

THE ATOMIC MASS OF TUNGSTEN.

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A REVIEW of the literature on the determinations of the atomic mass of tungsten will show that a careful examination of the methods employed is of fundamental importance. Fifteen experimenters have made determinations of this constant, but with widely varying results. The method of investigation, with few exceptions, has been to reduce tungsten trioxide in a current of hydrogen at a white heat, and then to reoxidize the metal thus obtained. Deviations occur not only in the results of the different experimenters but also, with few exceptions, in the different observations of the same experimenter. Clarke¹ closes his summary of all the work on the atomic mass of tungsten with the following words: "Farther investigation is required in order to fully establish the true atomic weight of tungsten."

Deviations in the results of any atomic mass determination are due either to an inaccurate method or to experimental errors. It is not always an easy matter, however, to determine the source of error in a given series of variable results; but with several series of results from different experimenters, the question can be decided with a reasonable degree of accuracy. If, for instance, we have several series of results by the same method from different experimenters, and if the different series, with the exception of one, agree with each other, the probability is that the deviations in the one series are due to experimental errors. If, on the other hand, deviations occur in each series, and are more or less similar, the probability is that the method is inaccurate.

Almost every series of results on the atomic mass of tungsten, obtained by the reduction of the trioxide in a current of hydrogen, and by the reoxidation of the resulting metal, shows a variation between the maximum and minimum results of from one to two units, and in exceptional cases the deviation is much greater. In view of these facts, it seems desirable to make a

¹ A Recalculation of the Atomic Weights, 1897.

careful study of the method which has usually been employed in this work, rather than add to the already large number of results; for, if the method is unreliable, no experimental skill can make the results trustworthy.

The following summary will show the lack of concordance in the results of the earlier determinations:

Berzelius¹ was the first to determine the atomic mass of tungsten. By reduction of the trioxide he obtained the value 189.6 as a mean of two experiments for the atomic mass of tungsten. The difference between the two results was 3.0. These results and those that follow are calculated on the basis of O = 16.

Schneider,² working with material which had been carefully purified, obtained two series of results for the atomic mass of tungsten, one by the reduction of tungstic acid and the other by reoxidation of the metal.

Reduction series.	Oxidation series.
184.18	184.21
183.37	184.16
184.01	183.36
184.28	<hr style="width: 50px; margin: 0 auto;"/>
184.45	Maximum difference 0.85
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Maximum difference	1.08

The quantity of material used in these experiments varied from two to six grams.

Marchand³ reduced the trioxide of tungsten and reoxidized the resulting metal; the following results were obtained for the atomic mass of tungsten:

183.91	}	Reductions.
183.96		
184.16	}	Oxidations.
184.51		
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Maximum difference		0.60

Borch⁴ made seven reductions of tungstic acid in a current of hydrogen, and two oxidations of the metal. The results were as follows:

¹ *Pogg. Ann.*, 8, 1, 1826.

² *J. prakt. Chem.*, 50, 152, 1850.

³ *Ann. Chem. Pharm.*, 77, 261, 1851.

⁴ *J. prakt. Chem.*, 54, 254, 1851.

Reductions.	Oxidations.
184.10	184.53
182.90	184.32
183.77	<hr/>
184.10	Difference 0.21
183.03	
183.77	
<u>183.91</u>	

Maximum difference 1.20

The quantities of material varied from two to eight grams.

By weighing the water obtained in the reduction of tungstic acid in hydrogen, Riche¹ obtained the value 174 for the atomic mass of tungsten as a mean of two experiments. The difference between the two was 1.78.

Dumas² reduced the trioxide of tungsten in hydrogen and obtained the following results for the atomic mass of tungsten.

184.00
183.42
184.16
183.76
183.62
184.80
184.16
<u>184.08</u>

Maximum difference = 1.38

The quantities of material varied from one to four and six-tenths grams.

Bernoulli³ reduced tungstic acid at a very high temperature in a current of hydrogen. The results were as follows:

Reduction series.	Oxidation series.
186.78	186.81
185.86	187.94
186.75	186.77
186.81	186.76
186.70	<hr/>
<u>177.73</u>	Maximum difference = 1.18

Maximum difference = 9.08

The maximum difference in the two series is 10.21. He found

¹ *J. prakt. Chem.*, 69, 10, 1857.

² *Ann. Chem. Pharm.*, 113, 23, 1860.

³ *Pogg. Ann.*, 111, 573, 1860.

that the greenish colored oxide gave the same results as did the yellow oxide.

Persoz¹ made two reductions of the trioxide of tungsten and obtained concordant results.

$$\begin{array}{r} 183.93 \\ 183.94 \\ \hline \text{Difference} = 0.01 \end{array}$$

Scheibler², from determinations of the water in barium metatungstate, obtained the value 184.00 for the atomic mass of tungsten. Maximum difference = 1.03.

Zettnow³ obtained the value 184.08 for the atomic mass of tungsten as a mean from four analyses of the tungstate of iron. From silver tungstate he obtained the value 183.80.

Roscoe⁴ made three reductions and two oxidations of the same sample of material, beginning with 7.8840 grams of tungstic acid. The results were as follows :

Reductions.	Oxidations.
182.72	182.49
183.71	183.87
<u>183.97</u>	<u> </u>
Maximum difference = 1.25	Difference = 1.38

From two analyses of tungsten hexachloride, Roscoe obtained the value 184.25 for the atomic mass of tungsten.

Waddell,⁵ from carefully purified tungstic acid, obtained by reduction in hydrogen the following values for the atomic mass of tungsten :

$$\begin{array}{r} 184.55 \\ 184.37 \\ 184.59 \\ 184.00 \\ 183.67 \\ \hline \text{Maximum difference} = 0.92 \end{array}$$

The quantities of material varied from one to four and a half grams.

¹ *Ann. Chim. Phys.*, [4], 1, 93, 1864.

² *J. prakt. Chem.*, 83, 324, 1861.

³ *Pogg. Ann.*, 130, 30, 1867.

⁴ *Ann. Chem. Pharm.*, 162, 368, 1872.

⁵ *Ann. Chem. J.*, 8, 280, 1886.

The material used in the work of Pennington and Smith¹ differed from that of all the preceding experimenters; in that the last traces of molybdenum were removed by gently heating the tungstic acid in a current of hydrochloric acid gas. The method of operation was also somewhat different from those of the earlier experimenters. The metallic tungsten used in the oxidations was obtained by the reduction of tungstic acid in a platinum crucible at a white heat, in a current of hydrogen, which was conducted through the lid of the crucible. The mean of nine results from the oxidation of the metal is 184.921 for the atomic mass of tungsten. The maximum difference in the series is 0.043. The quantities of material used varied from 0.43 to 1.08 grams.

Smith and Desi² weighed the water obtained in the reduction of tungstic acid, and from that calculated the atomic mass of tungsten. The mean of six determinations is 184.704. Maximum difference 0.071.

Schneider³ made a second series of reductions and oxidations. The material used in these experiments was freed from molybdenum by gently heating the tungstic acid in a current of hydrochloric acid gas. The values obtained for the atomic mass of tungsten were as follows :

Reduction series.	Oxidation series.
184.14	184.00
183.98	183.92
183.96	184.04
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Maximum difference = 0.18 Maximum difference = 0.12

The quantities of material varied from two to six grams.

Shinn⁴ obtained by oxidation of metallic tungsten the following values for the atomic mass of tungsten :

184.72
184.96
184.75
185.22
<hr style="width: 50%; margin: 0 auto;"/>

Maximum difference = 0.48

¹ *Ztschr. anorg. Chem.*, 8, 198.

² *Ztschr. anorg. Chem.*, 8, 205.

³ *J. prakt. Chem.*, 53, 288, 1896.

⁴ Thesis, University of Pennsylvania, 1896.

The quantities of material used varied from 0.10 to 0.22 gram of metal.

A glance at the foregoing results will show a remarkable variation. The extremely high value obtained by Berzelius is supposed to be due to the presence of alkaline impurities in the material used.

The observations of Schneider, Marchand, Borch, Dumas, and Waddell are very similar. The method of operation was the same in each case, and the material used was purified with considerable care. It is difficult to account for the variations which occur throughout these results. Molybdic acid is probably the only impurity that could have contaminated the material used in the experiments. Such an impurity would probably have lowered the separate results by the same amount, and hence would not have produced the variations. The deviations between the maximum and minimum results of the different experimenters are as follows: Schneider 1.08, Marchand 0.60, Borch 1.63, Dumas 1.38, and Waddell 0.92.

The results of Riche and Bernoulli differ widely from those obtained by other experimenters. The extremely low value obtained by the former is probably due to the method. The high results obtained by Bernoulli are more difficult to explain. The material used was carefully purified. The tungstic acid used in some of the experiments was of a greenish tinge. Some have assumed that this material was incompletely oxidized, and in this way account for the high results. Bernoulli found, however, that the greenish colored oxide and the yellow oxide gave the same results when reduced. Furthermore, neither the color of the original oxide nor the state of oxidation could affect the results obtained in the reoxidations of the metal. The results obtained by the latter method are higher than those obtained in the reductions. In view of these facts, the explanation which has been offered to account for these high results is entirely unsatisfactory.

Scheibler's results on barium metatungstate show a variation of more than one unit, and it must be added that the results obtained by the determination of the barium and tungsten in this salt were still more variable and were not used by Scheibler in calculating the atomic mass of tungsten. The two short series

of results on ferrous and silver tungstates by Zettnow are reasonably concordant.

Roscoe's experiments on the same sample of material are rather interesting. The material was reduced and reoxidized several times without being removed from the porcelain boat. The maximum difference in a series of five results is one and a half units. If the method employed by Roscoe is accurate, it is difficult to account for this variation.

The most concordant series of results on the atomic mass of tungsten is that of Pennington and Smith. The value obtained is higher than that obtained by most experimenters. Schneider¹ has attempted to account for the high values obtained in these experiments but, inasmuch as these results agree very closely with those obtained by Smith and Desi and Shinn, it is useless to offer an explanation for this high value until the true atomic mass of tungsten is known with greater certainty, at least until a series of concordant results has been obtained which differs from these.

Schneider's last determinations consist of two series of results, each series containing three observations. From these two short series of reasonably concordant results, Schneider concludes that the atomic mass of tungsten may be safely considered equal to 184.00. The evidence, however, is far from satisfactory. In view of the wide variations in the earlier determinations, the number of results in these experiments is entirely too small to establish anything with certainty in regard to the true atomic mass of tungsten. This fact is shown in the work of Waddell, who made five determinations. The maximum variation in the first three observations was only 0.22, while in the series of five the variation was 0.92. The same is noticed in the work of other experimenters. And in the present investigation, consisting of more than sixty determinations, a series of five concordant results were sometimes obtained, after which considerable variation was obtained. Attention will be called to this fact again in the discussion of the following observations :

PREPARATION OF TUNGSTEN TRIOXIDE.

The material used in the first few series of determinations was

¹ *J. prakt. Chem.*, 53, 283, 1896.

obtained from wolframite, from Zinnwald, Bohemia. The greenish-yellow oxide obtained by digesting this mineral for several days with aqua regia was washed with distilled water and afterwards dissolved in ammonium hydroxide. The solution was evaporated to crystallization and the ammonium tungstate which separated out was strongly ignited. The resulting oxide was again dissolved in ammonium hydroxide, the solution was evaporated to crystallization, and the resulting ammonium tungstate strongly ignited. The oxide thus obtained was placed in a porcelain boat in a combustion tube and gently heated in a current of hydrochloric acid gas to remove the last traces of molybdenum. The material was then reignited and placed in a large porcelain dish filled with distilled water. Ammonia gas was conducted into the water for several days, after which the supernatant liquid was siphoned off and evaporated to crystallization. The ammonium tungstate which separated out was ignited and the process repeated. The material obtained from the second crystallization was used in the first series of experiments.

REDUCTION SERIES.

Tungsten trioxide obtained by the method just described was used in these experiments. The reductions were made in a hard glass combustion tube in a current of hydrogen, which was first conducted through solutions of ammoniacal silver nitrate, potassium permanganate, alkaline lead nitrate, caustic potash, and finally through sulphuric acid and a tube containing anhydrous calcium chloride. The reduction in each case was continued for several hours at a temperature almost high enough to melt the glass tube. The porcelain boat which contained the oxide was protected from the glass tube by means of platinum foil. The weighings were made on a Troemner short-armed balance with a set of weights which had been previously calibrated. The balance is sensitive to the fortieth of a milligram. The results calculated on the basis of $O = 16$ are as follows :

	Weight of WO_3 . Grams.	Weight of W. Grams.	Atomic mass of tungsten.
1	1.64084	1.30100	184.05
2	1.79728	1.42550	184.044
3	2.60739	2.06788	183.98
4	4.57390	3.62890	184.33

At this point an unglazed porcelain tube was substituted for the glass tube, and the reductions that follow were continued for three hours at the highest temperature obtainable in a combustion furnace.

	Weight of WO_3 , Grams.	Weight of W. Grams.	Atomic mass of tungsten.
1	3.32320	2.63547	183.94
2	6.11056	4.84580	183.91
3	9.23802	7.32393	183.66

The last experiment was continued through a period of eight hours.

The first three results agree very closely and give 184.02 as a mean for the atomic mass of tungsten. The mean of the results with the glass tube is 184.10. The maximum deviation is 0.35. The mean of the results obtained with the porcelain tube is 183.84, with a maximum difference of 0.28. The maximum deviation in the whole series is 0.67.

OXIDATION SERIES.

The metal obtained in the foregoing reductions was used in these experiments. The oxidations were made in porcelain crucibles. The material was protected from particles of dust by means of a porcelain lid suspended a short distance above the crucible. The oxidation in each case was continued until there was no farther increase in weight.

	Weight of W. Grams.	Weight of WO_3 , Grams.	Atomic mass of tungsten.
1	1.70220	2.14400	184.94
2	1.37651	1.73393	184.86
3	2.05606	2.58951	185.00
4	1.10300	1.38933	184.91
5	1.85855	2.34143	184.75
6	7.28774	9.18730	184.15

The mean of the first five results of this series is 184.89. This value is almost identical with that obtained by Pennington and Smith. The mean of the whole series is 184.77. The maximum deviation is 0.85.

REDUCTION OF OXIDE OBTAINED BY THE IGNITION OF METAL.

Inasmuch as the value obtained in the oxidation series is almost a unit greater than that obtained by reduction, it was

thought advisable to make a series of reductions of the oxide obtained in the series of oxidations.

	Weight of WO_3 . Grams.	Weight of W. Grams.	Atomic mass of tungsten
1	2.02890	1.61071	184.88
2	2.15894	1.71388	184.85
3	2.35206	1.86740	184.94
4	1.39137	1.10351	184.01
5	1.92125	1.52487	184.66
6	1.46746	1.16383	183.99
7	5.01313	3.97560	183.93
8	6.11056	4.84580	183.91

The first three results of this series agree very closely and give 184.89 as a mean for the atomic mass of tungsten. The last three results are equally concordant and give 183.94 as the mean value. The mean of the whole series is 184.40. The maximum deviation is 1.03. The oxide used in these experiments was very light and fluffy. The material used in the last experiment was moistened and re-ignited to render it more compact.

OXIDATION OF METAL OBTAINED FROM THE SECOND REDUCTION.

The material obtained in the last series was used in these experiments.

	Weight of W. Grams.	Weight of WO_3 . Grams.	Atomic mass of tungsten.
1	3.96360	4.99460	184.53
2	2.63034	3.31647	184.01
3	1.60964	2.02804	184.65

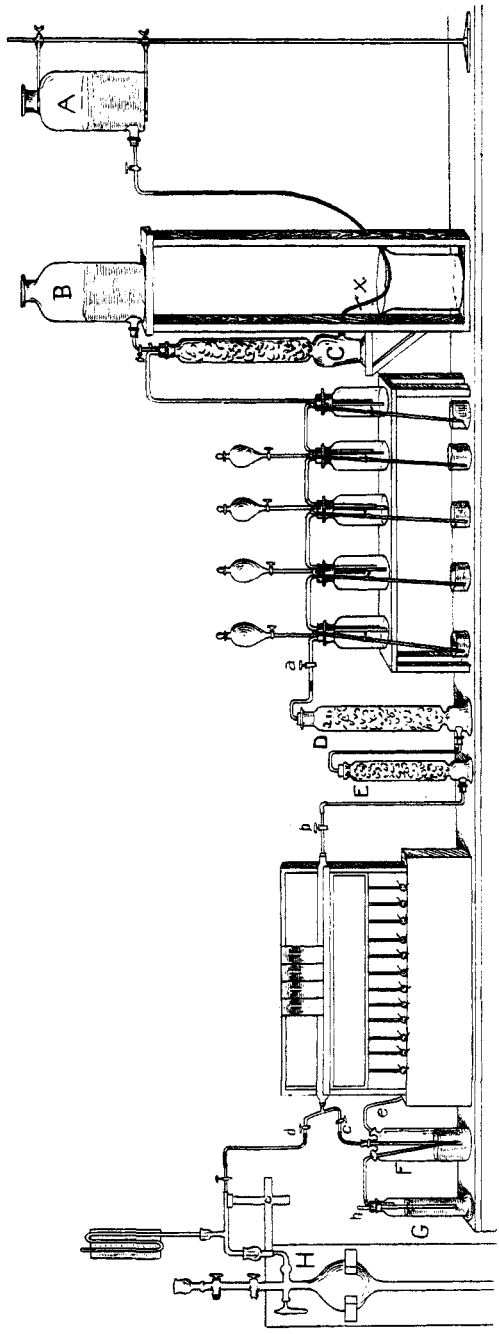
The variations in this series are similar in every respect to those of the preceding series.

In view of the wide variations in all the preceding work, an attempt was made to weigh the water formed in the reduction of tungsten trioxide. The moisture was collected in a small glass-stoppered U-tube filled with anhydrous calcium chloride. To this tube was attached another similar tube to prevent absorption of moisture from the air. Several determinations were made but the results were too discordant to establish anything. The removal of the last traces of air from the generator and wash-bottles was very difficult to accomplish, and hence the results were usually too high. The presence of air even in

small quantities would also affect the results in the reduction series. To overcome this difficulty, a different form of apparatus was constructed, the plan of which is shown in the accompanying sketch.

At the beginning of the operation, water, which had recently been boiled, was allowed to pass from the bottle *A* into the tower *C*, containing granulated zinc. When *C* was completely filled, the water passed through the small outlet tube into the first wash-bottle; after filling this it passed into the second, and so on. When the water reached the bottom of the cork in the last wash-bottle, the stop-cock at *a* was closed. The stop-cock in each of the separatory funnels was then opened and the water allowed to rise until the stems of the funnels were completely filled. In this way the air in the generator and wash-bottles was completely displaced by water. The stop-cock at the bottle *A* was now closed and sulphuric acid allowed to drop from the bottle *B* upon the zinc in *C*, the clip at *x* being opened at the same time. The hydrogen formed by the sulphuric acid and zinc, forced the water out of *C* into the beaker below, after which the clip at *x* was closed and the clip on the siphon of the first wash-bottle opened. When the water was removed from this bottle, the clip was closed and that of the second siphon opened and so on until the water in all these bottles was displaced by hydrogen. The separatory funnels were then filled with the different solutions used in purifying the hydrogen. The stop-cocks at *a*, *b*, and *c* were opened, while that at *d* was closed; this allowed the hydrogen to pass through the apparatus. The stop-cocks of the different separatory funnels were then opened and the solutions allowed to pass into the corresponding wash-bottles. The first bottle contained pure water, the second ammoniacal silver nitrate, the third and fourth potassium permanganate, and the fifth alkaline lead nitrate. The drying tower *D* was filled with anhydrous calcium chloride and caustic potash, and the tower *E* with alternate layers of glass wool and phosphorus pentoxide. These were substituted for sulphuric acid for, according to Dittmar and Henderson,¹ hydrogen when passed through sulphuric acid becomes contaminated, owing to the reduction of the acid by the hydrogen. From the drying

¹ *Proc. Phil. Soc.*, (Glasgow).



towers the hydrogen passed into a thin-walled, glazed porcelain tube, placed in a combustion furnace. The bottles *G* and *F* acted as a regulator; the outlet to *F* was connected to a suction tube *e*. When the suction was greater than the backward pressure of the wash-bottles, air passed in at *h* and through the columns of sulphuric acid in *G* and *F*. The length of these two columns of acid were adjusted so that the pressure exerted against the air passing through them was equal to the backward pressure of the wash-bottles. The Sprengel pump *H* was attached so that the metal might be cooled in a vacuum and thus prevent any occlusion of hydrogen. When the reductions were complete the stop-cocks at *b* and *c* were closed. The reservoir of the vacuum pump was exhausted and the stop-cock at *d* opened. This was repeated several times, until the vacuum was almost perfect.

This form of apparatus was used in all the reductions which followed. The air could be completely removed from the apparatus in a short time. The reductions were continued for a period of three hours at the highest temperature obtainable in a combustion furnace. When the quantity of material exceeded three grams the time was longer.

REDUCTION SERIES.

All the material resulting from the preceding experiments was ignited and digested for several days with pure aqueous ammonia. A residue was left, which gave the bead test for silica. It is evident from this, that tungstic acid, when reduced in a porcelain boat, takes up silica. The solution of ammonium tungstate was siphoned off and evaporated to crystallization. The crystals of ammonium tungstate were strongly ignited, and the resulting oxide used in the experiments. For the first time the metal was allowed to cool in a vacuum.

	Weight of WO_3 . Grams.	Weight of <i>W</i> . Grams.	Atomic mass of tungsten
1	3.55192	2.81560	183.55
2	4.59362	3.64461	184.34
3	4.30435	3.41459	184.21
4	2.64671	2.09900	183.95

The mean of these four results is 184.01. The maximum difference is 0.79.

OXIDATION SERIES.

The metal obtained in the preceding series of results was re-oxidized, and the following values obtained for the atomic mass of tungsten :

	Weight of W. Grams.	Weight of WO_3 . Grams.	Atomic mass of tungsten.
1	2.80958	3.54370	183.70
2	3.63095	4.57662	184.30
3	2.09740	2.64455	183.99

This series, like the preceding, is of little value, owing to the wide variation in the results.

Inasmuch as the removal of air from the present form of apparatus was a matter of little difficulty, another attempt was made to collect the water formed in the reduction of tungsten trioxide, and from its weight calculate the atomic mass of tungsten. The moisture was collected in a glass-stoppered U-tube filled with alternate layers of glass wool and phosphorus pentoxide. From a series of blank experiments, it seemed that any error introduced by the presence of air in the apparatus would be almost inappreciable. The following results were obtained :

	Weight of WO_3 . Grams.	Weight of H_2O . Grams.	Atomic mass of tungsten.
1	5.01313	1.16742	184.07
2	2.02890	0.47090	184.86
3	7.04192	1.63864	184.27
4	3.34204	0.77832	184.07

The variations in this series are similar in every respect to those of the different reduction and oxidation series.

The next line of investigation was to make a number of determinations with material obtained from different minerals and different localities.

REDUCTION OF TUNGSTEN TRIOXIDE OBTAINED FROM SCHEELITE FROM NEW ZEALAND.

The oxide was extracted from this mineral and purified in a manner similar to that described under wolframite. No trace of molybdenum was found even before the oxide was heated in hydrochloric acid gas. The results of seven reductions are as follows :

	Weight of WO ₃ . Grams.	Weight of W. Grams.	Atomic mass of tungsten.
1	3.41018	2.70410	183.83
2	2.99000	2.37084	183.80
3	3.11613	2.47047	183.67
4	4.32830	3.43118	183.56
5	4.66735	3.70050	183.72
6	4.29620	3.40623	183.71
7	3.39104	2.68885	183.80
8	2.93215	2.32515	183.87

The mean of this series is 183.745. The maximum deviation is 0.20. Considering the number of experiments, this is the most concordant series of results ever obtained by reducing the trioxide of tungsten and weighing the resulting metal. In experiments 2 and 7, the metal was cooled in a vacuum; in all the other experiments it was cooled in hydrogen.

OXIDATION SERIES.

The metal obtained in the preceding reductions was used in these oxidations. The results of six experiments are as follows :

	Weight of W. Grams.	Weight of WO ₃ . Grams.	Atomic mass of tungsten.
1	2.70219	3.40775	183.83
2	2.36771	2.98620	183.75
3	2.46705	3.11016	184.13
4	3.42163	4.31472	183.90
5	3.40086	4.28890	183.82
6	2.68249	3.38145	184.20

This series gives a mean of 183.94, with a maximum difference of 0.45.

REDUCTION OF TUNGSTEN TRIOXIDE OBTAINED FROM WOLFRAM-
ITE FROM CONNECTICUT.

The oxide was obtained from this mineral and purified by the method already described. The details of the work were the same as in similar series which precede. The results were as follows :

	Weight of WO ₃ . Grams.	Weight of W. Grams.	Atomic mass of tungsten.
1	3.14520	2.49330	183.58
2	3.10516	2.46141	183.51
3	4.17792	3.31244	183.83

Mean = 183.64

Maximum difference = 0.32

OXIDATION SERIES.

The metal was obtained from the preceding reactions.

	Weight of W. Grams.	Weight of WO ₃ . Grams.	Atomic mass of tungsten.
1	2.48088	3.12790	184.05
2	2.44588	3.08318	184.22
3	3.29370	4.15260	184.06

The mean of these results is almost one-half a unit greater than the mean of the reduction series. It seems that the results from oxidations are invariably higher than those obtained by reduction.

EXPERIMENTS ON MATERIAL OBTAINED FROM HUBNERITE FROM COLORADO.

The usual method of purification was used. Two reductions of the trioxide gave the following results:

	Weight of WO ₃ . Grams.	Weight of W. Grams.	Atomic mass of tungsten.
1	1.83600	1.45618	184.03
2	4.31878	3.42450	183.81

The metal resulting from these reductions was reoxidized.

	Weight of W. Grams.	Weight of WO ₃ . Grams.	Atomic mass of tungsten.
1	1.45184	1.83090	183.85
2	3.40470	4.29225	184.14

EXPERIMENTS ON MATERIAL OBTAINED FROM SCHEELITE FROM BOHEMIA.

The oxide was extracted and purified by the usual method. Two reductions were as follows:

	Weight of WO ₃ . Grams.	Weight of W. Grams.	Atomic mass of tungsten.
1	2.77363	2.19950	183.89
2	2.13327	1.69120	183.63

The reoxidation gave:

	Weight of W. Grams.	Weight of WO ₃ . Grams.	Atomic mass of tungsten.
1	2.18985	2.76060	184.17
2	1.68208	2.12070	184.08

Throughout this work, it had been noticed when tungsten trioxide was heated in a current of hydrochloric acid gas for some time that a considerable sublimate was formed, even when

molybdic acid was absent. Enough of this sublimate for an atomic mass determination was obtained as follows: Tungsten trioxide was heated for some time in a current of hydrochloric acid gas at a temperature of about 400°. The sublimate was removed from the tube, strongly ignited, and gently reheated in a current of hydrochloric acid gas. The small white sublimate formed did not respond to the test for molybdic acid. The portion left in the porcelain boat was removed from the tube and strongly ignited in the air for a period of ten hours. It was then reduced in a current of hydrogen and the following result obtained:

	Weight of WO ₃ . Grams.	Weight of W. Grams.	Atomic mass of tungsten.
I	1.12970	0.89610	184.13

Upon reoxidation, this metal gave 184.87 for the atomic mass of tungsten.

The results from the sixty-four determinations made in the present investigation, show a maximum deviation of one and a half units. A discussion of these results, with a view of arriving at the true atomic mass of tungsten, would be useless. To take the mean of all the results would be entirely unsatisfactory, and yet there seems to be no reason why any one result should be accepted in preference to any other. It will be noticed, in several instances, that three or four consecutive results agree very closely. These different series of concordant results, however, do not agree. The variations in these results are similar in every respect to those in the results of earlier experiments.

Various causes suggest themselves as possible factors in producing these variations. The lower values obtained in the latter part of the investigation are undoubtedly due to a better form of apparatus and a higher temperature.

The reductions were all made in a porcelain boat. During each determination the boat increased in weight by from one to three milligrams. It is difficult to determine whether this absorption of tungsten by the boat would affect the results or not. If the tungsten is absorbed as metal it would produce no effect on the results, if not absorbed as metal it would. It was shown in the first part of this investigation that the metal obtained in the reductions contained silica. This may, in part,

account for the higher values obtained in the oxidations. In view of these objections to the use of porcelain, a series of reductions were made in which a platinum boat was used. This, however, did not remove the difficulty; platinum absorbs tungsten and tungsten absorbs platinum, and the results obtained were just as variable as those obtained with the porcelain boat.

A series of observations on tungsten trioxide was next made with a view of determining whether or not this compound is suitable for atomic mass determinations.

The first point was to determine how rapidly this compound takes up moisture from the air. Several series of observations were made, and it was found in each case that the absorption of water was inappreciable. The rate at which the water was absorbed is best shown by the following series of weighings of tungsten trioxide, which had been left for several days in the open air. The oxide was first strongly ignited, then placed in a porcelain boat, carefully protected from dust, and left for four days in an open window.

	Grams.
Weight of the oxide at the beginning	5.34600
“ after one day	5.34605
“ “ two days	5.34620
“ “ three days	5.34625
“ “ four days	5.34630

From these observations it is evident that no appreciable error can be introduced by the absorption of moisture during the weighing of this compound.

A series of observations was also made to ascertain the action of light on this oxide. A weighed quantity of the material was placed in a desiccator and left for some time in direct sunlight. Weighings made at different intervals showed that no reduction had taken place. In working with this compound, it is unnecessary to cover the desiccator with a black cloth.

Upon examining the porcelain tube after a reduction, a slight sublimate was usually noticed. Whether the tungsten trioxide is volatile at that temperature, or whether the moisture formed in the reduction carried mechanically small particles of the oxide from the boat, was not determined. In either case an error is introduced, but in all probability a very small one.

A series of observations was next made to determine whether

or not tungsten trioxide contains nitrogen. A number of reductions were made in the usual way and the products set free were conducted through a U-tube containing pure water and a few drops of Nessler's reagent. The oxide used was obtained by strongly igniting ammonium tungstate for two days. Hydrogen was allowed to pass through the reduction apparatus for some time in order to completely remove the air. When the reduction was started, the solution in the U-tube began to assume a yellowish color, even when the temperature was comparatively low. Before the reduction was half completed, the solution was of a deep yellowish brown color. In some instances a slight precipitate was formed at the surface of the solution. Several observations were made, and the ammonium test distinctly obtained in each case. A series of blank experiments were made and no coloration was produced. The experiments proved conclusively that the oxide obtained by the ignition of ammonium tungstate contains nitrogen. No attempt was made to determine the quantity of nitrogen present. The oxide obtained by the ignition of metal was also examined and found to contain a trace of nitrogen. Whether the nitrogen in the former oxide was present as an oxynitride or as an ammonium residue, was not determined. If it exists as an ammonium residue, then hydrogen must also be present. A number of experiments were made by fusing the oxide with lead oxide and also with anhydrous sodium carbonate, with a view of converting any hydrogen present into water. Nothing definite was established, but there were some indications that a small quantity of water was formed. If the nitrogen is present in large enough quantities to affect the atomic mass determinations, it would probably lower the results and also produce variations, for it is not likely that the quantity would be the same in all cases.

In regard to the occlusion of hydrogen by the metal, nothing definite was established. The results obtained by cooling the metal in a vacuum were practically the same as those obtained when the metal was cooled in hydrogen.

It has been shown in the foregoing observations, that tungsten attacks the vessels in which the atomic mass determinations have been made, that the oxidation of tungsten is either slightly volatile, or that a small portion is carried mechanically by the

water formed in the reductions, and that the supposed trioxide of tungsten contains nitrogen and probably hydrogen. In view of these facts and of the fact that there is no means of determining when the reduction of oxide to metal is complete, and finally, in view of the fact that more than one hundred and fifty determinations have been made of this oxide, and nothing definite established, it is evident that the method usually employed in the determination of the atomic mass of tungsten must be regarded as unsatisfactory.

UNIVERSITY OF PENNSYLVANIA.

OBITUARY.

Mr. CARL H. SCHULTZ was born at Jutroschin-on-the-Orla, in the Province of Posen, on the 2nd of October, 1827. He began his education at the schools of his native town. In 1840 he entered the schools at Krotoschin, and later the gymnasium of Lissa. From there he went to the University of Breslau, from which he graduated in 1849. Being particularly fond of chemistry and natural philosophy, he continued the study of these branches for some time after the regular course was finished.

While in the tertiary course in the gymnasium, although only thirteen years of age, he gave private instructions in mathematics and later in chemistry.

In 1853, during the World's Fair in New York, he came to America, bringing with him very little money, but some strong letters of recommendation, and was not long in finding employment. His first situation was with the late Professor Benjamin Silliman, who had charge of the Chemical Department of the Exposition. Later he was appointed assistant to Dr. John Torrey, Professor of Chemistry at the College of Physicians and Surgeons, then in Crosby street. In 1854 the United States Assay Office appointed Dr. Torrey Chief Assayer, and he at once made Mr. Schultz his assistant. He not being a citizen of the United States was offered as an objection to his appointment, but he overcame this by taking out his first papers, and after the proper time, his second papers. Few men ever felt prouder of their citizenship or could have been more thoroughly American.

While at the Assay Office, besides his routine work of making