

ment was never more than 1 mm. Hence with the 14 K. white gold wire used under these conditions the faults would always have been less than 0.1 mm. That means that under ordinary conditions or even under bad conditions the temperature coefficient of the 14 K. white gold measuring wire will never be the cause of any noticeable error.

### Summary

White gold,<sup>1</sup> which has already partially replaced platinum in jewelry, replaces it advantageously in the alternating current Wheatstone Bridge when the latter is used in a chemical laboratory where constantan corrodes too rapidly. Constantan, exposed to the air of the laboratory, had to be cleaned after a few weeks, while white gold still gave perfectly good contacts after ten months.

Good surface qualities of the measuring wire are of the greatest importance, especially in modern laboratory technique where amplifiers are used in connection with very weak currents.

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## A REVISION OF THE ATOMIC WEIGHT OF TITANIUM. III THE ANALYSIS OF TITANIUM TETRABROMIDE

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In two recent papers<sup>1</sup> the purification and analysis of titanium tetrachloride are described. The atomic weight of titanium computed from the experimental results is 47.90, a value considerably lower than that obtained by Thorpe, 48.1, which has been in use for some time. As a check on our recent work we have prepared and analyzed pure titanium tetrabromide and have obtained the same value as that found by analysis of the tetrachloride. Although in outline the two methods are similar, yet the differences in the physical and chemical properties of the compounds involved make it improbable that both results are affected by constant errors to the same extent.

### Purification of Materials

Water, nitric acid, silver and bromine were purified by the methods usual when extreme refinement is necessary.<sup>2</sup>

Carbon was prepared from rock candy crystals, by charring, followed

<sup>1</sup> 14 K. white gold wire similar to the one described above can now be obtained from Baker & Co., Inc., Newark, N. J.

<sup>1</sup> (a) Baxter and Fertig, *THIS JOURNAL*, **45**, 1228 (1923); (b) Baxter and Butler, *ibid.*, **48**, 3117 (1926).

<sup>2</sup> See, for instance, Baxter and Grover, *ibid.*, **37**, 1028 (1915).

by ignition first in a covered porcelain crucible, then in an exhausted quartz tube.

Arsenic trioxide was several times recrystallized, once from very dilute hydrochloric acid, then from water. The product was chloride free.

Helium was very kindly provided by the U. S. Navy Department. It was purified and dried by being passed over concentrated sulfuric acid, hot calcium, hot copper oxide, hot copper, silver nitrate solution, solid potassium hydroxide, concentrated sulfuric acid and phosphorus pentoxide, in an all-glass apparatus. This gas may have contained a trace of hydrogen formed by decomposition of traces of water by the copper, but since this impurity could only result in the production of a small amount of hydrogen bromide in the synthesis of the titanium tetrabromide, it was allowed to remain.

Titanium tetrabromide was prepared by the action of bromine at a high temperature on (a) metallic titanium, or (b) a mixture of carbon and titanium dioxide. Because of the action of nitrogen on titanium at high temperatures, helium was used as the carrier of the bromine. The products of several experiments were combined for the final purification by fractional distillation.

Titanium dioxide kindly furnished by the Valentine Valspar Co. served as the starting point in every case. To prepare metallic titanium the powdered dioxide was mixed with a 50% excess of magnesium powder by grinding and the reaction was started by igniting the mixture in a muffle. The product was extracted with an excess of hydrobromic acid and the residue digested with two successive portions of fresh acid at nearly boiling temperature. Washing by decantation followed, with centrifugal settling of the rather finely divided titanium in order to promote efficiency. The clean metal was dried on an electric hot-plate and after powdering was ignited in a high vacuum.

In the preparation of the tetrabromide from titanium, the metal was contained in a hard glass tube connected at one end by a ground joint with the apparatus for purifying helium and charging it with bromine, at the other by means of a ground joint of large diameter with a glass bulb which served as condenser. The reaction tube sloped toward the receiver at all points. Because of the high boiling point of the tetrabromide, 238°, especial cooling of the condenser was unnecessary. The helium could be passed either directly into the reaction tube or through bromine in a bubbling flask and then over the titanium. In a run the apparatus was first swept out with helium. Then the current of helium was directed through the bromine, and the titanium was heated electrically to redness. At the same time the bromine was warmed to increase its vapor pressure. The product, judging from the color, was at first nearly free from bromine, but before long uncombined bromine began to accompany the tetrabromide to a marked extent. Two experiments of this sort were both interrupted by accidents to the apparatus so that the total resulting quantity of tetrabromide was not more than 60-70 g.

In a third experiment, instead of titanium, a mixture of ground, ignited titanium dioxide with a considerable excess of carbon was employed. The result of this experiment was satisfactory so far as yield is concerned although the former method gave

every indication of being equally good under favorable conditions. About 200 g. was obtained from this experiment.

The material produced by the two methods was next separately freed from a large part of the excess of bromine by exhausting the containers with an efficient water pump while at the same time the container was warmed in a paraffin bath and the liquid boiled vigorously to flush out as much of the residual air as possible. The containers were then closed by fusing a capillary connection. Both containers were then connected through special fused-in joints (a, Fig. 1)<sup>3</sup> to a large bulb which was also connected with a Hempel fractionating column terminating in a special joint. By means of a Gaede mercury pump this bulb together with the fractionating column was thoroughly exhausted and sealed off. In succession the special joint of each container was opened and the contents distilled into the receiving bulb. Then the container was sealed off by fusing a capillary. The combined sample, of about 100 ml. in volume, was a reddish-brown mass, partly liquid owing to the excess of bromine.

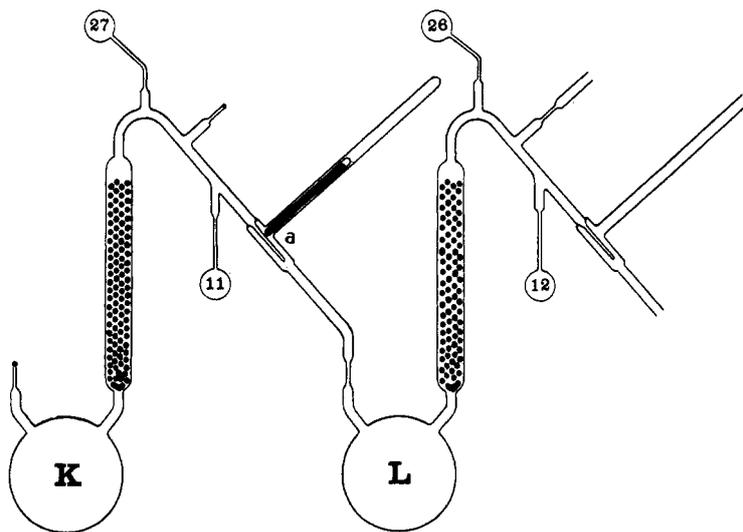


Fig. 1.

Fractional distillation in exhausted apparatus followed. The apparatus was modified slightly from one distillation to another but in general a distillation was carried out as follows. The material was contained in the exhausted bulb K (Fig. 1) attached through the Hempel column and the special joint to the receiving bulb L, which in turn was attached to a similar system also thoroughly exhausted. The special joint was then opened by means of the hammer weighted with mercury. The still K was warmed to about 150° in a paraffin-bath and the most volatile fraction of the tetrabromide was collected in the bulb 11 which was disconnected by sealing the capillary. The greater part of the tetrabromide was distilled into L, and the capillary was sealed. The residue in K was then collected in 27 and sealed off. After the receiver L had been connected to a similar exhausted system, the distillation process was repeated. During the distillation the fractionating column was jacketed with asbestos paper. Although

<sup>3</sup> (a) Bruner and Bekier, *Z. Electrochem.*, **18**, 369 (1912); (b) Briscoe and Little, *J. Chem. Soc.*, **105**, 1324 (1914); (c) Baxter and Starkweather, *THIS JOURNAL*, **42**, 907 (1920).

refluxing was very efficient, choking of the column was negligible. In all, 18 such fractional distillations were carried out. After the third, sixth and ninth distillation cracks in the apparatus necessitated transference by pouring to another bulb, which was exhausted while hot by means of a water pump and sealed off. The last nine distillations were, however, free from any such accident.

The complete course of the fractional distillation is shown in Fig. 2. The large lettered circles represent separate distillations, the small circles the fractions removed. The fractions to the right are the more volatile ones, while the fractions to the left are the less volatile ones. The fractions analyzed, as well as the atomic weights found in the analyses, are given in the figure.

Probable impurities in the crude tetrabromide included, besides bromine, hydrogen bromide from hydrolysis of the titanium tetrabromide when exposed to moisture in the air, carbon tetrabromide from action of bromine on charcoal and silicon tetrabromide from silicon contained in the titanium dioxide or from the glass. The boiling points and the effect on the atomic weight of titanium of one-tenth of one per cent. impurity of each are given in Table I.

The removal of the bromine was very rapid, for no evidence of its presence was obtained after the first three distillations. Presumably the still more volatile hydrogen bromide was removed at the same time. No tests for the other impurities were made, since all past experience with the distillation of inorganic halides has indicated that, when boiling points are as widely separated as in this case, separation is very rapid. Furthermore, the constancy in

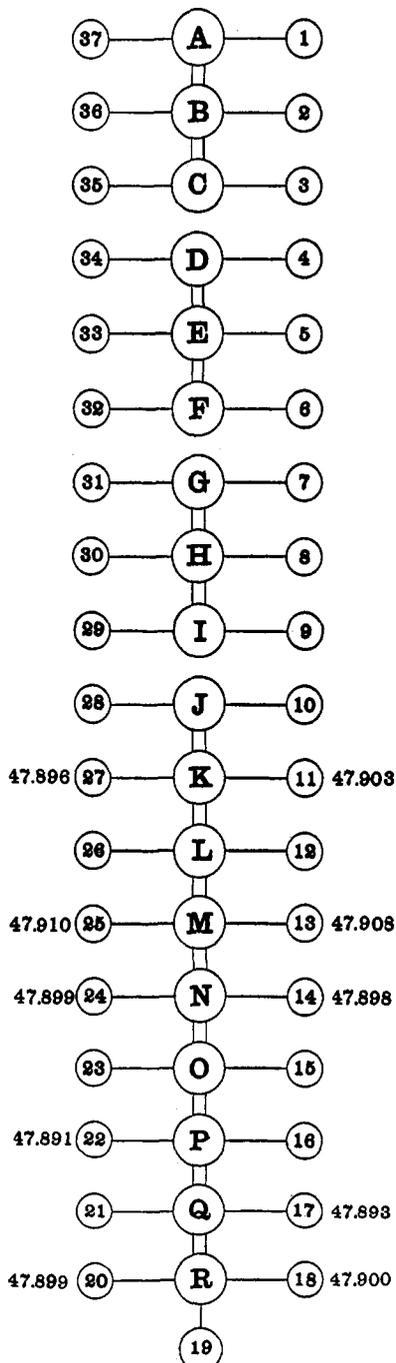


Fig. 2.

TABLE I

	B. p., °C.	Effect of 0.1% of impurity
TiBr <sub>4</sub>	230	....
HBr	-69	-0.050
Br <sub>2</sub>	59	- .055
CBr <sub>4</sub>	190	- .040
SiBr <sub>4</sub>	153	- .021

composition of the fractions of the tetrabromide after the initial stages in the fractional distillation is evidence in the same direction. At any rate it is clear that purification by this method had reached a limit.

The final product was a lemon-yellow solid at ordinary temperatures and melted to a somewhat darker liquid.

### Method of Analysis

The titanium tetrabromide was analyzed as in the case of the tetrachloride by solution in dilute nitric acid and comparison of the solution with silver. Since nitric acid slowly acts on the tetrabromide to liberate bromine, a small amount of arsenious acid was added to the nitric acid beforehand. Under these conditions no odor or color of bromine was ever detected.

A still more rigorous test for possible loss of bromine was made by dissolving one fraction of the tetrabromide in nitric acid containing arsenious acid, and drawing air slowly for two hours over or through the solution and then through a solution of ammonia. The latter was finally evaporated to small volume and tested for bromide by comparison with known quantities in a nephelometer. Various concentrations of bromide and nitric acid were used.

TABLE II

Concn. of TiBr <sub>4</sub> , %	Concn. of HNO <sub>3</sub> , normality	Bromide found, mg.	Concn. of TiBr <sub>4</sub> , %	Concn. of HNO <sub>3</sub> , normality	Bromide found, mg.
1.0	0.5	0.15	1.0	0.25	0.10
0.5	.5	.005	0.5	.20	.04
.5	.5	.3	.75	.18	.10
.5	.4	.05	.5	.12	.01
.5	.4	.15	.5	.12	.005
.5	.3	.10	.5	.12	.02
.5	.25	.005	.5	.12	.000
.5	.25	.005	.5	.10	.05

Since the loss of bromide from the solution seemed to be negligible at concentrations of nitric acid around 0.1 *N*, this concentration of nitric acid was used for the solution of the titanium tetrabromide.

The more important details of the method of analysis were as follows. In order to find the density of the glass bulb containing the tetrabromide,

it was weighed first submerged in water of known temperature, and then, after being cleaned and dried, by substitution in air of known density.<sup>4</sup>

The weighed bulb was next broken under one liter of 0.1 *N* nitric acid containing 0.1 g. of dissolved arsenious oxide in a heavy-walled, glass-stoppered flask, and the solution was allowed to stand for several hours. No turbidity ever appeared and the hydrobromic acid fumes formed at first were quickly absorbed by the solution. The solution was then filtered into the glass-stoppered precipitating flask or bottle, through a weighed platinum-sponge Gooch crucible, on which the fragments of the glass bulb were collected after they had been washed with pure water. In order to prevent the retention of titanous acid, the crucible and the glass were further washed with hot 6 *N* nitric acid, and after being washed with water and dried at 250° were weighed. A second treatment with nitric acid ordinarily did not produce a change in weight of more than 0.02 mg., but in four experiments a third treatment was necessary before constant weight was secured. This method of collecting and weighing the glass was found satisfactory in the analysis of titanium tetrachloride.

The weight of titanium tetrabromide was obtained as the difference between the weight of the bulb and the weight of the glass, both corrected to vacuum. Very nearly the exact weight of pure silver necessary to combine with the tetrabromide was dissolved in nitric acid with especial precautions to avoid loss by spattering and, after dilution until approximately 0.1 *N*, the solution was slowly added to the bromide solution, which at this stage also was as dilute as 0.1 *N* and in many cases no more than 0.05 *N*. Thorough shaking and standing for several days followed. With the aid of a nephelometer the bromide and silver in the solution were adjusted to equivalence by the addition of hundredth normal solutions. Several weeks always elapsed between the precipitation and the final adjustment of the end-point, so that occluded material had abundant opportunity for being extracted from the precipitate of silver bromide.

No attempt was made to estimate the silver bromide quantitatively, since in the analysis of the tetrachloride the silver chloride was found to be badly contaminated with titanium compounds.

Weights were standardized by the substitution method of Richards.<sup>5</sup> Vacuum corrections were applied as follows.

Weights	Density	Vacuum correction per gram
	8.3	
Silver	10.49	-0.000031
Glass	2.5	+ .000335
Air	0.001293 (0° and 760 mm.)	

<sup>4</sup> Baxter, *THIS JOURNAL*, **43**, 1317 (1921).

<sup>5</sup> Richards, *ibid.*, **22**, 144 (1900).

## Results

TABLE III

## ATOMIC WEIGHT OF TITANIUM

TiBr <sub>4</sub> :4Ag		Ag = 107.88			Br = 79.916		
Analysis	Sample of TiBr <sub>4</sub>	Weight of TiBr <sub>4</sub> in vacuum, g.	Weight of Ag in vacuum, g.	Weight of Ag added or subtracted in soln., g.	Corrected weight of Ag in vacuum, g.	TiBr <sub>4</sub> :4Ag Ratio,	Atomic weight of titanium
1	11	10.02147	11.76552	-0.00040	11.76512	0.851796	47.903
2	13	9.20373	10.80523	- .00030	10.80493	.851808	47.908
3	25	4.33488	5.08816	+ .00085	5.08901	.851812	47.910
4	27	8.22722	9.65971	- .00085	9.65886	.851780	47.896
5	14	9.59208	11.26112	+ .00004	11.26116	.851784	47.898
6	24	5.09864	5.98572	+ .00010	5.98582	.851786	47.899
7	17	5.29301	6.21401	+ .00010	6.21411	.851773	47.893
8	22	6.53582	7.67314	+ .00010	7.67324	.851768	47.891
9	18	6.14520	7.21432	+ .00015	7.21447	.851788	47.900
10	20	4.72253	5.54423	+ .00004	5.54427	.851786	47.899
						Average	.851788 47.900

## Discussion

The extreme deviation of the calculated values for the atomic weight of titanium is 0.019 unit, but six of the results fall within a range of 0.007 unit. The "probable error" of the mean is 0.0013 unit, but it is far from certain that the accuracy of the final average is as great as this, owing to constant errors which it is impossible entirely to eliminate.

If the results are arranged in the order of decreasing volatility of the fractions of tetrabromide no trend is apparent, for the average of the first five results is 47.900, and the average of the last five 47.899.

Fraction of TiBr <sub>4</sub>	Atomic weight of titanium	Fraction of TiBr <sub>4</sub>	Atomic weight of titanium
11	47.903	20	47.899
13	47.908	22	47.891
14	47.898	24	47.899
17	47.893	25	47.910
18	47.900	27	47.896

In his initial examination of titanium in the mass spectrograph, Aston<sup>6</sup> found doubtful indications of an isotope of mass 50 besides the main isotope of mass 48, but apparently this indication has not been confirmed. The atomic weight 47.90 is in accord with the general rule that the masses of individual isotopes fall short of integral values when the mass number is between 20 and 200, but leads to a "packing fraction" nearly three times as large as that corresponding to Aston's curve connecting packing fraction with mass number.<sup>7</sup> This discrepancy may be due to an undiscovered isotope of mass number less than 48.

<sup>6</sup> Aston, *Phil. Mag.*, **47**, 397 (1924).

<sup>7</sup> Aston, *Proc. Roy. Soc. (London)*, **115A**, 510 (1927).

Under the conditions of the distillation no separation of the bromine isotopes is to be feared, as the constancy in composition of the fractionated material also indicates.

The analyses of titanium tetrachloride and titanium tetrabromide thus agree in yielding the value 47.90 for the atomic weight of titanium.

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## NOTES

**Alkali Earth Metals in Saccharate Solutions and their Use in Alkalimetry.**—Theoretically it would be most desirable to find some substance the equivalent weight of which could be directly weighed out, put into solution and diluted to a given volume to yield a standard of predetermined normality that would not require standardization or adjustment. The writer has been carrying on some work in an attempt to realize, partially at least, this ideal.

To this end different materials that would yield calcium oxide have been converted to that substance or to calcium hydroxide and have been dissolved to form a standard solution in a 30% cane sugar. These attempts were successful in so far as the attainment of the final results were concerned, but so much time was consumed that the method was not considered practical. In the course of further investigations, it was found that samples of metallic calcium in the form of 0.05 inch wire and about 96% pure went into solution at the rate of 1 g. in about eight minutes, on the average. In the ten cases tried a solution of predetermined normality was obtained, employing, of course, a correction factor to allow for the impurities. The calcium was obtained from the General Electric Company and, though impure, was so uniform that samples from different parts of the lots were found to yield identical solutions. The chief impurity is metallic magnesium which, together with its oxide, is almost insoluble in 30% sucrose, a fact that might be employed in separating small amounts of magnesium from large percentages of calcium especially in the analysis of metallic calcium. It would seem easy to eliminate this impurity by employing pure calcium chloride as an electrolyte instead of that obtained as a by-product from magnesian bitters.

Another source of impurity is the rapid tarnishing of clean surfaces of metallic calcium when exposed to moist air, as reported in the literature. The film so formed is slow to appear in ordinary air and since it is very thin and consists of a high calcium compound, the error from this source seems negligible; however, it can easily be sandpapered off from the warm metal much as rust is removed from standard iron wire. The