ART. XXXIV.—*The Complexity of Tellurium*; by PHILIP E. BROWNING and WILLIAM R. FLINT.

[Contributions from the Kent Chemical Laboratory, Yale Univ.—cciii.]

ALTHOUGH the consensus of opinion among chemists at present seems to favor the homogeneity of tellurium* and an atomic weight of 127.5, the recent work of Marekwald,† and the last report of the International Committee on Atomic Weights‡ seem to suggest that possibly the question of the atomic weight at least has not been definitely settled.

The work described in this paper was suggested by the observation that when water is added in large amount to a solution of tellurium tetrachloride, this compound is hydrolyzed and the greater part of the tellurous acid is precipitated, while some of the tellurium remains in solution however large the amount of water present.

This observation was apparently first made by Berzelius§ and later the method applied in a limited degree by Brauner|| and by Baker and Bennett¶ to a process of fractionation.

It was further observed by us that the tellurium remaining in solution after the treatment with water and filtering may be completely precipitated as the dioxide by heating to boiling, treating first with ammonia and then with acetic acid in faint excess, as described in a previous paper from this laboratory.**

This procedure was applied with the result to be described, in order to determine whether by means of it any light might be obtained upon the possible complexity of tellurium.

About one hundred grams of crude tellurium, which had been extracted by hydrochloric acid from electrolytic copper residues, were subjected to a series of purification processes such as have been commonly used for the purpose of preparing pure material. This crude preparation was first twice fractionally precipitated by sulphur dioxide; then fused in portions, in hydrogen, with potassium cyanide, extracted with water and precipitated from solution by a current of air. It was next reprecipitated, by sulphur dioxide, from hydrochloric acid solution; was fused in hydrogen, and finally distilled, in a current of hydrogen, from porcelain boats in a porcelain tube.

* Kthner, Ann., xcccix, 1; Gutbier, Sitzungsber. phys-med. Soc. Erlangen, xxxvii, 270; Lenher, J. Am. Chem. Soc., xxx, 387.

† Ber., xl, 4730. ‡ J. Am. Chem. Soc., xxxi, 1.

§ Ann. Chim. Phys. (2), lviii, 113.

|| J. Chem. Soc., lv, 382.

¶ Ibid., xci, 1849.

** This Journal, xxviii, 112.

Ninety-two grams of this pure product were converted to tetrachloride and the solution, in as small amount of hydrochloric acid as possible, was diluted with four liters of boiling distilled water, and cooled. The precipitate, seventy-six grams of pure white, crystalline TeO_2 , was removed and the filtrate was heated again to boiling, after which ammonia and then acetic acid in the smallest possible excess were added. When cold, thirty-eight grams of TeO_2 were obtained, more finely crystalline than the preceding fraction, but also pure white. The filtrate from this fraction contained no tellurium detectable by stannous chloride, and was consequently discarded.

These two fractions were next separately refractionated by an exact repetition of the process above described, each fraction secured being likewise refractionated, the three fractionations thus providing eight fractions, of which the last, about 1.5 gram, was set aside. Fraction two was combined with three, four with five, and six with seven, and each portion of the material refractionated, as was also fraction one. From this point on, the fractionation was carried out after the usual plan of fractional crystallizations, intermediate fractions being combined before retreatment, and those at the latter end of the series being removed when small in amount (from one to two grams). In this manner ten fractionations were performed, as a result of which were secured about fifty-nine grams of dioxide from the first, or water, end, and fifteen grams from the last, or ammonia-acetic acid, end of the series. Each of these portions was refractionated once, the water fraction (50 grams) of the first being denominated alpha, and the ammonia-acetic acid fraction (13 grams) of the latter, beta. The alpha and beta fractions were lastly converted to basic nitrate, the former by one and the latter by two crystallizations, according to the method described by Norris, Fay, and Edgerly.* It is to be noted that in the process of fractionation the material of each fraction had been crystallized out of a large amount of distilled water.

The alpha and beta fractions were subjected to analysis by three different methods: (1) the basic nitrate method; (2) the Gooch and Danner modification of Brauner's permanganate process;† and (3) the ammonia-acetic acid method previously described.

(1) After bringing the basic nitrate to constant weight at 140° as recommended by Norris,‡ carefully weighed portions were heated in platinum with a gradually increasing temperature for a period of five to six hours. The crucibles were contained in porcelain radiators, a porcelain dish being supported

* Am. Chem. J., xxiii, 105.

† This Journal, xlv, 301.

‡ J. Am. Chem. Soc., xxviii, 1675.

above each in an inverted position to distribute the heat more evenly. Finally they were removed and ignited for a short time at dull redness until the dioxide had fused to a glassy condition. The weighings were conducted with properly standardized weights, by the method of vibrations, and the usual corrections were applied. The results are recorded in Table I.

TABLE I.

	2TeO ₂ . HNO ₃ taken gram.	TeO ₂ found gram.	Per cent TeO ₂ found
Alpha			
(1)	0.09575	0.07986	83.40
(2)	0.27354	0.22813	83.39
(3)	0.60237	0.50272	83.45
(4)	0.66288	0.55331	83.45
(5)	1.60542	1.33912	83.41
(6)	1.78565	1.48982	83.43
Beta			
(1)	0.08473	0.07081	83.57
(2)	0.23125	0.19256	83.63
(3)	0.87484	0.73306	83.79
(4)	0.39778	0.33232	83.56
(5)	0.39479	0.33005	83.60

The mean percentage of dioxide in alpha (83.42 per cent) gives an atomic weight of 126.53; that for beta (83.63 per cent), 128.97. It is thus apparent that the fractions are not homogeneous with each other, since they had been crystallized under precisely similar conditions, with due precautions to secure constancy of composition in each case, and with exactly similar treatment in the performance of the analyses.

(2) Analyses made by the permanganate process mentioned above confirmed this difference. The material was dissolved with two cubic centimeters of ten per cent potassium hydroxide and the solution was acidified with sulphuric acid (1:1), one cubic centimeter in excess, diluted to one hundred cubic centimeters with water, and treated with an excess of permanganate, oxalic acid being then added in excess. The mixture was then warmed nearly to boiling and the excess of oxalic acid determined by permanganate. The titrations were conducted in porcelain dishes. The results follow in Table II.

Computation from the permanganate required for the oxidation, in each case, gave a mean of 126.64 for alpha, and 128.77 for beta.

(3) A similar difference was again obtained by the ammonia-acetic acid process already referred to. The basic nitrate was dissolved with two cubic centimeters of hydrochloric acid, the

TABLE II.

	2TeO ₂ . HNO ₃ grm.	TeO ₂ theory grm.	TeO ₂ found grm.	Error on TeO ₂ grm.	TeO ₂ theory grm.	TeO ₂ found grm.	Error on TeO ₂ grm.
Alpha	(Te=126.5)				(Te=127.5)		
(1)	0.2537	0.2116	0.2119	+0.0003	0.2118	0.2132	+0.0014
(2)	0.2508	0.2092	0.2093	+0.0001	0.2094	0.2106	+0.0012
(3)	0.2521	0.2103	0.2102	-0.0001	0.2105	0.2115	+0.0010
(4)	0.2508	0.2092	0.2092	0.0000	0.2094	0.2105	+0.0011
(5)	0.2523	0.2104	0.2100	-0.0004	0.2107	0.2113	+0.0006
(6)	0.2511	0.2094	0.2092	-0.0002	0.2097	0.2105	+0.0008
Beta	(Te=128.9)				(Te=127.5)		
(1)	0.2504	0.2094	0.2095	+0.0001	0.2091	0.2077	-0.0014
(2)	0.2500	0.2090	0.2086	-0.0004	0.2087	0.2068	-0.0019
(3)	0.2505	0.2095	0.2095	0.0000	0.2092	0.2075	-0.0017
(4)	0.2505	0.2095	0.2095	0.0000	0.2092	0.2075	-0.0017
(5)	0.2504	0.2094	0.2100	+0.0006	0.2091	0.2083	-0.0008
(6)	0.2501	0.2091	0.2093	+0.0002	0.2088	0.2076	-0.0012

excess of acid removed as much as possible by careful evaporation; the dilution was with two hundred cubic centimeters of boiling distilled water, and the ammonia and acetic acid were added from burettes. Filtration was performed after standing over night. These results appear in Table III.

TABLE III.

	2TeO ₂ . HNO ₃ grm.	TeO ₂ theory grm.	TeO ₂ found grm.	Error grm.	Per cent TeO ₂
Alpha	(Te=126.5)				
(1)	0.2506	0.2090	0.2093	+0.0003	83.51
(2)	0.2505	0.2089	0.2088	-0.0001	83.35
(3)	0.2529	0.2109	0.2108	-0.0001	83.35
(4)	0.2510	0.2094	0.2093	-0.0001	83.39
(5)	0.2507	0.2091	0.2091	0.0000	83.41
Beta	(Te=128.9)				
(1)	0.2512	0.2101	0.2097	-0.0004	83.48
(2)	0.2514	0.2102	0.2103	+0.0001	83.65
(3)	0.2504	0.2094	0.2095	+0.0001	83.66
(4)	0.2507	0.2096	0.2095	-0.0001	83.57
(5)	0.2612	0.2101	0.2100	-0.0001	83.60

For alpha the mean percentage of dioxide is 83.40 per cent, or Te=126.31; beta, 83.59 per cent, or Te=128.81.

SUMMARY OF ANALYSES.

Process	Alpha	Beta
Basic nitrate	126.53	128.97
Permanganate	126.64	128.77
Ammonia—acetic acid	126.31	128.81
Mean	126.49	128.85

It is seen that an atomic weight of 126.5 gives more satisfactory results for alpha, while neither 126.5 nor 127.5 will answer for beta.

Besides the experiments with the basic nitrate, just described, the following experiments upon the dioxide are to be noted. Two portions of tellurium dioxide from each fraction, prepared by the ignition of the basic nitrates, were dissolved in equal amounts of hydrochloric acid and treated with equal amounts of boiling distilled water. The results given in Table IV indicate different degrees of hydrolytic susceptibility on the part of the tetrachloride prepared from these fractions.

TABLE IV.

	TeO ₂ taken gram.	TeO ₂ found gram.	Percentage precipitated
(1)	0.3000	0.2521	84. %
(2)	0.3000	0.2602	86.7%
(3)	0.3000	0.2772	92.4%
(4)	0.3000	0.2806	93.5%

(1) and (2) were obtained from one fraction and (3) and (4) from the other. (1) and (3) stood 22 hours before filtration, (2) 26 hours, and (4) 18 hours.

A sample of tellurium dioxide obtained from the tellurium tetrachloride by several hot water precipitations, according to the procedure for the preparation of the alpha fraction, was analyzed by the permanganate process already described. The results of the analysis of this specially prepared dioxide, as given in Table V, show a close agreement with the analyses of the basic nitrate prepared from the alpha fraction and recorded in Table II.

TABLE V.

	TeO ₂ taken gram.	TeO ₂ found gram.	Error gram.	TeO ₂ found gram.	Error gram.
		Te=126.5		Te=127.5	
(1)	0.3066	0.3064	—0.0002	0.3076	+0.0010
(2)	0.2723	0.2719	—0.0004	0.2729	+0.0006
(3)	0.2229	0.2228	—0.0001	0.2243	+0.0014
(4)	0.2220	0.2220	0.0000	0.2235	+0.0015

It consequently appears from the analyses by three different methods that, in the end fractions obtained by fractional hydrolysis of tellurium tetrachloride prepared from the carefully purified element, tellurium, seems to possess different atomic weights. It is not claimed that these atomic weights have been determined with the utmost accuracy. The two fractions, however, have been in each case treated exactly alike, in a manner entirely competent to show at least approximately whatever difference there might be. The preparations have been carefully examined to discover the presence of any impurities which might cause the difference, but no such impurities have been found. At present, therefore, there seems to be no explanation of the differences found other than the complexity of the original substance. The investigations just described are of necessity preliminary in character, and the results of a more extended study of this fractionation process, already begun by the latter of the two collaborators, will be published as soon as practicable.