd	3052.9	4 n			2791.9	8 nd	2793.2	8 n		
		3050.5	3 n					2778.0	0 n		
3046.0	8 nc	3047.4	8 n					2776.8	0 n	A?	
3022.1	2 sc	3023.2	4 n			2768.6	6 sc	2769.5	8 s		
3016.6	8 sd	3018.0	6 n			2766.5	6sd	2767.0	2 n		
3012.1	4 sd	3012.0	4 n			2766.0	4 se				
		3005.5	4 n					2758.8	0 n		

Hartley & Adeney.		Our measurements.		Other elements present in Hartley & Adeney's Tellurium.		Hartley & Adeney.		Our measurements.		Other elements present in Hartley & Adeney's Tellurium.	
Wave length.	Intensity and character.	Wave length.	Intensity and character.	Wave length.	Element.	Wave length.	Intensity and character.	Wave length.	Intensity and character.	Wave length.	Element.
2756.0	2 sc					2590.1	2 nd	2591.2	3 n		
2751.5	2 nd	2751.8	0 n			2585.0	2 nd	2585.2	3 n		
2745.0	4 sd	2745.5	5 n			2580.1	2 nd		8 s	2580.6	Ag
2743.0	4 sd					2578.0	2 nd	2578.6	3 n		
2739.5	4 sd	2740.0	4 n					2577.0	2 n		
2738.0	4 sd	2737.5	1 n			2574.8	4 sd	2575.0	1 n		
		2733.2	0 n			2572.4	4 nd	2572.4	2 n		
		2724.5	5 sn			2567.8	2 nd	2567.2	0 n		
2723.2	2 nd					2564.1	2 nd	2564.6	0 n		
2720.7	2 sd					2558.7	2 nd	2559.5	2 n		
2718.0	2 sd		6 sc	2717.9	Sb	2549.7	2 nd	2550.2	2 n		
2713.0	2 sd	2711.4	8 n			2543.7	6 sd	2543.5	1 n		
2710.2	8 nd					2536.8	2 nd		2 s	2536.7	Ag
2702.3	2 sd	2703.2	3 n			2533.8	2 sd		6	2533.6	Au
2700.3	2 sd		10	2701.3	Cu	2529.4	8 sc	2530.7	8 s		
2696.6	6 nd	2697.5	5 n			2528.3	2 nc		5 s	2526.9	Cu
2694.1	6 nd	2695.4	5 n			2525.6	2 sd		3 s	2525.2	Cu
2690.2	2 sd	2691.8	3 n					2523.1	1 n		
2688.2	2 sd	2689.0	0 n					2517.8	1 n		
2683.2	2 nd	2683.8	4 n					2511.7	1 n		
2679.8	2 nd	2680.0	4 n			2505.2	6 sd		10 s	2506.6	Cu
		2676.8	1 n						9 s	2506.4	Ag
2674.6	2 sc		2 sd	2674.0	Sb	2502.7	2 sd		3 s	2503.4	Au
2666.0	4 sd	2666.0	1 n					2500.0	5 sn		
		2661.6	3 n			2498.6	6 nd		3 s	2497.8	Cu
2659.4	2 b ^v d	2660.0	4 n			2491.3	2 sc	2492.0	3 sc		
2657.1	4 nd	2656.5	2 n			2490.8	2 nd		2 s	2490.4	Au
		2653.2	1 n			2488.7	2 sd		2 s	2488.3	Au
2648.7	2 nd	2649.5	5 n			2485.3	2 nd		3 s	2485.7	Ag
2647.0	2 nd	2647.6	4 n			2480.9	2 sd	2480.6	2 n		
2642.3	2 nd	2642.5	1 n			2479.6	2 nd				
2637.0	2 sd	2637.5	4 n			2476.7	2 nd	2477.8	1 n		
2634.7	6 nd	2635.4	8 n					2474.2	1 n		
2630.5	2 nd	2631.3	5 n			2473.2	6 sd		8 s	2473.7	Ag
2627.8	4 sd	2628.2	2 n			2469.0	2 nd	2469.8	5 sn		
2624.3	4 sd	2625.0	3 n			2462.0	4 nd		5 s	2462.6	Ag
2621.4	4 sd	2622.5	1 n			2460.2	4 nd		4 s	2460.0	Ag
2617.4	2 sc		2 s	2617.6	Au	2452.8	2 nd	2453.8	1 n		
2613.7	4 sd		6 s	2614.3	Ag	2447.8	6 sd		8 s	2447.7	Ag
2611.3	4 sd	2612.2	1 n			2444.3	2 nd	2445.0	2 n		
2604.4	2 nd	2605.4	4 n			2441.7	2 sc		6 s	2441.9	Cu
2599.4	2 sd	2599.0	4 n			2438.0	8 sc	2438.6	4 n		
2598.1	2 sd		9 sc	2597.5	Sb			2433.5	1 n		
2594.0	2 sd					2432.0	2 nc	2431.8	6 sn		

Hartley & Adeney.		Our measurements.		Other elements present in Hartley & Adeney's tellurium.		Hartley & Adeney.		Our measurements.		Other elements present in Hartley & Adeney's tellurium.	
Wave length.	Intensity and character.	Wave length.	Intensity and character.	Wave length.	Element.	Wave length.	Intensity and character.	Wave length.	Intensity and character.	Wave length.	Element.
2429.7	2 nd		7 s	2430.3	Ag			2299.8	1 n		
2428.2	2 sc		10 s	2428.1	Au	2297.5	2 nd	2297.3	2 n		
2426.7	2 nd	2426.4	4 n			2295.0	6 nc		6 s	2295.3	Cu
2425.0	4 nd		5 s	2424.7	Cu	2291.8	2 nd		4 s	2291.7	Cu
		2423.8	1 n			2288.6	2 nd	2288.5	2 n		
2420.3	2 nd	2420.0	4 s			2280.6	6 nd		8 s	2281.3	Ag
2418.5	2 nd	2418.3	3 n			2277.2	6 nd		6 s	2277.3	Ag
		2415.8	1 n			2275.7	6 nd		5 s	2275.8	Ag
2413.3	8 sc		10 s	2413.2	Ag			2272.5	5 n		
2411.4	6 sc	2411.8	4 n			2266.2	6 nc	2266.0	7 sn		
2403.7	6 nd	2403.7	3 n			2264.2	2 nd		3 b	2264.2	Cu
2400.0	6 sc		6 s	2400.5	Cu	2260.4	6 nc	2259.5	8 sn		
		2397.0	1 n			2256.6	6 nc	2256.2	7 sn		
		2393.0	1 n					2251.0	2 n		
2392.8	4 nd	2392.6	1 n			2250.0	6 nd		6 s	2250.2	Ag
2390.7	4 nd		5 s	2391.0	Ag	2248.0	6 sc		7 s	2248.0	Cu
2386.3	10 nc	2386.3	10 s			2247.3	6 nc		5 s	2247.6	Ag
2383.8	10 nc	2383.8	10 s			2243.3	6 b ^v c		7 s	2243.8	Cu
2377.0	2 nd		5 s	2377.1	Cu	2240.7	2 nd	2240.2	3 n		
2375.3	2 nd	2375.0	3 n					2238.2	3 n		
2370.3	8 sc		10 s	2370.6	Cu	2231.3	2 nc		5 s	2230.9	Ag
		2367.5	2 n			2230.3	2 nc		3 b	2230.5	Cu
2364.7	4 nd		10 s	2364.8	Au	2229.0	2 nc		3 s	2228.7	Ag
2362.8	4 nd		4 s	2362.8	Ag	2226.8	2 nd	2227.4	2 n		
				2359.9	Fe?	2223.2	2 nd	2223.2	1 n		
2359.8	4 nd		10	2359.7		2219.3	6 b ^v c		6 s	2219.6	Cu
										2218.8	Cu
2358.6	6 sd	2358.6	3 n								
2357.0	4 nd	2357.4	2 n			2216.0	2 nc	2216.3	3 n		
		2352.0	3 sn					2215.0	2 n		
2351.7	2 nd	2351.1	3 sn			2211.2	6 nd		5 s	2211.1	Cu
2344.3	2 nd	2344.5	3 n			2209.5	6 nd	2209.0	6 sn		
2340.3	2 nd	2340.4	3 n					2207.4	2 n		
2336.8	2 nd	2336.8	4 n			2202.8	2 nd		3 n	2202.3	Ag
2332.0	8 sd		8 s	2332.1	Ag	2200.1	2 nd		3 s	2200.1	Cu
		2327.6	3 n			2196.5	2 nd		3 s	2196.8	Cu
2325.5	8 sd		8 s	2325.8	Ag	2192.2	6 nc		5 s	2192.4	Cu
2321.0	8 sd		8 s	2321.1	Ag	2189.7	6 nd		5 s	2189.9	Cu
		2320.4	1 n			2186.9	2 nd	2186.8	4 sn		
2317.8	8 sd		8 s	2317.9	Ag	2182.0	2 nd		1 s	2181.3	Cu
		2316.8	1 n			2179.2	6 nc		5 s	2179.3	Cu
2310.1	2 nd	2310.2	2 n			2175.3	2 nd	2175.0	3 s		
		2308.8	2 n			2167.2	2 nd	2167.4	7 s		
2303.7	2 nd		4 s	2303.1	Cu	2165.7	2 nd		4 s	2166.1	Ag
2301.1	2 nd	2300.8	1 n			2159.7	2 nd	2160.0	6 sn		

Hartley & Adeney.		Our measurements.		Other elements present in Hartley & Adeney's tellurium.		Hartley & Adeney.		Our measurements.		Other elements present in Hartley & Adeney's tellurium.	
Wave length.	Intensity and character.	Wave length.	Intensity and character.	Wave length.	Element.	Wave length.	Intensity and character.	Wave length.	Intensity and character.	Wave length.	Element.
2149.7	2 nd		4 s	2149.1	Cu	2108.4	2 nd	2109.2	2 n		
2147.8	2 nc	2147.6	7 n			2103.6	2 nd		2 s	2103.3	Cu
2146.7	2 nd					2100.2	2 nd	2100.8	1 n		
		2143.3	6 sn					2082.2	7 n		
2142.7	2 nd	2142.6	3 sn					2081.2	2 n		
2136.5	2 nd		3 s	2136.1	Cu	2078.5	2 nd		2 s	2079.0	Cu
2135.0	2 nd		2 s	2134.5	Cu			2072.0	2 n		
2125.5	2 nd		5 s	2125.3	Au	2050.8	2 nd				
			3 s	2125.3	Cu	2039.2	2 nd				
2122.5	2 nd		3 s	2122.5	Cu				2 s	2037.3	Cu:
		2121.4	3 n			2032.7	2 nd		2 b	2031.3	Cu
		2119.8	3 n					2002.0	2 sn		
2119.0	2 nd		4 s	2119.3	Ag			2001.3	4 sn		
		2116.8	2 n					2000.0	2 sn		
2116.3	2 nd		2 s	2116.3	Cu			1997.8	1 sn		
2113.3	2 nd		3 s	2112.3	Ag			1994.5	3 sn		
			2 s	2112.5	Cu			1993.7	1 sn		
2110.5	2 nd		9 s	2110.8	Au						

A Study of the Residues.

It was noted in reviewing Flint's work that he reported a small amount of an unidentified substance in the final residues. The amount was too small to admit of thorough chemical investigation. We decided to make a careful chemical study of the final residues after precipitation with hydrazine hydrochloride and to apply the spectrograph for the purpose of determining the composition of them.

The filtrate from the twentieth fraction was reduced to less than 300 cc. by evaporation, and the usual amount of hydrazine hydrochloride added, and fraction twenty-one was thrown down. It weighed 2.22 grams. The filtrate was then further reduced in volume and fraction twenty-two, of 0.5 gram, was precipitated from the boiling solution by adding hydrazine hydrochloride. A twenty-third fraction consisted of a very slight precipitate, which was lighter in color and more finely divided than the preceding fractions. Fractions 21 and 22 were very difficult to fuse. Thinking it might contain some of the dioxide, fraction 21 was washed thoroughly in warm hydrochloric acid (1 : 2) in which the dioxide is soluble. A very little was dissolved, but the remainder seemed as difficultly fusible as ever. It was kept at red heat for 25 or 30 minutes, while hydrogen passed through it, and it was finally partly fused. Fraction 22 was mixed with part of fraction 20 and heated as was fraction 21.

After long continued heating, it was partially fused. The spectra of fractions 21 and 22 were compared with the spectrum of the redistilled tellurium and with the spectra of fractions 9 and 12. There was no difference except the copper lines in fractions 21 and 22. Fractions 21, 22 and 23 were then treated with nitric acid, sp. gr. 1.25. A brownish white residue remained insoluble which was found to be barium sulfate with a trace of tellurium. The nitric acid solution was evaporated to dryness three times with concentrated hydrochloric acid, and a second residue—barium sulfate—remained insoluble in the hydrochloric acid. The hydrochloric acid solution of tellurium tetrachloride was treated with hydrogen sulfide, a reddish brown color resulted, and a brownish black precipitate was formed. When the action seemed complete, ammonium hydroxide was added to excess. At first the mixture became milky, and a curdy white precipitate formed which completely hid the brownish black precipitate. This white precipitate was probably tellurium dioxide. The mixture then darkened and the precipitates went into solution. (There remained undissolved a small finely divided black residue—residue A). The solution was evaporated nearly to dryness and all of the tellurium was precipitated as a mixture of elementary tellurium and tellurous sulfide, and some ammonium salts crystallized out. The ammonium salts were extracted with water, the tellurium mixture was then boiled with concentrated hydrochloric acid, and hydrogen sulfide was evolved. The elementary tellurium was then treated with warm nitric acid and the insoluble residue filtered out, dried, and treated with carbon disulfide, which dissolved the sulfur. The remaining residue was soluble in nitric acid and was added to the above mentioned nitric acid solution. This nitric acid solution was evaporated to dryness twice with concentrated hydrochloric acid and taken up with dilute hydrochloric acid and precipitated with hydrazine hydrochloride. The tellurium thus precipitated was very difficultly fusible, but electrodes were finally obtained (we called this tellurium Z). The spectrum of tellurium Z was compared with that of pure tellurium—fraction 8—and a number of barium lines were found in its spectrum. The two copper lines still persisted also. Tellurium Z was then dissolved in nitric acid. A white residue remained which proved to be barium sulfate. The solution of tellurium Z was evaporated to dryness twice with concentrated hydrochloric acid and taken up in a slight excess of the acid. The tellurium was then precipitated by passing sulfur dioxide into the hot solution, and was washed, dried and fused as usual. It was perhaps a little more difficult to fuse than fractions 8, 9, 10, etc. These electrodes, which we called "tellurium Y," gave a spectrum which was compared with that of fraction 8. The two copper lines (3273.4 and 3246.8) were found in the spectrum of tellurium Y. Otherwise the spectra were identical.

The final filtrate, from fraction 23, was evaporated almost to dryness. It yielded several grams of a white crystallin substance which proved to be hydrazine hydrochloride. The crystals were removed and purified by recrystallization, and the mother liquors were returned to the filtrate which was then evaporated to dryness on a steam bath. A brownish residue remained which seemed to lack definit crystallin form, and had an odor suggesting organic matter. It was digested thoroughly with concentrated nitric acid and evaporated to dryness three times over a low flame. The color of the residue changed to a yellowish brown, and small bunches of octahedral crystals appeared in it. The residue was digested with hot water and the insoluble matter filtered out and dissolved in nitric acid, sp. gr. 1.25. It was found to contain considerable barium and traces of iron, aluminium and tellurium. The water solution gave a greenish yellow crystallin residue—rhombohedra and hexagonal pyramids. Hydrogen sulfide in an acid solution of these crystals gave a brownish color and finally a brownish black precipitate which responded to the tests for tellurium. It was carefully tested for copper with negative results. The filtrate gave doubtful indications for iron. A trace of barium was found to be present. The barium was removed from the entire residue and the solution evaporated to dryness. A greenish yellow crystallin residue remained which was quite hygroscopic. It was dissolved in water containing a few drops of hydrochloric acid and treated with ammonium hydroxide in the presence of ammonium chloride. A white, flocculent, semi-transparent precipitate formed which aggregated on boiling. On standing over night the color of the precipitate changed to a light brownish yellow. The filtrate was evaporated to dryness and heated until the ammonium salts were driven off and a very slight brownish residue remained tinged in two spots with green. The precipitate was thoroughly washed and dissolved in nitric acid, resulting in a slightly yellowish solution. This solution, which we called "unknown No. 1" was concentrated and its spectrum photographed. It gave a number of calcium and copper lines and several other faint lines which were not identified at this time, but later proved to be iron and silver lines. The solution was evaporated to dryness, the residue converted into chlorides and the presence of copper was indicated by the ordinary qualitative tests. The calcium was removed as oxalate in the presence of acetic acid. Ammonium chloride and an excess of ammonium hydroxide were added until a blue color indicated that the copper had gone into solution. There was a slight precipitate similar to the precipitate whose spectrum we had just examined. This precipitate was thoroughly washed and dissolved in nitric acid and included in solution which we called "unknown No. 2."

Residue A was dissolved by boiling with dilute nitric acid and treated with ammonium hydroxide in the presence of ammonium chloride. A

white, flocculent, semi-transparent precipitate formed. It changed in color to a light brownish yellow on standing. This precipitate was washed thoroughly, dissolved in nitric acid and included in solution called "unknown No. 2."

The filtrate from residue A was treated with sodium hydroxide and the ammonia boiled off. A heavy white precipitate formed which was filtered off and washed thoroughly. It dissolved in hydrochloric acid with effervescence. A portion of the hydrochloric acid solution gave a slight muddy color with hydrogen sulfide, and on adding ammonium hydroxide to the solution saturated with hydrogen sulfide a slight, blackish, flocculent precipitate appeared. Further examination showed that the heavy white precipitate was chiefly calcium and that the black flocculent precipitate contained a trace of copper. The calcium was thrown out as the oxalate, from the entire hydrochloric acid solution, and an excess of ammonium hydroxide added, and the solution boiled. A slight, white, semi-transparent precipitate formed which changed in color to a light brownish yellow. It was washed, dissolved in dilute nitric acid, and included in solution called "unknown No. 2."

The spectrum of the solution, "unknown No. 2," was compared with that of ammonium nitrate and the wave lengths of the extra lines determined. These lines indicated positively the presence of calcium, iron, copper and silver.

The study of the final residues has not developed any new evidence on the tellurium problem. In Flint's¹ discussion of his final residues he mentioned a yellow and green residue which he said suggested a possible contamination with iron and copper, but he could find not even the slightest trace of either by the usual tests. It was noted above that the residues from our final filtrate had a greenish yellow color and, again, that the filtrate from which ammonium hydroxide had thrown out a flocculent semi-transparent precipitate left a slight brownish residue tinged with green. This greenish yellow residue was also carefully tested by the usual tests for iron and copper, and gave negative results for copper and doubtful indications for iron. The spectrograph, however, showed the presence of both of these elements. Flint says further: "When an excess of ammonia is added to a solution of the green substance in hydrochloric acid, the precipitate obtained by neutralization of the acid is not completely dissolved by the excess of the alkali. The liquid filtered from this throws out a black substance, apparently tellurium, when acidified and treated with stannous chloride. The precipitate which did not dissolve in the excess of ammonia, when dissolved, after thorough washing, in hydrochloric acid, gives also a black precipitate with the same reagent." The semi-transparent precipitate which was thrown down from our final

¹ *Loc. cit.*

filtrate was also insoluble in an excess of ammonia; and when dissolved in hydrochloric acid, after thorough washing, threw out a black substance when treated with stannous chloride. The filtrate from the ammonia precipitate, after acidifying with hydrochloric acid, was slightly darkened when treated with stannous chloride. From a consideration of these facts it seems possible and even probable that Flint's residues did contain iron and copper, but in such slight traces as to escape detection by means less delicate than the spectrograph.

Since the results of Flint¹ were not confirmed by his method in the hands of Harcourt and Baker,¹ there is no keen disappointment that the results of the method set forth in this paper likewise do not harmonize with his conclusion that he had possibly separated a new element from tellurium.

The fact that the copper which came down in the last fractions was not removed by two subsequent precipitations one by hydrazine hydrochloride, and the other by sulfur dioxide, seems to argue for a large number of fractions as against complete single precipitations or a smaller number of fractions as in the processes of Gutbier¹ and Köthner.¹

The presence of barium and calcium in the residues is not regarded as significant. The barium was from the hydrazine hydrochloride, and the calcium was probably an accidental impurity or from the same source.

Conclusion.

In conclusion, the tellurium problem remains unsolved. We have mentioned three possible solutions, *i. e.*, (1) tellurium is an element, though abnormal; (2) tellurium is contaminated by an admixture of a higher homolog of tellurium having an atomic weight of about 212; (3) tellurium is, like didymium, a mixture of two substances differing but little in atomic weight and remarkably similar in other properties.

We have only added another link to the chain of evidence reaching back over 40 years of research and pointing almost uniformly toward the elementary nature of tellurium. However, the writers are prone to believe that a different answer will be forthcoming sooner or later. The higher homolog admixture does not seem feasible for the following reasons: If this higher homolog, dvtellurium, has an atomic weight of 212 and the correct atomic weight of pure tellurium is, let us say, 125.5, there would be present only about 2.25% of dvtellurium. It is believed that the above described rigorous treatment of 135 grams of material containing only 2.25% of a substance as different from true tellurium as dvtellurium must be from its position in the Periodic Table would have brought sufficient separation to have enabled us to detect it by means of the spectrograph.

On the other hand, if tellurium is, like didymium, a mixture of nearly equal parts of substances differing but little in atomic weight and re-

¹ *Loc. cit.*

markably similar in other properties, we should not expect the spectrograph to reveal this fact to us without more complete fractionation. And the writers believe, though it may not be well founded, that this third possible solution suggests the direction which future investigations of the tellurium problem should take.

Atomic weight determinations of the various fractions of tellurium which the spectrograph has shown to be free from all known impurities are now in progress in this laboratory.

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THE PREPARATION OF FERROUS CHLORIDE BY THE ELECTROLYSIS OF AN ETHEREAL SOLUTION OF FERRIC CHLORIDE.

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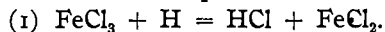
The electrolysis of ferric chloride in ether was attempted in the hope that a chlorine substitution product could be obtained. It was thought that metallic iron would separate at the cathode and that the chlorine liberated at the anode would act on the ether, producing monochlorether.

The ether used (U. S. P.) was treated with calcium chloride and sodium to remove water and alcohol, and then distilled. The ferric chloride was from Merck. It contained six molecules of water of crystallization.

The electrolytic cell was a glass bottle provided with a cork bored with three holes, one for a reflux condenser and the other two for glass tubes carrying platinum electrodes, 3 by 6 cm.

The continued electrolysis of a dilute solution of ferric chloride gave a green precipitate, separating out on the cathode, which increased in amount as more current was passed through the solution. No liquid product was observed. The solution, which was acid to litmus, was neutralized with acid sodium carbonate and distilled, but no new product, other than ferrous chloride could be detected. The green precipitate was found by analysis to contain: Cl, 34.7 and Fe, 28.5. It agreed in every respect with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$.

The conductivity of an ethereal solution of ferric chloride is at first slight, but rises rather gradually and at last remains fairly constant. This may be explained by the increase in the amount of the hydrochloric acid, the first molecules of which come from the slight hydrolysis of the very deliquescent ferric chloride. The amount of acid is increased, during electrolysis, in accordance with the equation



This accounts for the precipitation of ferrous chloride. The electrolysis of the hydrochloric acid formed would give hydrogen and chlorine. The latter might be expected to oxidize the ferrous chloride to ferric, but