

THE ATOMIC WEIGHT OF TELLURIUM; AND A CRITIQUE OF THE BASIC NITRATE METHOD OF DETERMINATION.

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This work is a continuation of the investigation of tellurium, begun by Dudley and Jones,¹ who made a spectrographic study of it. Our object, in the beginning, was to make atomic weight determinations of different fractions of tellurium precipitated by hydrazine hydrochloride and thus to confirm the conclusions reached by Dudley and Jones, that tellurium did not suffer decomposition when so treated; but later it was found desirable to make an investigation of the basic nitrate method for determining the atomic weight.

The tellurium used in this investigation was purified as described by Dudley and Jones.² There were in all twenty fractions of the tellurium; about six grams to the fraction, precipitated by hydrazine hydrochloride. The spectrograms taken of the different fractions showed no impurities, with the exception of the last one.

Unless otherwise stated, Kahlbaum's chemically pure reagents were used. Ammonia-free water was used for all dilutions.

Very concordant results have been obtained by Köthner,³ Norris⁴ and Flint⁵ with the basic nitrate method. Therefore, we began the work by using this method. Our procedure was as follows: The tellurium was dissolved in nitric acid (sp. gr. 1.25) and evaporated on a steam bath at about 70°. The basic nitrate which crystallized out was washed with concentrated nitric acid and then dried by heating at 120° in a current of air dried by sulfuric acid and phosphorus pentoxide. These crystals were then ground in an agate mortar. Portions were weighed in a platinum crucible and brought to constant weight by heating in a current of dry air at a temperature of 140° for periods of 24 hours each. The crucible was then placed over a low Bunsen flame and the temperature very slowly and gradually raised to the fusion point of the dioxide.

A Freas electric oven was used for drying the crystals and bringing the basic nitrate to constant weight. This oven was regulated to vary only a fraction of a degree. In order to draw the air over the basic nitrate, a specially constructed glass apparatus was made to fit into the oven.

The fractions Nos. 1 and 2, when dissolved in nitric acid, gave to all appearances the orthorhombic crystals of the basic nitrate but from the solution of the third fraction, there separated colorless crystals of perfect octahedral form. These proved to be crystals of tellurium dioxide.

¹ THIS JOURNAL, 34, 995.

² *Loc. cit.*

³ *Ann.*, 319, 1.

⁴ THIS JOURNAL, 28, 1675.

⁵ *Am. J. Sci.*, [4] 30, 209.

They dissolved with difficulty in a large excess of nitric acid (sp. gr. 1.25). But from this nitric acid solution of the dioxide, there would usually separate, on concentration, the orthorhombic crystals of the basic nitrate, but sometimes it would separate as the dioxide again.

Thinking that there might be some difference between the tellurium which came down in the octahedral form as the dioxide and that crystallizing in the orthorhombic form as the basic nitrate, samples of the two were reduced to the elementary state (tellurium) and spectrograms were taken of each. A comparison of the spectra was made but no difference was noted. In order to be sure of this point, it was decided to make atomic weight determinations of them, so whenever the dioxide crystals appeared they were separated from the liquid by decantation, washed with concentrated nitric acid, dissolved in nitric acid, sp. gr. 1.25, and the solution evaporated until the orthorhombic crystals separated. Sometimes the dioxide crystals would again appear on concentration, as previously mentioned. These were treated with more nitric acid (sp. gr. 1.25) and the operation repeated until only the crystals of the basic nitrate form were obtained. In fraction No. 15 especial effort was made to avoid the formation of any dioxide crystals, by dissolving in a very large excess of acid. Then only the orthorhombic crystals were obtained from the solution, but they were found to contain inclusions of the dioxide.

As the amount of basic nitrate obtained from the different fractions was not enough for a series of atomic weight determinations, the crystals of the fractions Nos. 1, 2, 3 and 4, and Nos. 5, 6, 7 and 8, etc., first separating in the orthorhombic form were put together and the crystals of the dioxide which were converted into the basic nitrate were grouped in like manner.

Portion.	Det. No.	$2\text{TeO}_2\text{HNO}_3$ Gms.	TeO_2 Gms.	% TeO_2 .	At. wt.
A Fraction Nos. 1, 2, 3 and 4	1	1.74464	1.46204	83.796	130.94
A Fraction Nos. 1, 2, 3 and 4	2	1.08072	0.90445	83.689	129.65
A Fraction Nos. 1, 2, 3 and 4	3	1.93538	1.61476	83.434	126.69
A Fraction Nos. 1, 2, 3 and 4	4	1.34715	1.60841	83.750	130.39
A Fraction Nos. 1, 2, 3 and 4	5	1.33704	1.59490	83.832	131.37
A Fraction Nos. 5, 6, 7 and 8	6	2.27174	1.91397	84.251	136.56
A Fraction Nos. 5, 6, 7 and 8	7	1.61049	1.35653	84.230	136.61
A Fraction Nos. 5, 6, 7 and 8	8	1.67029	1.40286	83.976	133.13
B Fraction Nos. 1, 2, 3 and 4	9	1.55380	1.38070	83.391	126.13
B Fraction Nos. 1, 2, 3 and 4	10	1.26647	1.05595	83.377	126.04
B Fraction Nos. 5, 6, 7 and 8	11	1.74197	1.45398	83.455	126.93
B Fraction Nos. 5, 6, 7 and 8	12	1.19549	0.99758	83.428	126.62
B Fraction Nos. 11 and 12	13	0.59279	0.49295	83.157	123.58
B Fraction Nos. 11 and 12	14	0.60778	0.50670	83.396	125.95
B Fraction No. 15	15	1.62585	1.39745	85.952	160.78
B Fraction No. 15	16	1.28903	1.09327	84.813	143.96

The preceding are the results obtained. For convenience of tabulation, the determinations of the portions first crystallizing as the dioxide are marked "A" and those separating from the original solution in the orthorhombic crystals of the basic nitrate, "B."

In all of the atomic weight determinations the weighing was made by the method of oscillations. The set of weights used was standardized and the weighings were reduced to vacuum.

As the results were so irregular the method was necessarily abandoned. According to our experience there is no certainty of the purity of the basic nitrate crystals. From a nitric acid solution the tellurium may crystallize as tellurous acid, tellurium dioxide and the basic nitrate of tellurium according to the temperature and excess of acid present. Thus the conditions for crystallization must be very exact in order to obtain pure crystals of either. What all of these conditions are, we are not prepared to say. The temperature may be regulated and before evaporation a large excess of acid may be present; but on concentrating the solution it often becomes supersaturated and there is not sufficient nitric acid present to form the basic nitrate with all of the tellurium. So the dioxide either crystallizes out or is held as an inclusion in the orthorhombic crystals of the basic nitrate. Such inclusions were observed on close examination with the microscope. Also when the dioxide and basic nitrate are together, some of the dioxide is always held between the basic nitrate crystals, which have a tendency to form rosette clusters. This tends toward high results, and with one exception determinations marked "A" gave high results. The crystals from the solution of fraction "B," No. 15, also contained these inclusions. Although, as said above, only orthorhombic crystals separated from this solution, still they gave the highest results, owing to the amount of dioxide included.

In all of the determinations marked "B" in which the basic nitrate was crystallized out after the dioxide crystals had been separated from the solution, low results were obtained. These low results were due to inclusions of the mother liquor, instead of the dioxide, as in the case of high results. These inclusions were also observed under the microscope. Baker and Harcourt¹ conclude from their investigations that some of the trioxide basic nitrate may be formed in small amounts along with the dioxide basic nitrate of tellurium, and in this way they attempt to account for the low results of Flint.

That some of the dioxide may be lost mechanically by the gases evolved when the nitrate is decomposed by heating should also be taken into consideration. But only in one or two instances was there any evidence of this on the lid of the crucible and these determinations were discarded. Then there is the uncertainty as to whether all the oxides of nitrogen

¹ *J. Chem. Soc.*, 99, 1311.

are driven off at the fusion point of the dioxide. For all of the reasons given above, we have come to the conclusion that this method is not dependable.

The Tetrabromide Method.

Owing to the failure of the basic nitrate method to give reliable results, we adopted the tetrabromide method for determining the atomic weight of the fractionally precipitated tellurium. The tetrabromide method presented by Baker and Bennett¹ is very simple and avoids the danger of loss due to transferring of material from one vessel to another and the authors got exceedingly concordant results.

Baker's "Analyzed Bromine" containing from 0.26 to 0.46% of chlorine was purified according to the method given by Stas. A pound of bromine was distilled over chemically pure zinc oxide and potassium bromide, ten times the amount of each, required for the chlorine present, being used. The bromine was then treated with phosphorus pentoxide in a separatory funnel and allowed to stand for several hours. Finally the bromine was drawn off and redistilled.

Each fraction of the tellurium which had been converted into the basic nitrate for the previous method was twice evaporated to dryness with hydrochloric acid, then dissolved in hydrochloric acid, diluted to the precipitating point of the tellurium dioxide with ammonia-free water and sulfur dioxide passed into the hot solution. The tellurium thus precipitated was filtered through hardened filter paper, washed first with hydrochloric acid, 1 : 1, then warm hydrochloric acid, 1 : 4, ammonia-free water until free of the chloride and finally alcohol followed by ether. This was dried in a vacuum over sulfuric acid in order to avoid oxidation of the finely divided particles of tellurium. More sulfur dioxide was passed into the filtrate and the process repeated until all of the tellurium was precipitated. The dried precipitated tellurium was then fused into sticks, after the method used by Dudley and Jones,² for the preparation of electrodes.

Portions of this fused tellurium were powdered in an agate mortar and placed in the lower bulb of the weighed tube, which was specially constructed of Jena glass according to the diagram given by Baker and Bennett.³ This was dried to constant weight by heating in the electric oven at 50° in a current of air dried by calcium chloride, sulfuric acid and phosphorus pentoxide. The air was then displaced by nitrogen. The nitrogen was obtained by passing air over red hot copper turnings, then through a potassium hydroxide solution of pyrogallic acid and was dried in the same way as the air. The purified bromine was run into

¹ *J. Chem. Soc.*, 91, 1849.

² *Loc. cit.*

³ *J. Chem. Soc.*, 91, 1857.

the upper bulb of the tube through a funnel with a drawn-out stem and then the tube was tightly capped. The bromine was run down into the tellurium a little at a time, until the tellurium was all converted into the tetrabromide and some excess of liquid bromine remained. This was allowed to stand for about 24 hours. The tube was then placed in the electric oven and heated to 50°, while a current of dry nitrogen was drawn through it. When no tests for bromine with potassium-iodide-starch-paper was obtained in the nitrogen drawn through the tube, the oven was allowed to cool to room temperature. The nitrogen was then displaced by dry air and the tube weighed. A similar tube was used as a counterpoise.

Concordant results were not obtained from the tellurium precipitated and cast in sticks as described. Notwithstanding washing with hydrochloric acid, drying in a vacuum and fusion in hydrogen, the tellurium contained some dioxide and, as was discovered later, some impurities. Parts of the series 1, 2, 3 and 4; 5, 6, 7 and 8; 11 and 12, A and B, were put together and distilled in hydrogen. A residue of about 0.1% was left in the boat. This residue was found to contain some carbon, which was very probably due to the hydrogen, although it was generated from chemically pure zinc and hydrochloric acid; a slight trace of iron which must have come from the can of liquid sulfur dioxide, as no iron lines were previously found in the spectra of the tellurium; some tellurium and microscopic fragments of glass, due to shattering the glass tube to remove the fused tellurium. This tellurium, when redistilled, left only a slight coloration in the boat, showing that the one redistillation was sufficient to purify the material. The results of the determinations are as follows: Br = 79.92.

	Wt. of Te. Gms.	Wt. of TeBr ₄ . Gms.	% Te in TeBr ₄ .	At. wt. of Te.
No. 1.....	0.479816	1.682387	28.520	127.550
No. 2.....	0.296341	1.037049	28.575	127.897
No. 3.....	0.433241	1.516746	28.563	127.819
No. 4.....	0.457782	1.605684	28.510	127.487
No. 5.....	0.321522	1.126939	28.530	127.612

The high results in these determinations were due to some tellurium which was left in the bulb unattacked by the bromine. This was caused by running the bromine into the lower bulb too rapidly; thus inclusions of tellurium were formed in the tellurium tetrabromide which could not be broken up by shaking the tube. It is best to start with smaller quantities of tellurium than those used above, because it allows better mixing of the material and thus brings the bromine into contact with all of the tellurium.

The remainder of the portions "A", fractions Nos. 1, 2, 3 and 4; "B," fractions 1, 2, 3 and 4; also the fraction No. 19 of the tellurium precipi-

tated by hydrazine hydrochloride were distilled separately in hydrogen and the atomic weight determinations gave the following:

	Det. No.	Wt. of Te. Gms.	Wt. of TeBr ₄ . Gms.	% of Te.	At. wt. of Te.
A Fraction Nos. 1, 2, 3 and 4....	1	0.300558	1.054251	28.509	127.481
A Fraction Nos. 1, 2, 3 and 4....	2	0.199807	0.700947	28.505	127.456
B Fraction Nos. 1, 2, 3 and 4....	1	0.22032	0.773048	28.500	127.425
B Fraction Nos. 1, 2, 3 and 4....	2	0.158161	0.554717	28.512	127.500
Fraction No. 19.....	1	0.436907	1.532360	28.512	127.500
Fraction No. 19.....	2	0.29811	1.045485	28.514	127.512
Average.....				28.509	127.479

These determinations show that there is no separation of the tellurium after 19 fractional precipitations by hydrazine hydrochloride and that there is no difference between the tellurium which crystallized from the nitric acid solution in the octahedral crystals as the dioxide and that separating in the orthorhombic crystals as the basic nitrate.

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CORRECTION.

The papers from this laboratory which appeared in the June JOURNAL require the following corrections:

P. 712, equation 75, for $2RT$ read $\frac{2n_aRT}{F}$, and p. 739, lines 33 and 37, for mm. read cm.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WYOMING.]

ANALYSES OF SOME WYOMING LARKSPURS. I.

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The poisonous character of some of the various larkspurs which are widely and abundantly distributed in the states of the Northwest has been the subject of several experimental studies. Chestnut and Wilcox¹ studied the influence of *Delphinium glaucum* and of *Delphinium bicolor* upon animals which were fed with these plants or with extracts prepared from them. These workers also had the opportunity for observing, to some extent, the economic importance of these particular species in Montana. During the season of 1900, one hundred cases of cattle poisoning produced by *Delphinium glaucum* were brought to their attention and of these fifty-six proved fatal. Because of the habitat of this plant on the mountain ranges, cattle alone are poisoned by it. The figures given are

¹ Div. Bot., U. S. Dept. Agr., *Bull.* 26, 65 (1901).