In order to produce agreement between the bromide and oxide series of analyses, it would be necessary to assume the unreasonably high value for the atomic weight of silver of 107.90.

If the bromide analysis is assumed to be correct and to yield the value 55.838 (Ag = 107.880), this would indicate incomplete reduction of the ferric oxide, to the extent of 0.0002 gram residual oxygen in the metal resulting from 5 grams of oxide. Such a result would not be at all surprising, however, when the great difficulty in completely converting one solid into another without intermediate fusion or solution is considered.

Whether the atomic weight of silver is taken as 107.880 or 107.870, the averages of the bromide and oxide results, 55.843 and 55.840, when expressed to two decimal places are identical.

The outcome of this research may be briefly expressed as follows:

1. Pure ferric oxide on reduction in hydrogen is found to contain 69.9427% of iron, whence the atomic weight of iron is 55.847.
2. Terrestrial and meteoric material are found to give identical results.
3. When the result of this investigation is combined with that of the analysis of ferrous bromide by Baxter, Thorvaldson and Cobb, the atomic weight of iron is found to be 55.84.

We are greatly indebted to the Carnegie Institution of Washington for generous pecuniary assistance in carrying out this investigation.

CAMBRIDGE, MASS.

THE ALLEGED COMPLEXITY OF TELLURIUM.[1]

BY WILLIAM CONGER MORGAN.

Received September 28, 1912.

The accepted atomic weight of tellurium, 127.5, is higher than that of iodine, 126.9, and the so called anomalous position of tellurium in the periodic system resulting therefrom has been the incentive to many a research inquiring as to the homogeneity of this element. Brauner in 1889[2] was led to believe that "tellurium is not a simple substance" and offered this as an explanation of the lack of uniformity in the results obtained by his many different methods of determining its atomic weight. The same year in the Faraday Memorial Lecture, Mendeleeff stated his belief that with true tellurium, the atomic weight of which is about 125, there is associated another element of higher atomic weight belonging to the sulfur group. For this he suggested the name dvitellurium.

Though much careful work has been done upon this problem, every subsequent investigator has acknowledged his failure to obtain any direct evidence of the complexity of tellurium until the publication of

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[1] Results presented before the Eighth International Congress of Applied Chemistry, September 7, 1912.

[2] *J. Chem. Soc.*, **55**, 382.

the work done by Flint.[1] By fractional hydrolysis of tellurium tetrachloride he claims to have separated two fractions. The true tellurium fraction, apparently pure material, gave an atomic weight of 124.3. From the higher fraction, inferentially still very impure, he obtains the atomic weight of 128.85.

These results have been called in question by Baker and Harcourt.[2] Previously having tried this method without success, they have since repeated part of the work of Flint and were unable to duplicate his results. Still more recently, Pellin[3] reports that he also has not been able to substantiate Flint's results.

In the following pages an attempt to repeat the work of Flint is briefly described. Though larger amounts of material were used and the method pushed to twice as great a number of fractions, no separation of any material with an atomic weight significantly lower or higher than the accepted value was accomplished.

In view of the preceding facts, a brief review of the evidence for the homogeneity of tellurium may not be out of place.

Material has been repeatedly prepared in which neither the spectroscope nor other method of analysis has detected any known impurity. Unknown impurities would belong most probably to the sulfur group. The possibility of impurities belonging to other groups has been reduced to a minimum by the work of Norris,[4] who purified his tellurium by causing it to replace sulfur in a derivative of sodium pentathionate, $Na_2S_4TeO_6$. This compound is stable in the presence of acids but is decomposed by alkalies with the formation of sodium tetrathionate and tellurium. The atomic weight of tellurium, so purified, is normal.

The probability of the presence of an element of the sulfur group with higher atomic weight than tellurium seems small in consideration of the following points.

Sulfur dioxide boils at —8°; selenium dioxide vaporizes between 200° and 250°; tellurium dioxide volatilizes at a red heat. A higher member of this series would doubtless be much less volatil. Fractional distillation of tellurium dioxide resulted in no separation.[5]

Hydrogen sulfide dissociates at 500°, hydrogen selenide at 270°, and hydrogen telluride at ordinary temperatures. A higher member would probably exist only at very low temperatures. Tellurium prepared from

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[1] *Am. J. Sci.*, 28, 347 (1909); 30, 209 (1910); also published *Z. anorg. Chem.*, 64, 112 (1909); 68, 251 (1910).

[2] *J. Chem. Soc.*, 99, 1311 (1911).

[3] *Atti della Reale Academia Dei Lincei*, 21, 218 (1912).

[4] THIS JOURNAL, 28, 1675 (1906).

[5] Norris, *Loc. cit.*

the hydride at ordinary temperatures is presumably free from a higher member and it gives a normal atomic weight.[1]

Sulfuric, selenic and telluric acids are increasingly insoluble in water. A higher member would presumably be still less soluble. Fractional crystallization of telluric acid effected no separation.[2]

The barium salts of these acids are increasingly soluble. A higher member would probably be still more soluble. Fractional solution of barium tellurate caused no change from the normal atomic weight in any fraction.[3]

As a result of the work published within the last dozen years, the evidence for the homogeneity of tellurium seems quite convincing.

Experimental.

Since the purpose of this work was to obtain evidence for or against the existence of two elements with different atomic weights in the fractions separated by hydrolysis of tellurium tetrachloride as claimed by Flint, and not to obtain atomic weight determinations of the highest degree of accuracy, the rapid volumetric method of determining tellurium as set forth in Gooch and Danner's[4] modification of Brauner's permanganate method was adopted.

In brief this is as follows: A weighed portion of fused tellurium dioxide is dissolved in potassium hydroxide and diluted to a definit volume. Measured portions of this solution are acidified with sulfuric acid and an excess of approximately tenth normal solution of potassium permanganate added. About half again as much of a standard solution of ammonium oxalate as is necessary to unite with the excess of permanganate is added immediately and the solution heated to 80°. The solution thereupon becomes clear and is titrated back with permanganate. From the actual amount of permanganate used, the molecular weight of tellurium dioxide is calculated and from this the atomic weight of the element.

Flint claimed to have reduced the atomic weight of tellurium from 127.5 to 124.3, a difference of 3.2 units. The permanganate method is accurate to within one drop of permanganate, which with a tenth normal solution means a difference of 0.45 in the atomic weight of tellurium. Whatever may be said against the use of volumetric methods in atomic weight determinations, the method used by us was sufficiently accurate to detect at least one-sixth of the difference for which we were looking.

As is set forth below, we failed absolutely to obtain any progressive diminution in the atomic weight of tellurium as claimed by Flint. Yet

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

[2] Baker and Bennet, *loc. cit.*

[3] Baker and Bennet, *ibid.*

[4] *Am. J. Sci.*, 44, 301 (1905).

the result of our atomic weight determinations constantly ran about 0.3 of a unit lower than the accepted value for tellurium. We did not have the time to ascertain the cause for this constant difference, but in the last days of our work we checked our volumetric results on one part of our material by the gravimetric basic nitrate method. One determination gave 127.5; the duplicate determination was accidentally lost. This one result indicates that our material is not different from that used by other investigators.

The experimental work was largely performed by Wallace K. Gaylord, Earl C. Lane and Margaret Engle under the direction of the writer. Our permanganate was standardized against purified oxalate and the ammonium oxalate against permanganate. Standardized burettes and Merck's blue label or Baker's analyzed chemicals were used throughout the work.

Through the courtesy of Mr. Walter T. Page, manager of the Omaha, Nebraska, plant of the American Smelting and Refining Company, ten pounds of tellurium were obtained. According to data furnished by the company, their tellurium bars run 99.8–99.9%, the remaining 0.1–0.2% consisting principally of selenium with traces of copper, lead and gold. The results of our work with the material used and of a careful qualitative analysis confirm this composition; for the only impurities for which definit tests could be obtained were selenium, copper and gold. No evidence of the presence of bismuth or antimony could be obtained. From the preceding statements it is evident that the material with which we started was remarkably pure when compared with that of other investigators using the residues from electrolysis.

Between five and six pounds of this material were dissolved in *aqua regia* and repeatedly evaporated to dryness with concentrated hydrochloric acid until chlorine could no longer be detected. The residue was dissolved in the least possible amount of concentrated hydrochloric acid and a preliminary hydrolysis according to the method of Flint run through with in order to get a general idea of the process. The solution, placed in large earthenware jars, was heated with steam and hot water added from time to time until a total volume of nearly twenty gallons of solution at the temperature of 100° was obtained. After standing over night, the solution was siphoned off from the heavy pure white crusts of tellurium dioxide, reheated with steam, neutralized with ammonium hydroxide and brought back to faintest acid reaction with acetic acid. After standing over night once more, the cold solution was siphoned and filtered from the additional tellurium dioxide which had separated.

The material obtained under these conditions is always much less dense than that which separates from the hydrochloric acid solution and, in the earlier hydrolyses, had a bluish cast due to inclusion of copper salts.

Since the solution, when tested with stannous chloride, still indicated the presence of tellurium, it was heated to boiling and treated with stannous chloride. In the first three hydrolyses this procedure was followed. After this it was learned that a slight increase in the amount of acetic acid present would cause the tellurium to separate completely as was stated by Browning and Flint.[1] Since the material thus separated was more soluble than any other and according to Flint should have a higher atomic weight, it was specially purified and determined as stated later.

The filtrate containing large quantities of ammonium chloride, when evaporated to dryness and gently heated, turned reddish, indicating selenium. After two hydrolyses, however, no trace of selenium appeared in this place.

When material which separated from the hydrochloric acid solution was used, except in the product of the first hydrolysis, no test for selenium could ever be obtained by the method of Norris, Fay and Edgerly[2] which is claimed to detect one part in one hundred and fifty thousand.

Flint states that the method of hydrolysis of tellurium tetrachloride is a very effective way of getting pure material. These preliminary results indicated that the impurities present in our material would be speedily removed and that the portion separating from the hydrochloric acid solution would rapidly reach a high degree of purity. We determined, therefore, to proceed with the hydrolysis as outlined by Flint, without previous purification of the material by distillation and other methods which, with large amounts of material, would be time consuming.

The total amount of tellurium dioxide obtained as the result of the preliminary hydrolysis just described was 2925 grams. This was subjected to fractional hydrolysis ten times repeated, following the directions and preserving the concentrations given in Flint's article, except that the solution was kept heated by passing in steam as previously noted. More than 90% of the tellurium dioxide was recovered each time from the hydrochloric acid solution and this fraction only was subjected to subsequent hydrolysis. The material was pure white. A portion taken after the fifth hydrolysis and one from the tenth hydrolysis, when fused, turned a light straw color. Atomic weight determinations were made from these portions. The first gave the result 127.20 as an average of two determinations. The second gave 127.24 as an average of four results.

The proportion of the original material obtained by us in the first fraction after ten hydrolyses was considerably larger than that obtained by Flint and it seemed probable that in his work he did not have "the

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[1] *Am. J. Sci.*, 28, 112.

[2] *Am. Chem. J.*, 23, 105 (1900).

least possible amount of hydrochloric acid" that will dissolve the dioxide, as his directions state.

In order to be certain that possible impurities were not affecting our results, we then set about purifying our material by the most approved methods. Nearly a kilogram of dioxide that had been fractionally hydrolyzed ten times was dissolved in hydrochloric acid and reduced by sulfur dioxide obtained from the liquefied gas. This process was repeated again and on a portion of the material so purified, atomic weight determinations showed no significant change; 127.23 was the average of seven determinations by two different individuals, the greatest variations being 126.86 and 127.49.

Five hundred grams of tellurium, that had been twice purified by sulfur dioxide after being ten times hydrolyzed, were oxidized with nitric acid, ignited and evaporated to dryness twice with concentrated hydrochloric acid. The residue was taken up with concentrated hydrochloric acid and again subjected to fractional hydrolysis ten times repeated. This work was carried on in Jena glass exactly as Flint directs except that some hydrochloric acid in excess of "the least possible amount" necessary to dissolve the dioxide was always present. In the light of our previous results, we made this change in order that we might approximate more nearly the proportions obtained by Flint in his work. After the tenth hydrolysis but 35 grams of dioxide remained. An atomic weight determination made from this material gave 127.2.

This 35 grams of dioxide, obtained after fractional hydrolysis twenty times repeated from material twice purified by the sulfur dioxide method, was then fused with potassium cyanide in an atmosphere of illuminating gas. The melt was dissolved in water and from the claret colored potassium telluride solution, elementary tellurium was precipitated by air purified by barium hydroxide. The tellurium so obtained was distilled from a porcelain boat in a quartz tube in an atmosphere of hydrogen prepared by electrolysis of barium hydroxide. The atomic weight of the distilled tellurium was unchanged from the values previously obtained, 127.22 being the average of seven determinations, the greatest variations being 127.12 and 127.55.

The most soluble portion of tellurium dioxide, obtained by stannous chloride from the earliest hydrolyses as previously stated, was purified twice by sulfur dioxide, once by potassium cyanide and then distilled. The atomic weight of this was not significantly different from the other portions. According to Flint, this material should have given higher results, yet the actual figures were slightly lower than any other obtained. The average of three determinations was 127.11.

The agreement between the atomic weight determinations made on material which had been purified only by hydrolysis of the tetrachloride and others made on material subjected to the most approved methods of purification indicates that the material with which we worked was pure; but even with the large quantities which we had, we were unable to find any indication of a progressive diminution of the atomic weight of tellurium.

UNIVERSITY OF CALIFORNIA, May, 1912.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, COLLEGE OF THE CITY OF NEW YORK.]

A STUDY OF THE SENSITIVENESS OF THE BEAD AND LEAD DIOXIDE TESTS FOR MANGANESE WITH SPECIAL REFERENCE TO THE INTERFERENCE OF IRON.[1]

BY L. J. CURTMAN AND A. D. ST. JOHN.

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The object of this work was to determin, first, the delicacy of the bead and lead dioxide tests for manganese when this metal alone is present and, second, the influence of iron on these tests, since in the ordinary qualitative procedure, the manganese and iron are tested for in the same precipitate.

The Bead Test.—The bead tests were made in the customary way; that is, a sodium carbonate bead on a loop of platinum wire of approximately 3 mm. in diameter with a volume of about 0.03 cc. was fused with a small quantity of the metallic compound, slightly cooled, and then touched while still quite hot to powdered potassium chlorate. A special procedure, referred to below as "reheating," consisted in bringing the carbonate bead containing the manganese compound and adhering potassium chlorate into the upper part of the Bunsen flame, heating to quiet fusion,[2] and finally cooling, preferably by contact with a cold surface, such as a porcelain plate, until almost cold. By this "reheating" process a more intense coloration was produced, and in cases where large amounts of iron were present, it had the effect of concentrating the coloration in certain parts of the bead notably near the wire.

Tests were first made to determin the minimum quantity of manganese which would give a green coloration to the bead. To this end, one drop (0.05 cc.) of a standard manganese chloride solution was carefully absorbed in a sodium carbonate bead that had been previously fused and cooled; the wet mass was then slowly and cautiously dried by heating the wire (away from the bead) and finally fused and brought in contact with potassium chlorate. This procedure obviated the apparent difficulty of in-

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[1] Read before Section I (Analytical Chemistry) of the Eighth International Congress of Applied Chemistry, September 11, 1912.

[2] Care must be exercised in this fusion to lose none of the bead through sputtering, which may be caused by the use of too much chlorate or by too rapid heating.