[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE ATOMIC WEIGHT OF TANTALUM.[1]

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Received July 1, 1910.

Introduction.

Of the previous determinations of the atomic weight of this element, those by Berzelius,[2] Rose,[3] Hermann[4] and Blomstrand[5] need not be considered, as their material was too impure to give results of value. The determinations of Marignac,[6] which appeared in 1866, were far more satisfactory. He analyzed potassium fluotantalate, K_2TaF_7, and the corresponding ammonium salt, $(NH_4)_2TaT_7$. In the case of the potassium salt he obtained the following percentages:

Ta_2O_5, 56.50, 56.75, 56.55, 56.56; K_2SO_4, 44.37, 44.35, 44.22, 44.24.

The ammonium salt gave the following percentages of tantalum oxide: 63.08, 63.24, 63.27, 63.42. These numbers were corrected for a small amount of potassium sulphate which was present in the oxide, due to the fact that he was unable to prepare the ammonium fluotantalate free from traces of the potassium salt.

If in the calculations the atomic weights of the elements involved are taken as given in the 1910 International Table the following values for the atomic weight of tantalum are obtained:

From the ratio, $K_2TaF_7 : Ta_2O_5$	182.4 to 184.6
From the ratio, $K_2TaF_7 : K_2SO_4$	181.6 to 182.9
From the ratio, $K_2SO_4 : Ta_2O_5$	181.9 to 183.0
From the ratio, $(NH_4)_2TaF_7 : Ta_2O_5$	180.5 to 183.8

It will be observed that there is a variation of several whole units between the individual determinations, yet for about forty years the accepted value of this constant was based on these results.

In 1906 Hinrichsen and Sahlborn[7] published a series of determinations in which metallic tantalum was burned to the oxide. The method has great simplicity, but it appears very doubtful to the writer if this metal can be prepared sufficiently pure for the purposes of atomic weight work. Their results follow on page 1128.

Here again there is a variation of over one unit between the individual determinations. Clarke,[8] after reviewing these various determinations

[1] Presented at the San Francisco meeting of the American Chemical Society.

[2] *Pogg. Ann.*, 4, 14 (1825).

[3] *Ibid.*, 99, 80 (1856).

[4] *J. prakt. Chem.*, 70, 193 (1857).

[5] *Acta Univ. Lund*, 1864.

[6] *Arch. sci. phys. nat.*, (2) 26, 89 (1866); also *J. prakt. Chem.*, 99, 23.

[7] *Ber.*, 39, 2600 (1906).

[8] A Recalculation of the Atomic Weights, *Smithsonian Miscellaneous Collections*, Vol. 54, No. 3 (1910).

of the value of this constant, remarks that its uncertainty probably amounts to as much as a unit.

Wt. of Ta.	Wt. of Ta_2O_5.	Per cent. O.	At. wt. Ta.
0.37200	0.45437	22.12	180.65
0.41278	0.50364	22.01	181.77
0.33558	0.40975	22.10	180.98
0.35883	0.43807	22.08	181.14
0.47554	0.58087	22.15	180.59
			Mean, 181.03

While carrying out an investigation on columbium[1] it was found possible to make a satisfactory determination of the atomic weight of that element through the conversion of its pentachloride into the corresponding oxide. Consequently the writer decided to carry out a similar investigation with tantalum chloride, and, in general, the methods used were very similar to those employed in the former work.

Preparation of Materials.

In the preparation of all materials used during the investigation great care was exercised in the cleaning of all containing vessels and especial care was taken to exclude dust. Whenever possible the apparatus used was made continuous by fusing the various parts together, and this was always the case where chlorine was being used. In the case of chemicals not especially purified, those of the highest purity obtainable were employed.

Chlorine.—The chlorine used, including that used in the preparation of the sulphur monochloride, was made by allowing hydrochloric acid to drip upon potassium permanganate contained in a large flask. The acid used was prepared by distilling the constant boiling mixture from large Jena retorts. During the first part of the distillation small quantities of potassium permanganate were added from time to time and the first portions of the distillate were rejected. The chlorine was passed through a wash bottle containing water, two containing sulphuric acid and finally through a tower one meter long containing glass pearls and so arranged that the latter could be moistened from time to time with concentrated sulphuric acid.

Sulphur Monochloride.—This compound was prepared by passing a stream of chlorine over molten sulphur which had been crystallized previously from carbon disulphide. The apparatus was so constructed that the liquid could be redistilled from the receiver without transferring the material. The first portions of the distillate were rejected and the final product was collected directly in sealing flasks through which a stream of dry, filtered air had been allowed to flow.

Nitric Acid.—The nitric acid used in the determinations was distilled

[1] Balke and Smith, THIS JOURNAL, 30, 1637 (1908).

twice from a platinum retort, the middle third of the distillate being retained in each case. The acid was preserved in quartz flasks.

Water.—The water used, including that employed in the final recrystallizations of the potassium fluotantalate, was prepared by redistilling the ordinary distilled water of the laboratory, after the addition of alkaline permanganate, from a still ordinarily used in the preparation of conductivity water.

Tantalum Chloride.—This compound was prepared by the ignition of tantalum oxide in a current of chlorine and the vapors of sulphur monochloride. The oxide used for preparations I and II was prepared from some of the potassium fluotantalate which had been obtained by Hall and Smith[1] from the columbite of South Dakota, and which was very kindly furnished me by Professor Edgar F. Smith.[2] This salt was recrystallized four times from water containing appreciable amounts of redistilled hydrofluoric acid, and only the first crops of crystals were used in the next crystallization. These operations were carried out in platinum and hard rubber dishes and hard rubber funnels were used in the filtration of the solutions. The final crop of crystals was heated in platinum dishes with concentrated sulphuric acid, which had been distilled from platinum, until most of the acid had been expelled. The residue was washed by decantation with large amounts of pure water. After this washing was complete, the mass was strongly ignited in platinum or quartz crucibles. Tantalum oxide prepared in this way has been shown to be pure.[3]

The oxide used for the third preparation of the chloride was obtained from the columbite of South Dakota as follows: The finely ground mineral was fused with potassium hydroxide in large iron crucibles; the mass was dissolved in water and the solution, after filtration, was treated with sulphuric acid, which precipitated the metallic acids. These were washed with water by decantation and then dissolved in an excess of hydrofluoric acid. The addition of potassium hydroxide to this solution gave a precipitate of potassium fluotantalate.[4] The final purifications were carried out as previously outlined.

The apparatus used for the preparation of the chloride is shown in Fig. I. The tantalum oxide (50–100 grams) was introduced into the hard Jena glass tube H, the ends of which were connected with the bulbs E and I by means of carefully ground joints which were lubricated with a trace of graphite. These joints were wrapped with several thicknesses

[1] THIS JOURNAL, 27, 1369 (1905).

[2] The author wishes to take this opportunity to express his appreciation for this and many other kindnesses shown him by Professor Smith.

[3] Balke, THIS JOURNAL, 27, 1140.

[4] My thanks are due to one of my students, Mr. Lloyd Almy, who carried out this preliminary work.

of asbestos paper and the bulb of a thermometer was inserted in the latter at G and the temperature regulated so as to prevent a deposition of the chloride at this point. A stream of chlorine was passed through the apparatus by means of the tube B for 3–4 hours, the entire apparatus being heated with a free flame in order to remove any traces of moisture which might be present. At this time the tube H containing the oxide was heated to a low red heat for the same purpose. Sulphur monochloride was then run into the bulb E through C and heated to boiling. The oxide was slowly converted directly into the chloride which together with the excess of sulphur monochloride collected in bulb I. When all of the oxide had been converted into chloride, leaving practically no residue in the tube H, the sulphur monochloride was driven on through the entire apparatus and collected in O. The tantalum chloride was then distilled over into the bulb J and the apparatus sealed off at L. The two-way stopcock was then turned so as to deliver chlorine through D. The tantalum chloride was heated to boiling and the entire apparatus heated, so that the residue of sulphur monochloride and some of the tantalum chloride was driven over into O. The entire amount of chloride was then distilled over into K and finally into the small bulbs N. The chloride in all the bulbs was then brought to the boiling point and a small amount distilled over into the receiver O to insure the re-

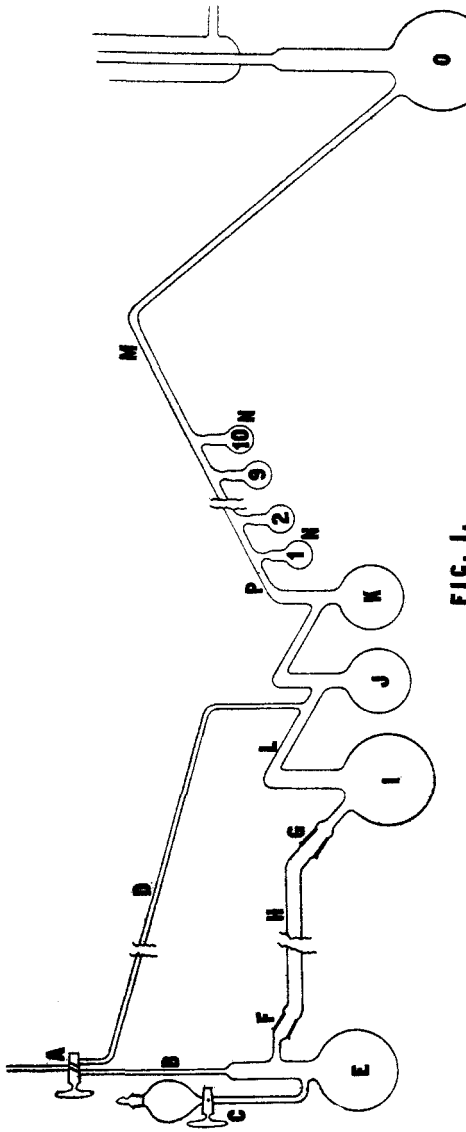

FIG. 1.

moval of the last traces of sulphur monochloride. When cold the apparatus was sealed off at P and M and finally the individual bulbs were sealed off. These contained from 5–20 grams of chloride.

The tantalum chloride so prepared was absolutely white in color, having none of the pale yellow tint which this compound is usually said to possess. When fused the chloride had a pale straw-yellow color. Five grams of this chloride were thrown into a flask containing bromine water, and the contents heated for several hours. The tantalum hydroxide was filtered out and the filtrate was evaporated to a very small bulk. This remained perfectly clear after the addition of a solution of barium chloride, which was taken to indicate that no sulphur remained in the preparation.

Density of Tantalum Chloride.—The density of this chloride was determined in carbon tetrachloride and the number 3.62 obtained. Tantalum chloride is somewhat soluble in carbon tetrachloride, and consequently a more satisfactory determination was obtained when heptane was used. This liquid did not react with the chloride nor did any of the latter dissolve. The following results were obtained:

Wt. of Pycnometer	10.2313
Wt. of Pycnometer + $TaCl_5$	23.6545
Wt. of Pycnometer + H_2O	35.2073
Wt. of Pycnometer + heptane	28.4050
Wt. of Pycnometer + heptane + $TaCl_5$	39.1710

$t = 27°$ Density of $TaCl_5 = 3.68$

Density of Tantalum Oxide.—As was found in the case of columbium oxide, the density of the tantalum oxide obtained from the present determinations varied quite appreciably, the numbers 8.62, 7.91, and 8.06 having been obtained. The density of this substance is not far from that of the weights used which were taken as having a density of 8.4 and it was found unnecessary to make a vacuum correction in the case of this substance.

Analyses of Tantalum Chloride.

The ratio studied was that of tantalum chloride to tantalum oxide, the transformation being made in quartz bulbs provided with tightly ground stoppers of quartz or glass. One of Ruprecht's best balances was used in the work and the weights were carefully standardized. All weighings were made by substitution, using a tare of the same material and very nearly the same weight as the object being weighed. The excess weight of the quartz bulb and its stopper over the tare was determined. By carefully tapping one of the small bulbs containing the tantalum chloride the latter was broken up into small pieces and by means of a file and a hot rod a crack was drawn about two-thirds of the way around the neck of the bulb. This bulb, together with the weighed

quartz bulb, into the neck of which had been slipped a wide-neck funnel tube, were introduced into a gas-tight box supplied with a removable plate-glass top. Two holes had been cut in the sides of the box and rubber gloves were attached on the inside. This box contained a large amount of calcium chloride, and a stream of air, which had been passed through large amounts of sulphuric acid and then filtered through glass wool, was passed through the apparatus for several hours. By slipping the hands into the gloves it was possible to remove the top of the bulb containing the chloride and introduce the latter into the quartz bulb without soiling the neck of the bulb. In this way it was possible to effect the only transfer of material involved in the determinations in an atmosphere of dry air. After replacing the stopper in the quartz bulb the latter was removed from the box and the excess of weight over the tare again determined. The bulb was next placed in a vacuum desiccator containing water and the air pumped out. In one or two days the chloride had completely hydrolyzed and the greater part of the hydrochloric acid produced had dissolved in the water outside of the bulb. A small amount of water and a few cc. of concentrated nitric acid were introduced into the bulb and the mass evaporated to dryness with the aid of the apparatus shown in Fig. II. The hood B was fastened to the neck of

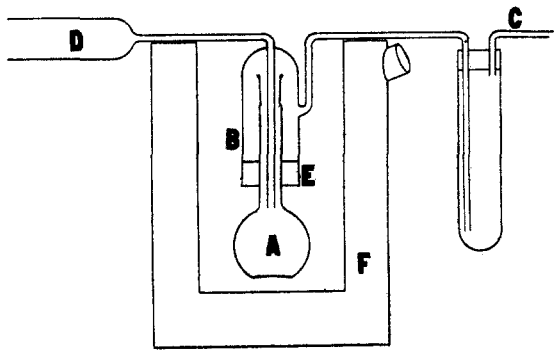

FIG. II.

the bulb by means of the split rubber stopper E, which was prevented from actual contact with the neck of the bulb by means of a strip of filter paper. F was a double-walled steam bath. D contained cotton to filter the air which was drawn slowly through the apparatus by means of a water pump attached at C. The mass was evaporated to dryness three times, a little water and a small amount of nitric acid being added each time. This insured the removal of the hydrochloric acid before the final ignition, which was made with a good blast lamp arranged so that both the air and gas were filtered through cotton in order to mini-

mize the amount of dust which might be blown against and adhere to the sides of the bulb. These ignitions were continued until no further loss of weight was observed. In making the calculations the atomic weight of chlorine was assumed to be 35.46. The temperature of the balance and the barometric reading were recorded in the case of the individual weights and these numbers were used in applying the vacuum corrections. In the calculation the density of tantalum chloride was taken as 3.68 and that of the weights as 8.4. As mentioned previously, no vacuum correction was applied in the case of the tantalum oxide, since this correction, which was smaller than the error in weighing, affected the fifth decimal only. The following table includes the results of all determinations made which were carried to completion without accident.

Series.	Bulb.	Wt. of $TaCl_5$ (vac.).	Wt. of Ta_2O_5 (vac.).	100 parts of $TaCl_5$ = parts of Ta_2O_5.	At. wt. of Ta.
II	3	12.99680	8.02326	61.733	181.49
II	5	9.24957	5.71104	61.744	181.60
II	4	10.17456	6.28133	61.736	181.52
II	1	17.99542	11.11014	61.739	181.55
II	2	11.70558	7.22693	61.739	181.55
III	4	6.24767	3.85658	61.728	181.46
III	3	7.26375	4.48398	61.731	181.48
I	2	15.88270	9.80465	61.732	181.49
					Mean, 181.52

Summary.

In eight experiments 91.51605 grams of tantalum chloride gave 56.49791 grams of tantalum oxide, corresponding in round numbers to 181.5 as the atomic weight of tantalum, a number one-half a unit higher than that now given in the international table. In conclusion, it may be as well to state that further work upon the value of this constant is in progress.

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. No. 57.]

THE IONIZATION RELATIONS OF SULPHURIC ACID.

BY A. A. NOYES AND M. A. STEWART.

Received July 22, 1910.

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