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ON THE ELEMENTARY NATURE AND ATOMIC WEIGHT OF TELLURIUM.

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SOME years ago Norris, Fay and Edgerly[1] undertook a study of the elementary nature of tellurium in order to discover, if possible, the cause of the anomalous relation of the element to the periodic law. Up to the time of the publication of the work reported by them, no systematic study of this problem had been described. A number of investigators had determined the atomic weight of tellurium, after what appeared to be a careful purification of the compounds to be analyzed. The methods of purification used, however, were not of such a nature as to be relied upon to free the compounds investigated from undiscovered elements. With this fact in mind an investigation was undertaken. Since the work was started, great activity has been shown in this field, and a number of papers have appeared on the atomic weight of tellurium. The most noteworthy is that of Köthner,[2] to which the reader is referred for a full historical account of the subject.

The work about to be described was inspired by a statement in the Faraday memorial lecture delivered by Mendeléeff in 1889. In discussing the periodic law Mendeléeff recounts the great service which the law has rendered in bringing about the correction of a number of atomic weights. In seeking to explain the

[1] Am. Ch. J. 23, 105.

[2] Ann. 319, 1.

high value of the atomic weight of tellurium, he expresses the opinion that the so-called element consists of two elements: one, true tellurium with an atomic weight of approximately 125, and the other, an element with a higher atomic weight, which would find a place in the periodic classification in the vacant space under tellurium. To this undiscovered element Mendeléeff gives the name dvitellurium. He sketches the chemical and physical properties of such an element as he had already done so successfully in other cases.

It was to test this hypothesis that the work which has been published and that described below were undertaken. In order to make the study of the problem complete, it seemed necessary to endeavor to discover first, whether an undiscovered element, which did not belong to the sulphur group, was present in tellurium, and second, whether the hypothesis of Mendeléeff could be given any experimental basis.

In seeking a solution of the first problem, a sample of tellurium, which had been freed from all known elements, was converted into a compound of the formula $Na_2S_4TeO_6$. This substance is a derivative of sodium pentathionate in which one sulphur atom has been replaced by one of tellurium. From this compound the tellurium was recovered by means of a reaction which is characteristic of pentathionates. Determinations of the atomic weight of the tellurium, which had been purified in this way, gave as a mean from several experiments the value 127.46.[1] This number was identical with that obtained with a sample of the element which had not been subjected to this particular method of treatment. As it is improbable that an element not in the sulphur group would show the power to replace, in part, sulphur in such a characteristic compound as sodium pentathionate, the conclusion can be drawn that tellurium contains no element which does not show the characteristic reactions of the sulphur group.

In order to test experimentally the hypothesis of Mendeléeff, carefully purified compounds of tellurium were subjected to fractionation. In the paper already published an account is given of the study of the products resulting from a fractional

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[1] For the atomic weights used in the calculation see p. 1683. If no vacuum correction is made and 14.04 is taken as the atomic weight of nitrogen this value becomes 127.62.

crystallization of the double bromide of tellurium and potassium. Atomic weight determinations of the element obtained from these products agreed with one another within the limits of accuracy of the method used. Notwithstanding this result the work was continued, as it was thought that the breaking down of the salt by crystallization might not have been effected on account of the fact that its constituents were isomorphous with each other. The method described below, which was finally selected to test the question, involved the study of the products resulting from the fractional distillation of tellurium dioxide.

Other investigators have used compounds which have been distilled. Brauner used sublimed tellurium tetrabromide in one of his atomic weight determinations. As the difference between the boiling-points of the bromides of selenium and tellurium is not great, it is evident that a long-continued process of fractionation would be necessary to free tellurium bromide from the analogous compound of dvitellurium. Since this work was started, Köthner has determined the atomic weight of distilled tellurium. The difference between the boiling-points of selenium and tellurium is such that it would be reasonable to expect that another element in the same family with a higher atomic weight would have a boiling-point not far from that of tellurium. It appeared from the above-mentioned facts that it was worth while to re-study the problem, if a better method could be found. The properties of the oxides of sulphur, selenium and tellurium are such, that it seemed that a study of tellurium dioxide would give results which would furnish a definite answer to the question as to the elementary nature of tellurium. Sulphur dioxide boils at —8°, selenium dioxide is volatile at 200–250°, and tellurium dioxide is converted into vapor slowly at a bright red heat. In the light of these facts it is highly probable that the oxide of another element in the same family, with a higher atomic weight, would be very much less volatile than is tellurium dioxide, if volatile at all at the temperature of the Bunsen flame.

The oxide investigated was prepared from a sample of nitrate which had been carefully purified. The source of the material and the methods of preparation and purification used are described in detail in the paper cited above. In the distillation of the oxide the process was stopped after about three-quarters of the product had been volatilized. The part which had distilled was redistilled, until as before three-quarters of it was collected. This process of fractionation was repeated five times. The oxide was distilled from platinum at the highest temperature obtainable with a Bunsen burner; under these conditions the oxide was collected at the rate of about 0.15 gram per hour.

The atomic weights were determined of the tellurium in the first residue, which should have contained the less volatile oxide, and of the tellurium in the oxide which had been sublimed five times. As a standard for comparison the atomic weight of the tellurium in a sample of oxide which had not been sublimed was determined. The method of determining the atomic weight which was used was that first described in the paper by Norris, Fay and Edgerly already cited, namely, the conversion of the nitrate into the oxide. This method has recently been used with success by Köthner.

The results were as follows: The average atomic weight obtained in the case of the tellurium from the undistilled oxide was 127.50. The average of three determinations of the value, when the oxide which had been distilled five times was used, was also 127.50. The original residue from the first fractionation gave the atomic weight 127.46. It is evident from these results that the fractional distillation effected no decomposition in the tellurium dioxide. The mean of all the values for the atomic weight, agrees well with the most trustworthy determinations which have been published, when these are calculated on the same basis.

The results seem to the writer to furnish positive evidence in favor of the elementary nature of tellurium. With a difference of about 250° between the boiling-points of sulphur dioxide and selenium dioxide, and a difference of 500° to 600° between the same constants for selenium dioxide and tellurium dioxide, it is evident, from all analogies in the properties of compounds of members of the natural families in the periodic classification, that the oxide of an element which should find its place in the formulation of the law in the vacant space under tellurium, should be very much less volatile than tellurium dioxide. Its separation by the process used should have been at least in part effected. Even if tellurium contains an element which does not belong to the sulphur family, the possibility of its oxide having the same volatility as that of tellurium dioxide is very remote. As there was no evidence of even the slightest change in the properties of the compound, or in the atomic weight as a result of the tests applied, and as these tests seem to be reliable and well suited to answering the question, the conclusion can be drawn that the statement that tellurium is an element rests upon a firmer experimental basis than heretofore.

EXPERIMENTAL.

The source and preliminary purification of the material used in this investigation are described at length in the paper already cited. A sample of the basic nitrate of tellurium which had been recrystallized three times from nitric acid was made use of in the work. From this the oxide was prepared by heating at increasing temperatures until all nitric acid had been removed.

About 25 grams of the oxide were fractionally distilled. The point at which tellurium dioxide volatilizes is so high it could not be distilled in a tube in the usual way. After tests of a number of methods that selected was as follows: The oxide was heated to bright redness in a platinum crucible, over which was placed a funnel with the stem bent at right angles. To this last was attached a glass tube provided with a cork and an exit tube, the open end of which was covered with filter-paper. A rapid stream of air was drawn through the tube and funnel. The tellurium dioxide which had been vaporized was swept through the funnel and was collected as a fine powder which settled in the tube and on the paper which covered the exit from the tube. When the crucible which contained the oxide was heated to bright redness, between 0.1 and 0.2 gram of the oxide distilled in one hour.

The distillation was started with about 25 grams of tellurium dioxide. This was heated until a residue of 7 grams remained. The 18 grams which had been vaporized were again distilled until there was a residue of about 3 grams. The twice distilled oxide was redistilled until about 12.5 grams had been collected. The process was repeated and 8 grams were distilled off. In the fifth distillation the oxide which was collected weighed about 6 grams.[1] The fractions of the oxide resulting from the distilla-

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[1] The author gladly acknowledges his indebtedness to Mr. C. F. Swan, of the Massachusetts Institute of Technology, who carried out the fractioning of the oxide, which was a tedious process, requiring a very long time for its completion.

tion, were converted into the basic nitrate, recrystallized twice from nitric acid, and finally purified for analysis as described below.

In endeavoring to test the question whether tellurium contains an unknown element which does not belong to the sulphur group, another method of purification was made use of. Facts which were reported by Norris and Fay in their papers on the volumetric estimation of selenium and tellurium suggested a convenient way of attacking this problem. It was shown that a reaction represented by the following equation takes place when selenium dioxide, sodium thiosulphate and hydrochloric acid are brought together in aqueous solution:

$$SeO_2 + 4Na_2S_2O_3 + 4HCl = Na_2S_4O_6 + Na_2S_4SeO_6 + 4NaCl.$$

The selenopentathionate is very unstable and cannot be obtained from solution. That the salt was present was shown by the fact that the solution exhibited all the reactions which are characteristic of pentathionates. Sodium pentathionate is stable in an acid solution, but is instantly decomposed when brought into contact with alkalies, being converted into sodium tetrathionate and free sulphur. The analogous selenium compound suffered decomposition in the same way and was converted into the tetrathionate and selenium.

It was also shown that similar reactions take place when the product of the reaction between tellurium dioxide, sodium thiosulphate and hydrochloric acid is treated with alkalies. A sample of pure tellurium dioxide was converted into the pentathionate derivative which was then treated with sodium hydroxide. It seemed highly probable that the precipitated tellurium so obtained was free from any element which did not have the power to replace sulphur in a pentathionate. The precipitate was treated with hydrochloric acid to free it from any hydroxide that may have been thrown down by the alkali.

In order to carry out the reaction successfully the substances are brought together in the quantities required by the chemical equation, with the exception that more hydrochloric acid than is called for must be used in order to keep the tellurium dioxide in solution. The solution must be dilute and cold in order to prevent decomposition of the sodium thiosulphate by the excess of acid. Addition of a small quantity of alkali to the acid solution causes the precipitation of a part of the tellurium present.

This precipitation continues until the solution is rendered alkaline. The tellurium obtained in the way outlined above was converted into the basic nitrate, which was crystallized twice and finally prepared for analysis.

In the final purification of the nitrate it was crystallized from dilute nitric acid (sp. gr. 1.25), which was prepared from purified materials. The water used for dilution was twice distilled, the last time from alkaline permanganate. The nitric acid used was a good sample of chemically pure acid, which was redistilled slowly from a platinum still, provided with a platinum condenser and receiver. The diluted acid was kept in bottles which had been repeatedly treated with warm nitric acid. The salt was crystallized in porcelain dishes which had been carefully cleaned with hot acid. Saturated solutions of the salt were evaporated at about 85° until reduced to about one-fourth their original bulk. The hot mother-liquor was immediately removed and the crystals were washed with redistilled concentrated nitric acid. The crystals were again dissolved in the purified acid and recrystallized.

It was found necessary, in order to obtain concordant results, to use, in determining the ratio between the weights of nitrate and oxide, only crystals which had been formed during the evaporation. In every case where the mixture of crystals and mother-liquor was allowed to stand over night before the crystals were removed, low values of the atomic weight, which varied with different samples, were obtained. It was evident that spontaneous evaporation caused the formation of crystals which contained mother-liquor.

The crystals which were removed from the hot solution were washed a number of times with redistilled concentrated nitric acid and were then ground to a very fine powder in an agate mortar, while still moist with acid. The finely ground nitrate was transferred by means of a platinum spatula to a well-cleaned porous tile, which immediately removed most of the acid clinging to the powder. The tile, with the nitrate which had been placed on it in a small pile, was placed in a desiccator which contained concentrated sulphuric acid and solid potassium hydroxide. The air was exhausted from the desiccator, which was left undisturbed for a day. The nitrate was then removed from the tile, care being taken to reject the portion which had come in contact with the tile. The product, which was at this stage in the form of a hard lump, was readily reduced to a fine powder by breaking it with a few strokes of a spatula. The nitrate was next kept for at least three days in a vacuum over phosphorus pentoxide.

This method of removing the excess of acid liquid from the nitrate is an improvement over that used by Köthner in his work. Köthner was of the opinion that as the acid was removed by evaporation from the crystals, they were partially decomposed to the oxide with loss of acid. This may have been the case when the acid was removed at an elevated temperature as Köthner did it. In order to prevent this decomposition he washed the crystals with mixtures of nitric acid and alcohol, using successively a larger proportion of alcohol in the mixture, until pure alcohol was used. This method is tedious and great precautions are necessary. In the preliminary work a number of samples were prepared by Köthner's method. These gave the same results as samples prepared as described above.

In determining the ratio between the weights of the nitrate and oxide, the usual precautions necessary for accurate results were taken. The weights were calibrated and a balance sensitive to 0.03 mg. was used. The weighings were made by substitution after the crucibles had stood in the balance case at least two hours. A crucible like those used to contain the nitrate was was used as a tare.

The samples of nitrate were heated in platinum crucibles to constant weight at 140° in a current of air dried by passing over phosphorus pentoxide. This first heating of the salt, which brought it to constant weight, was continued for four hours. The samples were weighed before and after this heating at 140°. In no case was the loss in weight as a result of heating for four hours greater than 0.1 mg. The decomposition of the nitrate was brought about slowly in order to avoid the loss of tellurium dioxide by mechanical removal along with gases evolved. The crucibles were heated about six hours at 250°, six hours at 300°, three hours at 350°, three hours at 400–450°. The crucibles, resting on pieces of platinum foil inside a large covered porcelain crucible, were next heated for four hours at the highest temperature procurable with a Bunsen burner. The oxide formed from the nitrate in this way was finally fused by the application of a free flame for a few seconds. A test showed that the oxide contained no nitric acid and the glassy condition produced by the fusion precluded the possibility of any enclosed gases.

The results of the analyses follow:

No.	Weight $2TeO_2.HNO_3$.	Weight TeO_2.	Atomic weight.
1	2.28215	1.90578	127.47
2	2.35429	1.96615	127.53
3	1.86853	1.56042	127.49
4	1.77348	1.48110	127.49
5	2.31048	1.92938	127.44
6	2.14267	1.78936	127.50
7	2.35523	1.96676	127.45
8	2.18860	1.82780	127.54
9	3.29158	2.74881	127.50
10	2.27516	1.89993	127.46
11	2.53164	2.11410	127.46
12	2.01327	1.68121	127.45
		Average,	127.48

In the second and third columns are given the apparent weights of the nitrate and oxide. In calculating the values of the atomic weight, a vacuum correction was made of +0.150 mg. for each gram of nitrate and +0.066 mg. for each gram of oxide. The specific gravity of tellurium dioxide has been reported as 5.76. The value of this constant for the basic nitrate of tellurium was found to be 4.26 at 22°/4°. The atomic weights used in the calculation were H, 1.0076; N, 14.01; O, 16.

When the results are calculated in the manner used by Köthner, namely, H, 1.01; N, 14.04; O, 16 and no vacuum corrections are applied, the average is 127.64. Köthner's average was 127.63.

The results given under numbers 1, 2 and 3, were those obtained with a sample of nitrate which had been purified by crystallization only. In the paper by Norris, Fay, and Edgerly it was stated that crystallization of the basic nitrate served to purify it from all other metals. These results confirm that statement. Köthner showed by a spectroscopic examination that the nitrate prepared by him contained silver and gold. When he determined the atomic weight of tellurium, using a sample of nitrate made from the metal which had not been distilled, he obtained as the atomic weight, the value 127.36, which differed by 0.27 unit from the value found when distilled tellurium was used. He considered the cause of this difference to be the presence of silver and gold in the nitrate which was prepared from undistilled tellurium. The results given above, which were obtained with a sample of nitrate which had been purified by crystallization alone, are practically identical with those obtained from a sample of nitrate prepared from the oxide which had been five times distilled.

The results obtained with the nitrate prepared from the tellurium which had been converted into the telluropentathionate are recorded in experiments numbered 4, 5 and 6. In the experiment numbered 7 the nitrate used was prepared from a sample of oxide which had been distilled but once, while in experiments 8 and 9 the oxide from which the nitrate was made had been distilled five times. In numbers 10, 11 and 12 are recorded the results of the analyses of samples of nitrate prepared from the residue from the first distillation. If the dvitellurium of Mendeléeff had been present, the atomic weight of this fraction should have been much higher than 127.48.

The results show clearly that the application of the methods studied effected no decomposition of tellurium. As these methods would have shown the presence of an unknown element with the properties which have been assigned to dvitellurium by Mendeléeff, the conclusion can be drawn that no such element is present. The work adds to the experimental evidence in favor of the elementary nature of tellurium.

The atomic weight found agrees well with the most reliable values, which have been determined by others.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE CARRYING DOWN OF AMMONIUM OXALATE BY OXALATES OF THE RARE EARTHS.

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A RAPID and convenient method for approximate atomic weight determinations of the trivalent metals of the rare earths is the "permanganate" method, in which the ratio $M_2O_3 : 3C_2O_3$ is determined. In this process a known weight of the oxalate of the rare earth is ignited to oxide and the latter is weighed. Then