LXXII.—On the Atomic Weight of Tellurium.

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THE atomic weight of tellurium has been determined twice; in the first place by Berzelius, and secondly by von Hauer. The former (Pogg. Ann., 1834, 32, 16) oxidised a known weight of tellurium with dilute nitric acid, and weighed the dioxide formed, obtaining the numbers 128.13, 127.96, and 127.95 (O = 15.96). Berzelius calculated his number from the latter two experiments which give Te = 127.955. The method employed by him for purifying his tellurium was that of distilling in hydrogen the tellurium obtained from potassium telluride. Subsequently von Hauer (J. pr. Chem., 1858, 72, 98) determined the atomic weight of tellurium by the analysis of a double bromide of tellurium and potassium, the amount of bromine in the salt being ascertained by precipitation with silver nitrate. As a mean of five experiments varying between Te = 126.86, and = 128.49, von Hauer obtained the number 127.74 as the atomic weight of tellurium (Br = 79.75, K = 39.04).

Dumas (Ann. Chem. Pharm., 1860, 113, 30) from experiments not published in detail, concludes that Te = 129.

Deville and Troost (*Compt. rend.*, **56**, 871) determined the density of tellurium vapour as 9.00 at 1390°, which gives Te = 130.5.

The present investigation was undertaken with the view of ascertaining whether a careful repetition of Berzelius's experiments, made with pure tellurium, would yield a number agreeing with the hitherto adopted atomic weight, or whether it would harmonise with Mendelejeff's classification (Ann. Chem. Pharm., 1871, Supp. Bd., 8, 133).

According to this classification, we should expect tellurium to have an atomic weight lying between that of iodine = $126\cdot53$, and that of antimony = 122, thus taking its place in the same series as sulphur and selenium, the atomic weight which Mendelejeff assigns to it being 125. The experimental results which I have obtained agree closely with those of Berzelius and von Hauer, according to which tellurium has a higher atomic weight than that of iodine, and must, therefore, be placed after this element in Mendelejeff's system.

Preparation of Pure Tellurium.—100 grams of crude tellurium was obtained from Trommsdorff, and a preliminary examination of this showed that it contained copper, bismuth, antimony, tin, &c., as impurities.

The following mode of purification was adopted:-The powdered substance was mixed with three times its weight of dry sodium car-

bonate and three times its weight of sulphur in a porcelain crucible; this was placed inside a fire-clay one and the mass fused in a small furnace. The mass when cold was exhausted with boiling water and filtered from a black insoluble residue; this last contains the sulphides of copper, bismuth, &c.; the deep-yellow filtrate may contain the sulpho-acids of tellurium, selenium, arsenic, tin, and antimony, the tellurium existing as sodium thio-tellurite, Na₂TeS₃. After boiling down, the filtrate was acidified with acetic acid, which precipitates the sulphides of tellurium, tin, &c. The precipitate obtained consisted chiefly of tellurium disulphide, and was nearly black. After filtering it was well washed with water containing sulphuretted hydrogen, and was then brought into a basin and oxidised. The best oxidising agent was found to be pure strong nitric acid, which rapidly dissolved the sulphides, with separation of sulphur. The solution was boiled to dryness, a white mass of tellurium oxide, mixed with sulphur, being left. This was twice treated with strong hydrochloric acid to expel nitric acid; finally an excess of strong hydrochloric acid was added, and, after filtering, a bright-yellow solution was obtained. This was concentrated, put in a flask and warmed, and a solution of sodium sulphite added by degrees, the whole being frequently shaken. In this way a black finely-divided precipitate of tellurium is obtained, any selenium in solution being at the same time precipitated. The precipitate was completely washed, first with dilute hydrochloric acid. and finally with water, and was then dried in an air-bath at 110°. To free this from selenium and sulphur, it was mixed with five times its weight of pure potassium cyanide in a porcelain crucible, this being closed with a lid having a small hole drilled through it to allow of the passage of a tube. Fusion was effected in a small furnace, a current of coal-gas being passed into the crucible throughout the operation and until the crucible was quite cold. The mixture fuses, evolving white fumes to a slight extent, and solidifies on cooling to a dark porous mass. On addition of water this dissolves to a splendid deep claretcoloured solution, which at once deposits some tellurium as a fine powder. The concentrated solution placed in a flask deposits on standing part of the tellurium in the form of long needle-shaped crystals, and a larger portion as a fine amorphous powder. When air has free access, as in a wide-mouthed vessel, or when air is passed through the solution, all the tellurium is deposited in the amorphous form. Both forms are insoluble in hydrochloric acid and in carbon disulphide. The tellurium was finally filtered off, washed completely with water, and dried in an air-bath. In the above processes the sulphur and selenium go into solution as selenio- and thio-cyanates of potassium, the tellurium existing as potassium telluride, the solution of which is decomposed by air with separation of tellurium. The

final purification consisted in distilling the tellurium thus obtained in a current of pure hydrogen obtained by passing the gas generated in the usual way through wash-bottles containing :—(a, b) silver nitrate; (c) caustic soda; (d, e) boiled sulphuric acid; then over pumice soaked with strong sulphuric acid, and, lastly, over platinum-black heated to All the joints of the apparatus were well paraffined and tied redness. with copper wire, and the whole was arranged so as to give a constant supply of hydrogen for many consecutive hours. The tellurium obtained as described was placed in a porcelain boat, and this in a slightly inclined combustion-tube connected with the hydrogen apparatus. A stream of hydrogen was first passed through the tube for some hours; the tellurium was then gradually heated, and soon fused to a metallic-looking mass, volatilising at a higher temperature in yellow vapours which condensed in the cooler parts of the tube. A small portion is deposited in long needles, the remainder as a metallic mass which solidified on cooling and is crystalline on the surface. A small black residue was left. On redistillation the tellurium left no sensible residue: the distilled tellurium thus obtained easily separates from the tube; it is very bright, has a silver-like lustre, and does not tarnish when kept in a stoppered bottle.

The distilled tellurium used for the final determinations was fused a second time with potassium cyanide in a current of hydrogen; the potassium telluride extracted with water, freed from air as far as possible by boiling, and the tellurium collected in two portions (1) that which precipitated on the filter (marked A), and (2) that which precipitated after the solution had passed through the filter (marked B). Finally, the tellurium obtained from each of these two portions was again distilled in hydrogen. No appreciable difference in the atomic weight was found in the results obtained when using the portion once purified, that twice purified, or either of the portions A and B.

The reagents used were water, nitric acid, and hydrochloric acid.

Pure water was obtained by re-distilling ordinary distilled water from a platinum retort, and condensing in a hard glass vessel. It left no sensible residue on evaporation.

Pure nitric acid was obtained by distilling the commercial acid until free from chlorine; the acid thus obtained was twice re-distilled, and before its final use was again distilled from a platinum retort and condensed in a platinum vessel.

Pure hydrochloric acid was obtained by distilling the strong acid obtained by passing hydrochloric acid gas into water, in a platinum retort connected with a hard glass receiver.

The pure acids on evaporation in contact with air leave a small residue, due to the fixation of foreign matter from the air, this being almost completely volatile at a low red-heat. The residue left on evaporation was estimated and allowed for when necessary. The final distillations of the reagents were always made just before they were used.

Means of Weighing.—A set of normal weights, by Staudinger, of Giessen, was first carefully calibrated by weighing by vibration. The following table was thus arrived at, one of the 10 gram pieces being taken as normal.

Table of true Relative Weights.

D = denomination of weight. W = true relative weight.

D.	W.	D.	W.
100	 100.00064	$0.5 \ldots$	0.49997
100'	 100.00054	0.2	0.50000
50	 50.00024	0.1	0.10000
20	 20.00015	0.1'	0.09997
10	 10.00000	0.05	0.04998
10'	 9.99998	0.02	0.01997
5	 5.00004	0.01	0.00999
2	 1.99997	$0.01'\ldots$	0.00999
1	 1.00004	* 0.01''	0.01000
1'	 0.99999	* 0.01′′′	0.01002
1″	 1.00001	* 0.01''''	0.01001

The balance used is by Oertling, and is fitted with a special arrangement for increasing its accuracy. An arrangement of two right angled prisms, into which the pointer screws, is placed on a line with the centre knife edge. By total reflection from these prisms two ivory scales placed on either side of the balance-case are seen through a telescope fitted into the front of the balance case; one of these (A) is divided into 100 divisions, the other (B) has a single mark across its The prisms and scales are so arranged that when the centre. pointer is at the centre division of the ordinary scale (C), the mark on scale B is continuous with the centre division of scale A, and as the pointer (hence the prisms) moves, the mark on scale B moves along the scale A in such way that one division of the ordinary scale corresponds to five divisions of scale A. Since it is easy to read accurately to half a division of scale A, it is thereby possible to read directly and without error to tenths of an ordinary scale division.

The following numbers indicate the sensibility of the balance : δ = weight in milligrams, corresponding to one division of the ordinary scale, *i.e.*, to five of the scale A.

Load in grams.	б.
0	0.066
10	0.066
30	0.072
50	0.013
75	0.084
100	0.096

The method of weighing used was that of vibrations. The position of rest with no load on the pans was first observed; the object to be weighed is then slightly more than balanced, and the position of rest again taken; half milligram weight is then removed and the resting point taken, and finally the position of rest with nothing on the pans is again noted. In this manner the sensibility of the balance is ascertained at each weighing, and it becomes possible to weigh with very great accuracy. Generally three swings of the pointer were observed, the first one (or two) being neglected as not sufficiently regular.

The objects to be weighed (unless hygroscopic) were always left in the balance case some time before weighing, and until they became quite constant in weight.

Experiments on the Oxidation of Tellurium with Nitric Acid.

Berzelius showed that by using nitric acid of sp. gr. 1.25 containing 40 per cent. HNO₃, tellurium is dissolved, with formation of the dioxide which separates out; and that only a very small quantity of the trioxide is formed at the same time.

Nitric acid of the above strength dissolves tellurium rapidly in the cold; nitric acid of sp. gr. 1.47, containing 83.5 per cent. HNO₃, has at the ordinary temperature no action, but on warming on a water-bath the action proceeds slowly up to a certain point, when it becomes rapid. The amount of TeO₃.3H₂O formed, varies according to the strength of acid used, as will be seen by the following table :---

Experiment.	Acid, sp. gr. 1.47.	Water.	Percentage increase at 100-110°.
Ī	18 ^{,5} c.c.	4 c.c.	48.47
I I	excess "	0 "	46.27
III	6 ,,	6 "	25.15
IV	5 ,,	0,,	49.98
V	2 ,,	2 ,,	25.22

The percentage increase for $\text{TeO}_2 = 24.9$; for $\text{TeO}_3 = 37.5$; for $\text{TeO}_3.3\text{H}_2\text{O} = 79.7$.

When using nitric acid of sp. gr. 1.25, the amount of tellurium taken influences the reaction. With small quantities all the tellurium

is dissolved; if larger quantities be used, the action is not complete; the tellurium dioxide formed is nearly insoluble in nitric acid and in water, and appears to coat over the tellurium, and thus protect it from further action. Thus the following numbers were obtained :---

Experiment.	Weight of Te taken.	Weight of unoxidised portion
Ī	$8.\overline{2}548$ grams.	0.88 gram.
II	4·8067 ,,	0.0285 "
III	2.6507 ,,	0.0005 "

When telluric acid, $TeO_3.3H_3O$, is heated to 180° it loses 2 molecules of water, and the H_2TeO_4 left loses on further heating first the remaining water and then one atom of oxygen. Between 180° and 350° there is a gradual loss in weight, no distinct temperature being noted at which the trioxide begins to lose oxygen and become dioxide. To completely convert all TeO_3 into TeO_2 it is necessary to heat it cautiously in a covered crucible over the flame until the oxide just begins to fuse round the edges; the mass then consists of pure tellurium dioxide, and no loss by volatilisation occurs.

The method employed for converting a given weight of tellurium into tellurium dioxide was as follows: Pure tellurium was finely powdered in an agate mortar, and weighed in a platinum crucible. after drying at 100-105°. Strong nitric acid, or this mixed with water, was then very gradually added by means of a pipette, a watchglass being placed over the crucible to prevent loss by spirting. After the action had ceased, the acid was evaporated to dryness on a waterbath, the watch-glass being left on until it had been washed perfectly clean by the acid which condensed and ran back, as shown by its drying in the air without the least residue being left on it. 1 c.c. of acid was finally added, and the whole evaporated again to dryness. The crucible was then slowly heated in an air-bath up to 350°, there being a gradual loss of weight corresponding with the decomposition of TeO₃.3H₂O by heat. Thus the following results were obtained, giving the increase of weight observed on 100 parts of tellurium :---

Ter	nperature.	Ι.		II.	
	(100°	48.5 per	cent.	49.9 per	cent.
Percentage	180	35.6	••	36.2^{-1}	••
increase at	230	31.6	**	$32 \cdot 9$	
	350	$25 \cdot 3$,,	26.5	,,

In the first experiment distinct crystals of $TeO_3.3H_2O$ were obtained, the gradual conversion of which into dioxide was plainly seen. Finally the oxide was cautiously heated over a lamp in such a way that no loss through volatilisation occurred, until the weight became

constant. The tellurium dioxide obtained is not sensibly hygroscopic.

The following results were obtained in this way: (0 = 15.96).

			Percentage	Atomic	
Experiment.	Te taken.	${ m TeO}_2$ found.	of Te.	weight.	Error.
$I.\ldots.$	2.21613	2.77612	79.83	126.31	-1.49
II	1.45313	1.81542	80.04	128.03	+0.23
$1II.\ldots$	2.67093	3.33838	80.01	127.73	-0.02
IV	4.77828	5.95748	80.21	129.34	+1.54
\mathbf{V}	2.65029	3.31331	79.98	127.59	-0.21
	М		14 197.00		

Mean atomic weight = 127.80.

In No. I the oxide was only heated to 350°, so that the last traces of TeO₃ were not decomposed : it was afterwards fused, during which there was slight loss, the atomic weight calculated from the weight of the oxide after fusion being 129.2. In Experiments IV and V, oxidation was not complete; the unoxidised tellurium was estimated by dissolving out the dioxide with hydrochloric acid, washing by decantation, and weighing the residue dried at 105°. This weight was deducted from the weight of oxide found, and from the weight of tellurium taken, and the atomic weight deduced from the corrected numbers, which are those given above. In No. IV the insoluble portion weighed 0.02846 gram, in No. V 0.00044 gram; in this last case the error caused by neglecting this altogether affects the atomic weight in the second decimal place only.

The mean of these five experiments gives the number 127.80, with a probable error of 0.32, whilst that of II, III, and V, which are the most trustworthy, is 127.78 with a probable error of 0.09.

Experiments I, II, and III, were made with tellurium once purified, IV and V with that twice purified. The occurrence in some experiments of a small unoxidised portion seemed to point to impurities: some pure tellurium was, therefore, distilled in hydrogen until about one half had been carried over; the operation was then stopped, and the more and the less volatile portions collected and acted on with nitric acid. No sensible difference was found in the two cases.

Portions of pure tellurium, and of that which remained unoxidised, were also examined with the spectroscope, but no difference between the two spectra could be detected.

Experiments on the Oxidation of Tellurium by Aqua-regia.

To obviate the error occasioned by the possible incomplete oxidation when nitric acid alone acts on tellurium, aqua-regia was next employed as oxidising agent. This necessitated the use of porcelain in place of platinum vessels, and it was found that the former always underwent a slight loss of weight, but this never amounted to as much as a tenth of a milligram in the course of a single experiment.

By the action of aqua-regia on tellurium a mixture of TeO_2 and $\text{TeO}_3.3\text{H}_2\text{O}$ is formed. As before, a weighed quantity of tellurium was taken and treated exactly as above described, with the exception that the nitric acid was replaced by aqua-regia. The tellurium dissolves quickly, aqua-regia being added until no further action goes on; on evaporation to dryness a white mass was left. Nitric acid alone was next added; this again evaporated to dryness; and the addition of acid and subsequent evaporation once more repeated.

The percentage increase at 140° was found to be as follows :---

I.	II.	III.	IV.
42.6	47.3	37.4	36.2 per cent.

On raising the mass to a higher temperature, nitrous fumes are evolved, and on gradual heating in the air-bath and finally cautiously heating over a flame, pure tellurium dioxide is left. The following numbers were thus obtained :---

Experiment.	Te taken.	TeO ₂ found.	Percentage of Te.	Atomic weight.	Error.
- I	2.85011	3.56158	80.02	127.88	-0.03
Π	3.09673	3.86897	80.04	128.00	+0.09
III	5.09365	6.36612	80.01	127.77	-0.14
IV	3.26604	4.08064	80.04	127.98	+0.02

The mean atomic weight is, therefore, 127.907, with a probable error of 0.053.

Experiments I, II, and III, were made in a porcelain crucible; No. IV in a small glass flask, placed with the neck in a nearly horizontal position. In this way any possible loss by spirting, when the acid acts on the tellurium, was avoided, and the heating could also be carried on with greater ease and less fear of loss than before.

I and II were made with the same sample of tellurium, after distilling in hydrogen and collecting in two portions. I was made with the more volatile portion; II with the less volatile portion. All these four experiments were made with twice purified tellurium, I and II with that marked A; III and IV with that marked B.

Analysis of Bromide of Tellurium and Potassium.

As a check upon the atomic weight determined as described, I have analysed the compound K_2 TeBr₆ in the manner that von Hauer describes. The crystallised salt was prepared according to his method as follows:—Equivalent quantities of tellurium and pure potas-

sium bromide were placed in a flask, and water added until the potassium bromide dissolved. Pure bromine was then gradually run in, and the flask shaken frequently. The bromine disappears, as does the tellurium, slowly, and an orange-yellow liquid is formed. A small yellow deposit forms at the same time. The liquid is decanted from this, and the excess of bromine evaporated off on a water-bath. The concentrated hot solution deposits on cooling crystals of the double salt, which crystallises exceedingly well. To recrystallise the salt, it was dried and then dissolved in a small quantity of hot water; tellurous acid then separates out at first but redissolves, unless there be an excess of water, when it remains permanent. Mr. Baker has kindly made the following measurements and determination of the crystalline form for me :---

Rhombic.-Forms observed P.0P.∞P∞. Type pyramidal; or + $\frac{P}{2}$, $-\frac{P}{2}$, the former often greatly predominating. Faces of P perfectly smooth and with a brilliant lustre; those of the basal plane and brachypinacoïd uneven. Axes $\ddot{a}: \dot{b}: \dot{c} = 1.0000: 1.4901: 1.3658.$



On heating to 120°, the salt loses water and becomes orange-coloured; it remains quite constant in weight between 120° and 160° .

For analysis a weighed quantity of the anhydrous salt was dissolved in dilute nitric acid (strong nitric acid liberates bromine) and precipi-The resulting silver bromide tated with a solution of silver nitrate. was washed many times with dilute nitric acid, and finally with water; it was then dried and weighed in the usual way.

The following results were thus obtained (Ag = 107.66; Br = 79.75; K = 39.04).

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Experiment. T	K ₂ TeBr ₆ taken. 1.70673	AgBr found. 2:80499	Percentage of Br. 69:93	Atomic weight. 127:61	Error. + 0.78
II	1.75225 2.06038	2.88072	69·96 70·07	127.40 126.33	+0.57 -0.50
IV	200958 $3\cdot29794$	5 ± 0739 $5 \cdot 43228$	70.09	120.33 126.07	-0.30 -0.76
\mathbf{v}	2.46545	4.05742	70.03	126.72	-0.11

The mean of these determinations gives Te = 126.83, with a probable error of 0.198. This is somewhat lower than von Hauer's mean number obtained in a similar way, and also lower than the number obtained by the oxidation method. Von Hauer found, as a mean of five experiments, 69.92 per cent. of bromine, the mean percentage which I obtain being 70.02.

Experiments I and IV were made with one sample, twice crystallised; Nos. II, III, and V, with another sample three times crystallised. In all cases only the distinct crystals were selected and used for analysis.

The conclusions which I draw from the three series of experiments is that the atomic weight of tellurium does not lie between those of iodine and antimony, but is greater than that of the former element, which must, therefore, precede tellurium in Mendelejeff's classification.