XLI.—Experimental Researches on the Periodic Law. Part I. Tellurium.

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On the Atomic Weight of Tellurium.

THE atomic weight of tellurium has been determined by Berzelius, who for this purpose oxidised tellurium with nitric acid, and weighed the tellurium dioxide left on ignition. He obtained the following numbers: 128.9 (in 1812), 128.9 (in 1818), and 128.3 (in 1832). In the year 1857, v. Hauer, by analysis of the potassium tellurium bromide, found Te = 127.9.* Up to the present time, the round number Te = 128 has generally been accepted as the true atomic weight of tellurium. (See the atomic weight recalculations by Clarke, Washington, 1882; L. Meyer and Seubert, Leipsic, 1883; and Ostwald, Lehrbuch, Leipzig, 1884.)

In the periodic system of elements, however, tellurium lies in Series VI, between antimony = 122 and iodine = 127, and it was therefore assumed by Mendeléeff, that the true atomic weight of tellurium lies between these numbers, and is about 125, as follows:—

Sb.	Te.	I.	
122	125	127	

According to the recent determinations made by J. P. Cooke, as well as those of Stas, these elements have the following atomic weights, Sb = 119.96 and I = 126.86, and we may therefore expect that the atomic weight of tellurium will be still smaller than the above, namely, about 123.5.

* All atomic weights used in this paper refer to the standard O = 16, for reasons published by me in the *Chemical News*, **58**, 307, and *Ber.*, **22**, 1186, of May 27th, 1889. My arguments were, I may say, accepted as valid by Horstmann (*Berl. Ber.*, **22**, R. 85) and Ostwald (*ibid.*, 1021), although not by Lothar Meyer and Seubert (*ibid.*, **22**, 872-879). The numbers used are O = 16, S = 32.07, Cu = 63.3, Br = 79.963, Ag = 107.938.

This circumstance caused Wills (*Chem. Soc. Journ.*, Trans., 1879, 704-713) in 1879 to redetermine the atomic weight of tellurium. By the oxidation of tellurium with nitric acid (I), Wills obtained numbers varying between Te = 126.63 and 129.66. Oxidation with aqua regia (II), gave Te = 128.09 and 128.30. Lastly, analysis of potassium tellurium bromide gave Te = 126.39-127.93. Wills concludes from his experiments "that the atomic weight of tellurium *does not lie* between those of iodine and antimony, but is greater than the former element, which must, therefore, precede tellurium in Mendeléeff's classification."

I may be allowed to remark that the differences between the maxima and minima of the numbers obtained by Wills as the atomic weight of tellurium differ in the Series I (see above) by 3.03 units, in Series II by 0.21, and in Series III by 1.57 units, those of the three series showing a distance of 3.27 units and, as 21.4 per cent. of Wills' numbers are *lower* than the atomic weight of iodine, it is certainly strange to see that from such discordant results a conclusion of such great theoretical importance should be drawn.

It has been shown lately by Basaroff (J. Russ. Chem. Soc., 1887, 61-73), that in the same manner as the elements follow each other in the periodic system, their atomic weights are found to increase, so that the regular variation of quotients obtained by dividing the atomic weight of an element by that of the next lower one may be represented graphically in a satisfactory manner, and it was therefore still more probable that the said regularity should hold good also in the case of tellurium, and that a lower value would be obtained for its atomic weight than that of iodine, I = 126.86.

The object of the following research was to undertake a thorough revision of the atomic weight of tellurium, and to that research I have devoted the greater part of my spare time during the past six years.

It was to be expected that tellurium would not remain an exception to the periodic law, for although nearly one-third of the known elements would not have fitted into the periodic system with their originally accepted atomic weights, yet hitherto it has been found that these atomic weights are at fault, and not the system. These apparent exceptions are: Li, Be, Sc, Ti, V, Co, Ga, Y, Nb, Mo, Ru, In, Sb, Cs, La, Ce, Ta, Os, Ir, Pt, Bi, Au, Th, and U.

Preparation of Material.

Two kinds of material were used for the preparation of pure tellurium: Hungarian tellurium ores, nagyagite, sylvanite, and petzite and Hungarian crude tellurium. After bringing the tellurium into solution in the form of chloride, it was precipitated in the usual way with sulphur dioxide in the elementary state, and this precipitate, after drying, was fused with potassium cyanide in order to get rid of any selenium which might be present, although none could be detected in it,* and also of traces of the heavy metals which are carried down with the tellurium on precipitating it with sulphur dioxide. From the claret-coloured solution of potassium telluride, tellurium was precipitated by means of a current of air. Lastly, it was placed in little porcelain boats which were introduced into a wide Bohemian glass tube, surrounded by wire gauze, and then distilled in a current of hydrogen. Minute traces of tellurides of the heavy metals were left behind.

The distilled tellurium forms a crystalline mass of silvery lustre which does not change its colour on exposure to the air. During distillation, part of the tellurium combines with hydrogen, forming tellurium hydride which, before escaping from the heated tube, is again decomposed with deposition of beautiful needle-shaped crystals of the element measuring 1 cm. or more in length; the hydrogen formed, however, always contains some gas of an extremely disagreeable odour which behaves like tellurium hydride, and has very poisonous properties.

By this costly process, large quantities of tellurium were prepared, the properties of which are those required of pure tellurium, according to the present state of our knowledge; it may be redistilled in hydrogen without leaving any residue, and no impurities can be detected in it by qualitative analysis.

Determination of the Atomic Weight.

It was my intention to determine the atomic weight of tellurium by as many independent methods as possible, but in the course of this investigation it was found to be very difficult to devise methods which would answer the purpose. In this, as in many other respects, tellurium approaches its next horizontal "atomanalogue," antimony, of which Berzelius said in 1812: "I have never worked with a material with which it was so extremely difficult to obtain constant results." (Schweiger, 6, 149.)

All the reagents used in the course of the present investigation, as hydrochloric, nitric, and sulphuric acids, were subjected to fractional distillation from platinum vessels, and the water employed was redistilled with alkaline permanganate, and the steam cooled in a platinum condenser; the set of weights used was corrected by the method of vibrations.

* Having been probably volatilised by the repeated evaporations with strong hydrochloric acid employed to get rid of nitric acid.

A. Conversion of Tellurium into the Dioxide.

Tellurium was oxidised (a) with nitric acid; (b) with aqua regia.

(a.) Oxidation with Nitric Acid.—The finely powdered tellurium was treated in Experiments 1 and 2 in a platinum crucible with dilute nitric acid, in which it readily dissolves. The crucible was covered with a watch-glass, in order to avoid loss by spirting. After the reaction was over, the contents of the crucible were evaporated to dryness on a water-bath, and then heated slowly up to 400°. It was observed, however, that the basic tellurium nitrate formed loses its last trace of nitric acid at a temperature at which part of the tellurous anhydride contained in the crucible begins to volatilise, the watch-glass becoming covered with a white substance.

Experiment No. 3 was carried on in a flask of hard Bohemian glass (previously boiled with aqua regia) so that the volatile portions were condensed in its colder neck. This method was abandoned, as it did not give constant results.

Exp.	Tellurium.	Te dioxide.	Atomic
No.	grams.	grams.	weight.
1	1.9509	2.4437	$12\bar{6}.7$
2	0.9212	1.1523	127.6
3	1.2947	1.6267	124.8

(b.) Oxidation with Aqua Regia.—Weighed quantities of pure powdered tellurium were placed in a round-bottomed flask of hard Bohemian glass, Fig. 1 (previously boiled for many days with aqua regia), and, after introducing some hydrochloric acid, nitric acid was

F1G. 1.



added gradually. As, however, large quantities of the finely divided spray of the solution are carried over with the escaping gases, the neck of the flask was closed with a glass tube, b, containing bulbs in the middle, the wider end of which was tightly ground into the neck of the flask, the narrow end dipping into a small beaker containing nitric acid. The escaping gases are thus forced to pass through the nitric acid contained in the small bulbs and in the beaker, and in this way the escaping spray of tellurium solution is completely condensed.

The arrangement of this simple apparatus is seen from Fig. 1, and it was used several times during the course of the present investigation when weighed quantities of substance had to be dissolved. without any of the latter being carried off with the escaping gases.

On evaporating the solution of tellurium in aqua regia, some of the tellurium tetrachloride formed is volatilised-a circumstance which was overlooked by Wills-and, further, during the evaporation, organic substances contained in the air may be condensed in it, causing a subsequent reduction at a higher temperature. In order to avoid these sources of error, the solution of tellurium was evaporated in a current of pure, dry air in an apparatus the arrangement of which is seen from Fig. 2. Air from the open was aspirated through potash solution, e, a long layer of cotton-wool, f, over pumice-stone soaked



with sulphuric acid, g, and then passed through a tube, h, containing red hot platinum sponge. This tube ended in d, which is ground into the flask a containing the tellurium solution, and heated in an airbath, b, the bottom of which was protected from the direct action of the radiant heat by a screen, c, made of asbestos cardboard. The glass bulbs i and flask k serve for the condensation of the acids escaping from the flask a. The various single pieces of which this apparatus

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The distilled mixture of hydrochloric and nitric acids, on evaporation with sulphuric acid, gives several milligrams of basic tellurium sulphate (see below, B), but it is a question whether the whole of the escaping tellurium can be collected in this way. However, on neglecting even this small quantity of tellurium, the atomic weight will be found to be higher by 1.2 units. After evaporation to dryness, the residue in the flask was repeatedly evaporated down with nitric acid in a current of air at 110°, and finally heated to 440°. It was found, however, that at the point at which tellurium trioxide decomposes into the dioxide and oxygen the dioxide begins to volatilise; moreover, when the "tellurium dioxide" after weighing was treated with hydrochloric acid, a white residue was always left, and this would not dissolve in the acid even on continued boiling !

Exp.	Te.	TeO_2 .	Atomic
No.	grams.	grams.	weight.
4	2.3092	2.9001	125.0
5	2.8153	3.5332	125.5
6	4.0176	5.0347	126.4
7	3.1613	3.9685	125.3
8	0.8399	1.0526	126.4

B. Conversion of Tellurium Dioxide into the Basic Sulphate.

As Marignac (Archives Sc. Phys. Nat. [3], 10, 17, separate copy) had succeeded in determining the atomic weight of bismuth by the conversion of the oxide into the sulphate, a similar method was tried For this purpose, tellurium dioxide was with tellurium dioxide. dissolved in hydrochloric acid, and the solution (containing always some undissolved white substance) was evaporated to dryness with a slight excess of sulphuric acid. As soon as the hydrochloric acid had been driven off, beautiful, glistening crystals-rhombic scales-of basic tellurium sulphate, Te₂O₄SO₃, were left. Sometimes beautiful, regular crystals-combinations of the cube with octohedron-were observed, but these seem to be another salt. It was remarkable that when this operation was carried on in platinum crucibles lower results were obtained (Experiments 9, 10, 11), whereas in glass or porcelain vessels (Experiments 12 and 13) the excess of sulphuric acid could not be driven off without the sulphate undergoing partial decomposition, so that the results obtained were very high.

Exp.	TeO2.	Te ₂ SO ₇ .	Atomic
No.	grams.	grams.	weight.
9.	2:4437	3:0570	127:5
10	1.0526	1.3202	125.5
	1.1523	1.4461	125.0
12	5.0239	6·2182	136.4
	2.9818	3·7197	129.4

C. Conversion of Tellurium into the Basic Sulphate.

Tellurium was first converted into the dioxide, and the latter into the sulphate. Experiments 14—19 were made in platinum crucibles, and they give again lower results than Experiment 20 which was made in a glass flask.

Exp.	Te.	Te_2SO_7 .	Atomic
No.	grams.	grams.	weight.
14	1.9509	3.0570	127.1
15	0.9212	1.4461	126.4
16	0.8399	1.3202	125.9
17	0.5836	0.9166	126.2
18	0.5243	0.8261	$125 \cdot 1$
19	1.5464	2.4402	124.6
20	5.1674	8.9271	130.0

The method was given up as, in spite of the greatest care, it was found to be impossible to obtain constant results.

D. Synthesis of Silver Telluride.

Chemically pure silver (preparation see below) was weighed in a porcelain boat, and tellurium vapour passed over it while it was heated in a porcelain tube in a current of carbon dioxide. The latter was purified by passing it over hot sodium carbonate, and then over red hot silver and copper wire. On allowing it to cool in a current of the same gas, silver telluride having approximately the composition Ag₂Te remained in the boat as a fused, crystalline mass of metallic lustre.

Experiment 21.—1.1434 grams of silver gave 1.8019 grams of silver telluride (containing 0.6585 Te). From this the atomic weight Te = 124.3 is calculated. It may be that the interior of the mass contains ancombined metallic silver which escaped the action of the tellurium vapour, and therefore a fresh portion of finely divided silver was mixed with an excess of powdered tellurium, and this mixture was first fused in a current of carbon dioxide, and then strongly heated.

It was found that the silver telluride obtained was more brittle and

more easily fusible than that just described, and that it contained an excess of tellurium over that required by the formula Ag_2Te ; whereas, when its composition approaches that formula, it does not melt even at a strong red heat, and is far less brittle.

Experiment 22.—From 0.5382 gram of silver, the following quantities of telluride were obtained :—

	Time of heating	Telluride.	Atomic
	in hours.	grams.	weight.
(a.)	4	0.8602	129.5
(b.)	7	0.8589	128.6
(c.)	15	0.8560	127.5

In order to drive off any excess of tellurium which might have remained in the interior of the fused mass, the telluride was powdered and heated again for five hours. It did not fuse again, and its weight was finally 0.8513 gram. This corresponds with Te = 125.6.

Experiment 23.—1.0796 grams of silver was mixed with an excess of tellurium and heated in the way described. After three hours, 1.8906 grams of silver telluride was formed; after 11 hours, 1.7194 grams. Hydrogen does not reduce this compound to pure silver, on the contrary, silver seems to combine more readily in its presence with an excess of tellurium, and the latter is given off with greater difficulty. The result was 1.7187 grams, calculation from which gives Te = 127.8.

Experiment 24.—In order to obtain a very high temperature, a Fletcher tube-furnace, acting with or without blast, was used. The boat containing the tellurium and silver was heated for half an hour to redness, and then, for 10 minutes only, to a yellow heat, as otherwise the boat fuses to the inside of the porcelain tube. 0.4917 gram of silver yielded 0.7835 gram of telluride, from which Te = 128.1.

It is seen from these experiments that at a point at which the silver telluride contains for 2 atoms of silver 127.5 to 128.1 parts of tellurium, the excess of the latter is driven off with the greatest difficulty. If, however, the surface of the telluride is artificially increased, dissociation of the silver telluride begins to take place.

The partial synthesis of silver telluride does not give results sufficiently exact for the determination of the atomic weight of tellurium.

E. Synthesis of Copper Telluride.

Copper combines with tellurium with far greater energy than silver does, so that a telluride of the composition Cu_2Te absorbs further quantities of tellurium if heated in its vapour, this absorption again

going on better in an atmosphere of hydrogen than in one of carbon dioxide.

The copper employed in these experiments was prepared by Hampe's method (Zeit. anal. Chem., 1874, 352), that is, electrolysis of a copper solution from which the impurities had been removed by partially precipitating with potassium hydroxide. Before experiment, the pure copper was heated in a current of hydrogen and allowed to cool in an atmosphere of carbon dioxide.

As the polytellurides of copper formed at first (they are interesting compounds and alloys) give off the excess of tellurium above that required by the formula Cu_2Te with far greater difficulty than the silver polytellurides, the full heat of the Fletcher blast tube-furnace had to be employed. The mixture of copper and tellurium was contained in a small porcelain boat, the outer glaze of which had been removed by etching with hydrofluoric acid. This boat was placed in a larger one, filled up to the edge with Calais sand, and this second boat was placed on a layer of sand in the porcelain tube in order to avoid the chance of the different porcelain vessels fusing together. The synthesis of the copper telluride was effected in the same manner as that of the silver telluride, the temperature being of course considerably higher.

Of the numerous experiments made, only a typical one need be mentioned here.

Experiment 25.—The copper telluride was weighed after being heated for a definite length of time to a yellow heat, and then heated again. It will be seen that the quantity of tellurium given off is smaller the more nearly we approach a telluride of the composition Cu_2Te .

From 0.5033 gram of copper, the quantities of telluride given in the second column were obtained :—

	Time of heating.	Copper telluride.	Loss of Te per minute.	Atomic weight.
(a.)	5 min.	1.1316	_	
(b.)	15 ,,	1.0533	0.0078	—
(c.)	25 ,,	1.0207	0.0033	130.2
(<i>d</i> .)	30 ,,	1.0108	0.0020	127.7
(e.)	35 ,,	1.0044	0.0013	126.1

The copper telluride, prepared by fusion in a current of carbon dioxide, is a steel-blue, crystalline mass, the surface of which was in Experiment 25(e) covered with small blisters, which seems to prove that the compound Cu₂Te contains a small quantity of free copper.

On continued heating of the copper polytellurides to redness in a

current of hydrogen, beautiful rhombohedra of a telluride possessing a steel colour and great lustre were obtained.

F. Synthesis of Gold Telluride.

Polytellurides of gold (alloys of gold and tellurium) are crystalline compounds of a silvery lustre. Heated to redness in a current of carbon dioxide, they easily dissociate, leaving finally a mixture of white gold telluride, Au_2Te , with yellow gold. I shall not give here any account of the individual experiments, as they cannot be used for the determination of the atomic weight of tellurium.

All these briefly mentioned metallic tellurides obtained by synthesis are interesting instances partly of definite compounds, partly of alloys. They confirm the law enounced by Beketoff ["Researches on the Phenomena of Displacement," Charkoff, 1865 (in Russian)] in 1859 and 1865, that the affinity of two heterogeneous bodies to each other is the greatest when the weights of the masses taking part in the reaction are equal. This is seen from the following group:—

$$Cu_2 : Te = 126 : 126$$

 $Ag_2 : Te = 216 : 126$
 $Au_2 : Te = 394 : 126$

and at the same time it may be remarked that the stability at a high temperature considerably decreases from the highest member (Cu_2Te) to the lowest (Au_2Te).

G. Analysis of Tellurium Dioxide.

Pettersson and Ekman have determined the atomic weight of selenium by the reduction of selenium dioxide with sulphurous acid and weighing the selenium precipitated. The same method was used by me for the determination of the atomic weight of tellurium.

Pure tellurium dioxide was prepared by dissolving distilled tellurium in aqua regia, evaporating the solution several times with distilled nitric acid, and fusing the residue in small portions in a platinum crucible. After a short fusion, the tellurium dioxide is obtained in the form of a brittle, crystalline mass of a milk-white or cream colour, which becomes yellow or brownish-yellow as soon as the fusion is continued more than is absolutely necessary.

Weighed quantities of the powdered dioxide were dissolved in hydrochloric acid in the glass apparatus, Fig. 1 (p. 385), in order to avoid loss by the volatilisation of the tetrachloride formed. The yellow solution obtained was mixed in the same flask with concentrated sulphurous acid, and it was remarked that the tellurium precipitated is some-

times so finely divided that it forms a transparent solution of a dark greenish-blue, blue, or violet colour.* The solution was heated to $60-70^{\circ}$ and completely saturated with sulphur dioxide; this caused a separation of tellurium in a flocculent state. After heating the solution for some time in order to produce complete reduction and separation, the precipitate was washed first with dilute sulphurous acid and then with water, but the finely separated tellurium is so easily oxidised that a small portion always goes into solution, so that the filtrate, after concentration and treatment with sulphurous acid, always gives small quantities of tellurium. This tendency of finely divided tellurium to oxidation is so great, that after standing for some time with cold hydrochloric acid in contact with air, considerable quantities pass into solution as tellurium tetrachloride, whereas tellurium alone is insoluble in cold hydrochloric acid.

The oxidation of tellurium is more apparent when it is dried at 100°, as is seen from the following :----

Experiment 26.—3.8745 grams of tellurium dioxide were reduced in the manner described, and dried on a weighed filter at 110°. Theory (see H) requires 79.93 per cent. Te. The quantity of tellurium obtained weighed—

(a.)	After 2 hours		3.1249	grams	=	80.63	р. с.
(b.)	After further 6 ho	ours	3.1279	,,	=	80.71	,,
(c.)	,, ,,		3.1396	,,	=	81.01	"

This large increase in weight is partly due to the cause mentioned below.

The results obtained on drying the precipitated tellurium in a vacuum or in a current of carbon dioxide are not much better, as after fusion of such tellurium in a current of pure hydrogen, drops of water are obtained, proving that the tellurium has been partly oxidised during washing.

Finely divided tellurium passes through glass-wool, asbestos, or even artificial pumice-stone, so that, in order to avoid the use of weighed paper filters, the method of reversed filtration was used for its collection with a slight modification, which will be understood from the accompanying drawings, Figs. 3 and 4. The upper part of the stand⁺ carrying the crucible can be taken off, and is so arranged that the crucible carrying the liquid to be filtered cannot be easily upset, a circumstance of great importance when, for example, the

^{*} Selenium gives, under similar circumstances, solutions of a beautiful intense blue colour.

⁺ This stand was made of excellent workmanship by Messrs. Jos. and Jan Fric, mechanicians, Prague.

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filtration of silver bromide is effected in a nearly dark room. The tellurium was washed finally with alcohol and dried at 110° in an atmosphere of hydrogen.





Unfortunately it was found here that considerable quantities of sulphuric and hydrochloric acid are carried down with the tellurium from the solution in which it is precipitated, but these could be removed to a very great extent by heating it, after taking out the filter, in a current of hydrogen to about 300°. The results are then pretty nearly accurate, as seen from-

Experiment 27.-2:5489 grams of tellurium dioxide, after reduction with sulphurous acid and drying at 130° in a current of hydrogen in the same flask which served for its precipitation, gave (a) 2.0389 grams of tellurium. From the filtrate (b), 0.0047 gram was obtained. VOL. LV. 2 F

The portion (a) was heated in a current of hydrogen at 300° in a flask similar to that represented by a, d in Fig. 2 (p. 386), and it was found that the escaping vapours gave with silver nitrate solution a white, and not a black, precipitate, a proof that only hydrochloric acid and no tellurium hydride was formed. The loss of weight was equal to 0.0062 gram, so that the real weight of the tellurium was 2.0374grams.

From this, the atomic weight of tellurium is calculated as Te = 127.5, and the percentage composition of the dioxide as

Tellurium	79.93
Oxygen	20.07
	100.00

H. Analysis of Tellurium Tetrabromide.

The methods described under Aa, Ab, C, D, E, and F, gave for the atomic weight of tellurium numbers varying but little from the theoretically expected number, Te = 125, and from these results it would have been correct to assume that number as the true atomic weight of tellurium—as the author actually did for some time especially had there been a better agreement between these numbers, a circumstance which, as shown above, was unfortunately never met with in the case of tellurium.

Of all the methods hitherto mentioned in this paper, that described under F alone seems to yield favourable results, although with some difficulty; here, however, we have the most unfavourable case of an atomic weight determination, viz., weighing the tellurium, resulting from an analysis, in the elemental state.

I expected to obtain good results from the analysis of tellurium tetrabromide, as the gravimetric, and especially the volumetric estimation of combined bromine are, according to Stas (see especially his latest classical research, *Mémoires de l'Académie Royale de Belgique*, **43** [2], 1—105), the most exact of all quantitative determinations. This method has been applied lately with great success to the determination of the atomic weight of antimony by J. P. Cooke (*Proc. Amer. Acad.*, **13**, 1—71; **15**, 251—255; and **17**, 13—22), in the case of aluminium by Mallet (*Phil. Trans.*, 1880; *Chem. News*, **45** and **46**), for titanium by Thorpe (this Journal, Trans., 1885, 108), and in the case of gold by Thorpe and Laurie (Trans., 1887, 565).

Neither the gravimetric nor the volumetric determination of chlorine in chlorides answers the same purpose on account of the comparatively great solubility of silver chloride in water, and in the solutions employed, as is shown in a most remarkable research pub-

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lished by Stas ("Recherches de Statique Chimique," Ann. Chim. Phys. [4], 25, 22-94; [5], 3, 145-188 and 289-327).

Preparation of Pure Bromine.

The pure bromine employed was prepared by two methods, the first being that recommended by Stas. For this purpose commercial bromine was first repeatedly shaken with water, dissolved in a concentrated solution of calcium bromide (prepared from the same bromine, calcium hydroxide, and ammonia), precipitated with water, and dried over calcium bromide and oxide. The last trace of water was removed with phosphorus pentoxide, which had been resublimed in a current of dry air.

The second method consisted in distilling potassium bromide (350 grams) dissolved in water (500 grams) with a quantity of chromic mixture (150 grams of potassium dichromate dissolved in 600 grams of pure sulphuric acid and mixed with 500 grams water) insufficient for its complete decomposition. In order to avoid dangerous explosions resulting from the heat developed by the reaction, the large retort containing the mixture was immersed in a large vessel of water at about 65°. The quantity of crude bromine obtained in this way from the above mixture weighed 210 grams instead of the theoretical amount of 235 1 grams.

In order to purify this bromine from the last traces of iodine and chlorine, a process recommended by Stas (*Mém. Ac. Belge*, **43**, 90-93), but not sufficiently known to chemists, was used. This consists in distilling 400 grams of bromine from a mixture of 300 grams of water, 250 grams of potassium bromide and 25 grams of granulated zinc oxide (prepared by heating pure basic zinc nitrate to a white heat). The same mixture may be used for the rectification of two successive portions of bromine of 400 grams each. The bromine obtained was dried over anhydrous calcium bromide and oxide, and the last trace of water was removed by means of anhydrous barium oxide.

The bromine prepared by either of these methods was distilled in an apparatus consisting entirely of glass. It was found to boil at 63°, but on treating a portion of it with potassium hydroxide the smell of an organic bromine compound could be perceived, probably bromoform or carbon tetrabromide, due to the action of bromine on particles of dust and filter-paper, unavoidably present in the reagents used (cf. Hamilton, Trans., 1881, 48). We must regard with admiration the great care taken by Stas, when he prepared bromine which was quite free from any carbon compound containing bromine.

Preparation of Tellurium Tetrabromide.

In order to prepare the tetrabromide, a combustion-tube of the best Bohemian glass was used, which was sealed and rounded at one end and was widened conically at the open end; into the latter were carefully ground (a) the tube of a Drechsel gas wash-bottle, and (b) a glass tube of a similar diameter, drawn out a little at the other end and sealed to a \bigcup -tube.

The sublimation-tube was placed vertically in cold water, several grams of pure bromine poured into it, and then very finely powdered tellurium was gradually added in small portions, shaking the liquid contents from time to time. In order to remove the excess of bromine, the Drechsel "Aufsatz" was inserted into the open end and the tube was heated in warm water while a current of dry carbon dioxide was passed through; the tellurium tetrabromide was then left in the tube as a beautifully yellow, loose mass. The product, however, is not pure, as it contains in its interior some free tellurium which has escaped the action of the bromine. On heating this mixture to a higher temperature, tellurium dibromide is formed thus : $TeBr_4 + Te$ $= 2 TeBr_2$. The tetrabromide cannot be fused or boiled at the ordinary pressure without undergoing partial decomposition into free bromine and the greenish-black dibromide, $TeBr_4 = TeBr_2 + Br_2$. The lower compound gives a deep-violet vapour.

After numerous experiments, the following method was used for the preparation of pure tellurium tetrabromide for analysis. The glass tube a, Fig. 5, containing the yellow tetrabromide, was connected



FIG. 5.

with the tightly ground tube, b, which, by means of a drying tube, c, filled with pumice moisted with sulphuric acid, was connected with a pump. The greater portion of the lower part of the sublimation-tube a was heated in an air-bath, ee, made of pieces of asbestos cardboard joined by means of platinum wire. The bath could be covered with a mica plate, dd, in order to watch the behaviour of the bromide with rise of temperature, and in the same level as the sublimation-tube a thermometer, f, was placed horizontally. A vacuum was then made in the tube, and its temperature raised to 200°. At this temperature, the more volatile dibromide could be separated by fractional sublimation from the less volatile tetrabromide, which remained behind in the lower part of the tube, and it was found possible to drive the subliming dibromide quite out of the tube a into the tube b. On now raising the temperature of the air-bath to about 300°, the tetrabromide is found to sublime without leaving any residue, and to condense on the colder walls of the tube in the form of beautiful, fiery-red, crystalline crusts which become orange-coloured on cooling. If there had been any oxybromide present, it would have decomposed, leaving a residue of tellurium dioxide, thus: $2\text{TeOBr}_2 = \text{TeBr}_4 +$ TeO₂, as shown by special experiments with a bromide prepared from superficially oxidised tellurium.

The crusts of pure tetrabromide are very brittle, easily detached from the walls of the tube, and not hygroscopic when weighed in a small weighing bottle made of thin glass, closed with a well-ground stopper; an empty bottle of equal size was always placed on the other pan of the balance. By the method of vibrations, the weight of the substance could be determined within a few hundredths of a milligram.

The bromide dissolves easily in a solution of tartaric acid (2 parts) in water (2 parts) without leaving any appreciable residue, but on using a more dilute solution, decomposition takes place accompanied by the separation of sparingly soluble telluric acid. The orangecoloured solution contains tellurium tetrabromide, but on addition of water its colour disappears and it then contains a hydrobromic acid solution of tellurium tartrate. Had the bromide contained any trace of oxybromide, telluric acid would have been left undissolved.

In a preliminary experiment, a tartaric acid solution of tellurium tetrabromide was precipitated by silver nitrate in the ordinary way and the silver bromide weighed.

Experiment 28.—3.1591 grams of tellurium tetrabromide yielded 5.3612 grams of silver bromide. From this Br = 72.22 per cent. This would correspond to an atomic weight of Te = 123.0. Subsequent exact experiments, however, have shown that the percentage of bromine is in reality only = 71.48, so that the silver bromide must have been too heavy by 0.0552 gram.

A detailed examination into this source of error has shown that it is due to two circumstances.

Firstly, it was found that in concentrated solutions containing tellurium, tartaric acid, and bromine, silver nitrate gives a precipitate consisting of silver bromide, which settles rapidly, and also of glistening, crystalline scales, which separate slowly from the liquid and are deposited on the surface of the first precipitate. They consist of tellurium silver tartar emetic, and have probably the composition $(C_4H_4O_6)_2Ag_2(TeO), 2H_2O$, as shown by the following analysis: ---

Experiment 29.-0.4660 gram gave 0.1913 gram silver chloride.

Calculated.	Found.
31.2	30.9

The analogous citrate seems to have a more complicated formula, $(C_6H_5O_7)_2Ag_3H(TeO), 2H_2O$.

Experiment 30.-0.6491 gram gave 0.3205 gram silver chloride.

Calculated.	Found.
36·7	37.1

The tartrate exhibits the most complete analogy to antimony, for Cooke has observed that in a tartaric solution of antimony tribromide, silver nitrate causes the formation of $(C_4H_4O_6)Ag(SbO),H_2O$.

In order to avoid the formation of silver tellurium tartar emetic and its precipitation along with the silver bromide, the precipitation of silver bromide was effected in the presence of a sufficient quantity of water and of nitric acid, in which this substance is easily soluble; and all excess of silver nitrate was avoided, as the substance is formed only when an excess of silver nitrate over that required to form silver bromide is present.

The second cause of the higher weight of the silver bromide precipitated in Experiment 32 is the circumstance that silver bromide readily carries down with it foreign substances contained in the solutions from which it is precipitated; it acts in this way with tellurium tartrate, as is seen from its becoming black in contact with zinc and water. This can be avoided only when, following Stas' directions, the silver bromide is vigorously shaken with the solution from which it has been precipitated, and with the water containing a little nitric acid used for washing it—of course in perfect darkness. Indeed, it is found that in this way a pure silver bromide, containing no tellurium, is obtained.

Several preliminary experiments carried out in this way, gave results approaching the truth, but they are omitted in order to avoid everything superfluous, although the first experiments seemed to point to insurmountable difficulties.

Experiment 31.—3.82048 grams of tellurium tetrabromide, after being dissolved in tartaric acid, were precipitated with the requisite amount of silver nitrate, washed by repeatedly shaking, and the silver bromide was collected by the method of reversed filtration. Its weight was 6.41734 grams = 71.482 per cent. of bromine. From this, the atomic weight of tellurium is calculated as Te = 127.61.

After this, the combined gravimetric and volumetric method was used for the analysis of tellurium tetrabromide.

On Pure Silver and its Properties.

Pure silver was prepared by two methods given by Stas.

A. Purest silver from the Mint was dissolved in distilled nitric acid, and the solution of the fused nitrate precipitated with distilled hydrochloric acid. After washing the chloride by prolonged agitation, it was boiled with aqua regia, and reduced with pure milk-sugar and sodium hydrate. The metal was boiled out with dilute sulphuric acid, digested with ammonia, and fused under borax and nitre in a Paris crucible. After pouring it into moulds of kaolin, the bars were rolled out into thin ribbons, between hard steel rollers well oiled, and the thin plates cleaned with sea-sand, ammonia, and alcohol. After cutting into pieces of about a gram and its subdivisions, they were treated with hydrochloric acid and ammonia, and finally heated in a porcelain crucible nearly to the melting point of silver.

B. Ordinary alloy of silver and copper from the Mint containing 0.900 of the former metal, was dissolved in nitric acid, and the mixed nitrates of silver and copper fused for some time. The fused mass was treated with dilute ammonia, and the solution filtered after standing for several days.

After adding double the amount of ammonium sulphite necessary to precipitate the solution of silver (which contained less than 2 per cent. of the metal), and allowing it to remain in closed vessels filled up to the neck, very nearly the whole of the silver was precipitated in beautiful crystals, having apparently the form of hexagonal pyramids (in reality tesseral). The remainder of the silver was thrown down on heating the solution. The precipitation is complete, the total loss amounting to about 0.5 per cent. After washing, the silver was placed in contact with strong ammonia, and digested in a closed flask for many weeks. On evaporating the solution, a non-explosive black substance was obtained, which on treatment with hydrochloric acid gave silver chloride. The filtrate from the latter contained a small quantity of copper, amounting, as found by colorimetric estimation, to about 0.0002 per cent, of the silver employed.

The silver was then fused in the usual way with borax and nitre, poured into a mould made of kaolin, the bars treated with fusing potassium sodium carbonate, and washed successively with boiling hydrochloric acid and ammonia. One portion was distilled in a furnace made entirely of lime, but only a small quantity was thus obtained from want of a platinum blowpipe, one made of hard glass having been used. Another portion which served for the atomic weight determination, was fused in a furnace made of lime, and granulated by pouring from a considerable height into distilled water.

The colour of this silver was beautifully white, and its standard fineness is, according to Stas = 99.997, the distilled silver being = 100.000.

On the Occlusion of Oxygen in Silver of M. Stas.

Dumas (Ann. Chim. Phys. [5], 15, 289-304), as is generally known, found that silver-which had been hitherto regarded as pure-when heated in a Sprengel vacuum gave up considerable quantities of oxygen, so that the standard fineness becomes 99.992 to 99.975 instead of 100, according as to whether 57 up to 174 c.c. of occluded oxygen = 0.008 to 0.025 per cent. by weight are given up by 1 kilo. of the metal.

This circumstance is theoretically of the highest importance, silver being in reality the standard of the atomic weight determinations of Stas, and consequently of many others depending upon these. But if the silver used by Stas had not been pure, the atomic weight of silver would be only Ag = 107.929 instead of 107.938 (Ostwald's number) or even only Ag = 107.911, according to the amount of oxygen, the maximum difference amounting to 0.027. In the same way the whole of Stas's numbers will be affected, and, indeed, Mailet (Phil. Trans., 1880, 1003; Chem. News, 45 and 46) and Clarke ("Recalculation of the Atomic Weights," 262) applied this "Dumas Correction" to the numbers obtained by Stas. But certainly Sebelien ("Beiträge zur Geschichte der Atomgewichte," 90) is right in remarking: "Eine Correction der Stas'schen Zahlen einführen zu wollen hiesse nur dessen classisches Werk verderben, ohne Garantie daf r erhalten zu haben, der Wahrheit näher gekommen zu sein."

Mallet (*loc. cit.*) prepared his pure silver by a method slightly different from that of Stas, and on heating it in a Sprengel vacuum he obtained for 1000 grams of silver 34.63 to 30.12 c.c. of a gas. The silver was placed on a layer of lime, and the gas does not seem to have been analysed, being taken by Mallet for oxygen without any remark. The only chemist who has in this respect investigated silver prepared by Stas's method was J. D. van der Plaats ("Mand-

blad voor Natuurwetenschappen," 1886, No. 2, blz. 25-32). He gives the full history and literature of this subject, and finds that pure silver does not change its weight when heated in a current of air, hydrogen, or carbon monoxide. On heating in a Sprengel vacuum, no loss of weight took place, but from 10 grams of the metal as much as 2 c.c. of a gas were obtained, this being regarded by the author as air, for 0.5 c.c. were absorbed by phosphorus. It is to be regretted that only 10 grams of silver were employed in this beautiful research, for, calculated for 1000 grams of silver, the above quantity becomes 200 c.c. of gas, and is therefore larger than the maximum obtained by Dumas. Van der Plaats concludes with the following interesting passage: "Enkele weken geleden vernam ik echter, hoe Dumas voor zijn dood de overtuiging heeft verkregen, dat door zijne proeven de aanwezigheid van zuurstof in zilver niet bewezen is."

In order to settle that interesting question, I have investigated the bars of silver prepared by Stas's second method. I constructed a Sprengel air-pump, provided with a system of air-traps, in order to avoid the mercury carrying air with it; the single parts of the apparatus were, of course, fused together, or, when Bohemian glass had to be connected with soft Thuringian glass, mercury joints were used. (See S. P. Thompson,* "The Development of the Mercury Air-Pump," London, 1887 and 1888.)

In the preliminary experiments, about 3 c.c. of a gas—air—were obtained for every 100 grams of silver, but it was found later on that this was due to surface condensations and to moisture. It was therefore necessary to insert between the pump and the tube containing the silver a \bigcup -tube filled with pumice stone containing sulphuric acid. (Phosphorus pentoxide was not used, as it was found to contain some trioxide, the vapour of which might contaminate the silver.)

Experiment 32 was carried on with all possible care. For this purpose, $153 \cdot 2133$ grams of pure silver in bars was heated nearly to its melting point, and, after cooling, placed in a combustion tube of the hardest Bohemian glass, made for this purpose at the celebrated works of J. Kavalier (Sázava). The inner diameter of the tube was 19 mm., the walls were of $2 \cdot 2$ mm. thickness, and the end, which was not connected with the air-pump, was drawn out conically. In the first place the silver contained in the tube was heated at 150° , while a current of carefully dried and purified air was drawn over it, and as soon as it was cold the tube was sealed up at the conical end. A vacuum was then made in the tube, and the next day it was again pumped out.

When a vacuum as perfect as possible was established, the tube

^{*} I am indebted to the author for the copy of this most interesting paper.

containing the silver was heated to 450° , the pump acting all the time, and the gas given off was collected in a carefully graduated microeudiometer, 1 mm. of the scale of which corresponded to 0.076 c.c., so that, by means of a telescope, the volume of the gas collected was 0.219 c.c. at 0° and 760 mm.* The microeudiometer was now replaced by a fresh one, and the temperature raised to the strongest red heat which could be applied to the tube without its form changing, and the tube was pumped out at this temperature during six hours. (This is the duration of Dumas' experiment, but it was far longer than was necessary for my purpose.) The volume of gas given off between 450° and a red heat was found to be = 0.844 c.c.

It was possible to analyse this small quantity of gas very accurately by Bunsen's method, using the microeudiometers mentioned above, and in this way it was found to consist of 0.586 c.c. of oxygen and 0.298 c.c. of nitrogen, the latter value corresponding to 0.312 c.c. of air, so that the quantity of oxygen given up by the silver at a red heat amounts to 0.532 c.c.

Experiment 33.—In order to apply a correction to the very small volumes of gas in question, it was necessary to study the way in which my "Sprengel vacuum" behaves on heating. An experiment identical with the foregoing was therefore made, using an *empty* glass tube, under perfectly similar conditions. The volume of the gas collected was = 0.249 c.c.

Experiment 34 was made with the silver which had been heated at 150° as above in Experiment 32, and then to a red heat. The volume of the gas was = 0.215 c.c. (air). Experiment 34 gave 0.215, Experiment 33 gave 0.249, Experiment 32 gave 0.219 up to 450° . These three quantities are identical, so that the last one is not to be accounted for in Experiment 32.

The net result is that $153 \cdot 2133$ grams of silver when heated to redness in a Sprengel vacuum give off 0.312 c.c. of air, probably condensed, and 0.524 c.c. of oxygen. Its weight is 0.0007609 gram = 0.0004996 per cent., so that the composition of the silver in question is—

> Silver 99·9995 Oxygen 0·0005 100·0000

The same silver, according to Stas, has a standard fineness of 99.997, that of distilled silver being 100.000; and that of the least

* All volumes given below are reduced to normal temperature and pressure.

pure silver of Stas being 99.994. In these two cases, the differences between the samples of purest silver are, therefore, 6 to 12 times larger than that due to the "occlusion" of oxygen. The last-named impurity cannot be determined either by titration or by the change of weight before and after heating, since small traces of silver are volatilised and condensed in the colder part of the tube. Moreover, some mercury vapour may become condensed in the hot silver on cooling, so that, before using it for the atomic weight determinations, it must be remelted in a lime crucible and poured into water.

But, as the very slight impurities of the undistilled silver of Stas, amounting to 0.003-0.006 per cent., were not regarded in his fundamental researches, the silver prepared by his methods having been declared by Stas as "absolutely pure," it is seen that the classical researches of Stas, which will for ever remain a model of exact investigation, do not require the correction proposed by Dumas, due to an occlusion of oxygen in silver, its quantity being practically nought.

I feel convinced that the distilled silver gives absolutely no oxygen when heated in a vacuum, the very small amount found by me being due to some otherwise inappreciable impurity contained in my silver.

Determinations of Bromine in Tellurium Tetrabromide.

The tetrabromide obtained by sublimation in a vacuum was weighed, as above stated, most exactly, and dissolved in the same vessel in two to four times its weight of a solution of 1 part of pure tartaric acid in 1 part of water. Then, from Experiment 31, the quantity of silver necessary for the complete precipitation of the bromine, was calculated and weighed out most exactly, and dissolved in about five times its weight of nitric acid of sp. gr. 1.24, either in the apparatus, Fig. 1, or in the flask in which the precipitation had to be These vessels were Gay-Lussac's silver test-flasks of effected. 200-500 c.c. capacity but equal diameter. They could be closed with tightly ground and carefully polished stoppers, having a sharp cone at their lower part projecting into the flask, this causing a quicker division of the flocks of silver bromide on agitation. The agitation was effected by means of the apparatus seen in Fig. 6, which could be set in action by a water engine a, b, c. The flask fis contained in a layer of black cloth and in a tightly closed box, e_{i} suspended by an elastic rubber spring, g. The agitation must be continued for many hours, not only for clearing the liquid, which takes place in a few minutes, but because the silver bromide gives up its impurities, especially tellurium, only when the flocculent precipitate has been entirely converted into the pulverulent modification.

After clearing, the very small excess of silver or bromine present in the liquid was determined by standard decinormal solutions. The

FIG. 6.

silver solution used for this purpose was prepared by dissolving 1 gram of pure silver in nitric acid and making up to 1 litre with water distilled over alkaline permanganate. The potassium bromide solution was prepared by dissolving 1.10340 grams of pure potassium bromide in water and making up to 1 litre. The bromide was prepared from the purest medicinal preparation by evaporating its solution to dryness with *pure* bromine and then fractionally dissolving in water and recrystallising. (See Kruss, Annalen, 238, 241.) Before weighing, it was heated to redness in a double platinum crucible.

The titration was effected by means of carefully graduated narrow pipettes, open at their lower end and closed at the top by a rubber

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tube, on opening which and letting air in carefully, the liquid can be allowed to drop out without coming into contact with greased stopcocks. The operation was effected in a perfectly dark room, but the liquid to be tested was lighted by a beam of yellow light. The light must contain chemically active rays, otherwise the slight turbidities become invisible. Red light—in general light of less than A = 550—does not answer the purpose. If large quantities of the standard solutions are added, slight decomposition of the silver bromide takes place, so that the limit of complete precipitation changes in such a way that after some time the liquid again yields a precipitate with silver solution. This is completely avoided in my case, the volume of the standard solution to be added amounting to a few drops only, and being sometimes nonght.

In this way the following experiments were made, every one of which required several days for completion.

Exp.	TeBr.	Ag.	Br.	Atomic
No.	grams.	grams.	p.c.	weight.
35	2.14365	2.06844	71 ·483	127.60
36	1.76744	1.70531	71.478	127.63
37	1.47655	1.42477	71.484	127.59
38	1.23354	1.19019	71.479	127.63
		Mean	71.481	127.61

From these experiments it is seen that the number representing the atomic weight of tellurium is Te = 127.61, this number being *larger by* 0.75 than the atomic weight of iodine !

Indeed, from a purely experimental point of view, the present work may be regarded as completed, and 20 years ago no one would have doubted that tellurium now belongs to those elements, the atomic weight of which is very exactly determined.

This is, however, not the case when we regard the matter in the light of chemical philosophy, for tellurium with such an atomic weight would be a striking exception to the periodic law, being in fact the first element the properties of which are *not* a function of its atomic weight !

This anomaly might, however, be only apparent, and might be possibly explained in one of the following ways :---

(a.) The Atomic Weight is badly Determined.—Such an assumption is impossible, the determinations, carried on volumetrically (Experiment 35—38), agreeing completely with the gravimetric determination, so that an error of four units $(127 \cdot 6 - 123 \cdot 6 = 4 \cdot 0)$ cannot be assumed to have taken place, such an error being 200 times as large as the largest deviation from the mean $= \pm 0.02$.

(b.) The Bromide may contain some Oxybromide.—This was very improbable, as the metal and the bromide were obtained by sublimation. The absence of oxygen in the bromide was shown by complete analysis.

Experiment 39.—4:4392 grams of tellurium tetrabromide were dissolved in hydrochloric acid and precipitated by sulphurous acid. The tellurium was collected by reversed filtration. In this way 1.2764 grams = 28.75 per cent. of tellurium was obtained. The result is slightly high on account of an unavoidable admixture of tellurium dibromide.

Experiment 40.—3.6247 grams of tetrabromide were reduced with sulphurous acid and the tellurium heated in the flask in a current of hydrogen at 200°, hydrobromic acid being found to escape. In this way, 1.0350 grams of pure tellurium was obtained = 28.55 per cent.

From this and the Experiments 35-38, therefore, the composition of tellurium tetrabromide becomes :--

Tellurium	28.55
Bromine	71·4 8
Total	100.03

Tellurium tetrabromide contains no oxygen and consequently no oxybromide.

(c.) The following is the third possible explanation. Tellurium is not a homogeneous body, but contains an admixture of foreign substances which have a higher equivalent than the bromine equivalent of tellurium. (This equals $127.6 \div 4 = 31.9$, but ought to be about = 31.) These admixtures might be partly known elements such as Se (equivalent from SeBr₂ = 39.5), Sb (eq. = 40), Bi (eq. = 69.3), and partly hitherto unknown elements of the same natural group as Mendeléeff's dwiselenium = 166 and dwitellurium = 214. Some of their properties may be predicted from their position in the periodic system.

Before assuming that tellurium forms a striking exception to the periodic law, and that this law consequently loses a great deal, if not all, of its authority, I have thoroughly investigated the question as to whether tellurium is a complex substance or not. For, if the periodic law is true, we may conclude by *deduction*^{*} that tellurium contains a foreign substance which renders its "atomic weight" higher.

^{*} Applying the periodic law, the author showed by the process of *deduction* eleven years ago that the atomic weight of beryllium is not Be''' = 13.6, as was assumed by Nilson and Pettersson, but Be'' = 9.1, in spite of its low specific heat, just as the existence of the simple molecules $AlCl_3$, &c., has been foreseen. It is remarkable that the author's paper on this subject was not mentioned by Nilson

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Attempts to Decompose Tellurium.

An attempt to decompose the metal by fractional distillation gave no results in the hands of Wills (*loc. cit.*).

First Method.—Tellurium tetrabromide was subjected to fractional sublimation in a vacuum. The more volatile portion gave Te = 127.60 and 127.63 (see Experiment 35 and 36); the less volatile portion Te = 127.59 and 127.63 (Experiments 37 and 38).

Second Method.—A considerable quantity of crude tellurium was dissolved and precipitated by sulphurous acid. The tellurium obtained was fused in many portions with potassium cyanide, and the claret-coloured solution was precipitated fractionally by passing in a current of air.

The single portions of tellurium obtained were distilled in a current of hydrogen and converted into the bromide, which was most carefully analysed as above.

Exp. No.	Fraction No.	TeBr ₄ . grams.	Ag ₄ . grams.	Br. p. c.	Atomic weight.
39	. I.	3.07912	2.97064	71.472	127.67
4 0	. I.	5.47446	5.28157	71.472	127.67
41. .	. II.	3.30927	3.19313	71.482	127.60
42	. IV.	7.26981	7 ·0 1414	71.477	127.64
43	. IV.	3.52077	3.39667	71.47]	127.67
			Mea	n	127.65

The experiments agree so remarkably that the concordance could not be closer if the tellurium were absolutely homogeneous; the largest deviation from the mean falling *almost* within the unavoidable experimental errors.*

Experiment 44.—For applying the correction for weighing in a vacuum, the sp. gr. of tellurium tetrabromide was taken in pure anhydrous benzene at 15° C., the numbers referring to water = 1 at 4° C. in a vacuum.

Sp. gr. of benzene	0.88456
Weight of tellurium bromide	3 [.] 40584 gram.
Weight of benzene displaced	0.69904 "
Sp. gr. of TeBr ₄ $d\frac{15^{\circ}}{4^{\circ}}$	4 ·310

and Pettersson when they had experimentally confirmed both the above suppositions.

* An error of \pm 0.1 milligram of silver (= two drops of its standard solution) causes, with 1 gram of the substance, a difference in the atomic weight of \pm 0.05, with 5 grams of substance a difference of \pm 0.01.

Loss of weight in air of 1 gram (Prague)-

Tellurium tetrabromide	0.274
Silver	0.112

The atomic weight of tellurium in a vacuum is obtained by adding to the numbers obtained in air +0.07.

Third Method.—A hydrochloric solution of pure tellurium dioxide (preparation see under G) was fractionally precipitated with ammonia, and eight fractions were thus obtained.

Fraction 9 was precipitated from the last filtrate with sulphurous acid in the presence of hydrochloric acid.

Fraction 10.—After boiling off the excess of sulphur dioxide, the solution was precipitated with hydrogen sulphide. A brownish-red sulphide was obtained, the small quantity of which did not permit me to ascertain its nature.

The tellurous acid obtained in the single fraction was converted into the element, and this as well as the bromide prepared from it were purified as above by sublimation.

Exp. No.	Fraction No.	TeBr ₄ . grams.	$Ag_4.$ grams.	Br. p. c.	Atomic weight.
45	1.	$2\overline{\cdot}35650$	2.27363	$7\hat{1}.477$	127.64
46	4.	1.51931	1.46564	71.465	127.71
47	9.	1.43985	1.38942	71.488	127.57
			Mear	1	127.64

This again would seem to point to an identity of the single fractions.

In the following experiments, the tellurium was only dried and fused in a current of hydrogen, but not distilled. The tetrabromide was only freed from the dibromide by fractional sublimation in a vacuum, but it was not converted into vapour, as it decomposed with the formation of a deep-violet vapour and of a large quantity of the greenish-black dibromide. This tetrabromide possessed a peculiar greenish colour, and its solution in tartaric acid was greenish-brown. The substance differs in properties and composition completely from the normal tellurium tetrabromide, as seen from the following experiments :—

Exp.	Fraction	$TeBr_4$.	$Ag_4.$	Br.	Atomic
No.	No.	grams.	grams.	р. с.	weight.
48	1.	1.85162	1.77858	71.160	129.63
49	2.	1.46740	1.38428	69.886	137.72
50	9.	1.48180	1.42573	71.279	128.88

The results obtained allow us to draw the following remarkable conclusion.

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If tellurium, obtained by any process of fractionation whatever, be subjected to distillation in a current of hydrogen, and the tetrabromide be prepared from this by sublimation in a vacuum, its analysis always gives the same atomic weight for tellurium. So that on comparing the quantities of the tetrabromide with those of the corresponding silver, as used in Experiments 35-38, 39-43, and 45-47, the following result is obtained :--

TeBr ₄ . grams.	$Ag_4.$ grams.	At	Tellurium. omic weight
34.59027	33 [.] 37355		127.64
Experimen "	nt 46, maximum 47, minimum	•••	$127.71 \\ 127.57$
Difference	· · · · · · · · · · · · · · · · · · ·	•••	0.14
Probable e	error of the mean resul	•• t*.	± 0.07 ± 0.008

If, however, the tellurium be only fused in a current of an indifferent gas, and the tetrabromide be not sublimed, higher numbers will be obtained. In this way in the Experiments 48, 49, and 50 we got Te = 129.63, 137.72, and 128.88.

The differences are too large to be due to experimental errors, as the difference between 137.72 and 127.64 = 10.18 is 144 times larger than the largest deviation from the mean, and 1272 times as large as the probable error of the mean result. But also in the case of the smallest number, 128.88, the corresponding numbers are 17 and 155 times larger.

It is therefore very probable that on distilling tellurium in a current of hydrogen, and the tetrabromide in a vacuum, one constituent of tellurium escapes partly, the presence of which in the last three cases renders the atomic weight higher.

The fact is a very remarkable one, although it would have been hardly remarkable except for the existence of the periodic law, that in the greater number of cases the "combining weight" (we cannot say atomic weight!) of tellurium remains constant, so that the quantity of matter which takes part in the reactions as "tellurium" weighs 127.6, oxygen weighing 16.

Tellurium is a true "Gadolinium" + of the hydrogen sulphide group.

* Calculated from the formula $\pm 0.6745 \sqrt{\frac{S}{n(n-1)}}$, where S = sum of the

squares of the errors, n = number of experiments; here n = 12.

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⁺ Compt. rend., 103, 795. The mixture of yttrium, erbium, and ytterbium oxides, showing apparently a constant molecular weight in different minerals, was called "Gadolinium" oxide by Nordenskiöld. Rammelsberg (Berl. Akad., 30, 549) has shown that this assumption contradicts the result of his analyses.

I. Analysis of the Dibromide.

A large amount of time and work was expended on the study and analysis of tellurium dibromide, my aim having been to determine the atomic weight of tellurium by as many independent methods as possible. I expected that the quantity of bromine combined with 100 parts of tellurium in the dibromide, and that in the tetrabromide would stand exactly in the proportion 1: 2.

The dibromide was prepared by fusing the tetrabromide with an excess of powdered tellurium, and sublimation either in a vacuum or in a current of carbon dioxide, $TeBr_4 + Te = 2TeBr_2$. It forms a blackish-green or black crystalline mass, or a black powder, or, after careful sublimation, needles of a pale steel colour. The powder is olive-green, with a yellowish tinge. The appearance, indeed, seems to show that the substance is a mixture either of several allotropic modifications, or of different compounds. On treatment with tartaric acid solution, tellurium tetrabromide dissolves, forming a yellow solution, which, however, is sometimes greenish-brown from the presence of another substance,

$$2 \mathrm{TeBr}_2 = \mathrm{Te} + \mathrm{TeBr}_4.$$

The dibromide must be finely powdered under the tartaric acid solution, otherwise some of the dibromide may escape decomposition, as seen from the following.

Experiment 51.—1.3856 grams of the dibromide was only extracted with tartaric acid, and the solution gave 1.6730 grams of AgBr = 51.38 per cent. bromine. The following experiments were made with tellurium dibromide of different preparations. The bromine was determined as silver bromide, which was collected in a dark room by reversed filtration :—

Exp.	$TeBr_2$.	AgBr.	Br.
No.	grams.	grams.	р. с.
52	0.5526	0.7160	55.14
53	0.8322	1.0726	54.85
54	2.3741	3.0693	55.02
55	1.00872	1.29556	54.658

After dissolving the insoluble washed residue of tellurium in dilute nitric acid in the apparatus Fig. 1, it was tested for bromine, but silver nitrate gave only a small, flocculent, greyish-violet precipitate, which was neither silver bromide nor silver tellurium tartrate.

The percentage of bromine calculated for Te = 127.64 in the dibromide ought to be Br = 55.62. All the results obtained were lower, the highest (Experiment 52) pointing to an atomic weight of Te = 130, the lowest (Experiment 55) to Te = 133.

From the analyses of tellurium tetrabromide, dibromide, and the observations regarding them, the following conclusion may be drawn:—

Tellurium is not a simple substance.

The question arises, whether the numbers, obtained by the synthesis of the dioxide and the sulphate of tellurium, giving Te = 125-126 (see Experiments 1-19), are to be regarded as inaccurate?

This I deny most decidedly. On the contrary, I regard these experiments as another proof of the complex nature of tellurium. For a mixture of several elements—probably three, as seen from the result of the fractionation with ammonia—may be expected to possess an affinity for oxygen different from that which they have for bromine, and indeed, the stability of the mixed bromides obtained from different fractions is very different.

The next task consists in studying the nature of the foreign admixtures of tellurium, in order to prepare pure, real tellurium, which remains to be discovered.*

I should be much obliged to my brother chemists if they would kindly leave this problem to be worked out by me for some time to come, as only now, after six years' labour, have I begun to overcome some of the difficulties connected with the research, and I expect to encounter even more serious ones in the future. Nothing is more hurtful to true science than the hasty publication of incomplete and unverified results, and I hope I may not be forced by circumstances to adopt such a course.

Some of the results, unpublished here, have been communicated by the author to the Chemical Society at the meeting of June 6th, 1889.

* The behaviour of acid tellurium solutions towards hydrogen sulphide is another proof of its compound nature. The first drops of sulphuretted hydrogen water cause a reddish-brown coloration of the solution, showing a peculiar fluorescence, due probably to the formation of a colloidal sulphide. On adding some more sulphuretted hydrogen water, a reddish-brown precipitate is thrown down, the solution remaining reddish-brown. As soon as the gas is present in excess, the volume of the sulphide (?) diminishes: it becomes black, and consists now of a mixture of tellurium and sulphur. After extracting the latter with carbon bisulphide, the precipitate still contains several per cent. of sulphur, probably in the form of a sulphide.