

- 12 And moreover by them my son, be warned:
Of making many books there is no end :
And much anxious thought
Is a weariness of the flesh.

The end of the discourse, the whole, listen to :

- 13 Fear God :
And keep His commandments :
For that is the whole (of) man.
14 For God will bring every deed into judgment :
With every hidden thing,
Whether it be good
Or whether it be evil.

The Atomic Mass of Tungsten.

By Mary E. Pennington and Edgar F. Smith.

(Read before the American Philosophical Society, November 2, 1894)

A study of the literature relating to this subject discloses the fact that while, in most instances, every effort was made to eliminate foreign matter from the material employed in the numerous investigations which have been conducted at various times, several doubtful points continue. The object of this communication is to direct attention to one of these possible sources of error, viz., the presence of traces of molybdenum, and to present results obtained after its evident removal.

The earlier investigations relating to the atomic mass of tungsten are rather numerous ; but of these that of Schneider is without doubt deserving of the most confidence, chiefly for the pains taken in preparing pure material for the later experiments. The author offers satisfactory evidence of the absence of possible contaminating substances, and in writing of the presence of molybdenum employs these words : " Molybdän endlich nicht, weil die Molybdänsäure in heftiger Glühhitze flüchtig ist " (*Journ. prakt. Chemie*, 50, p. 158). The experience of chemists generally is that a complete separation of tungsten trioxide from molybdenum trioxide cannot be attained in this way. Indeed, an examination of the experiments recorded by Schneider discloses the fact that he, while engaged in reducing strongly ignited tungsten trioxide, several times discovered on the anterior portion of the reduction or combustion tube " ein weissliches Sublimat." This sublimate Schneider attributes to tungsten chloride, but the question may well be asked, Was it not molybdic acid?

Waddell has made the most recent contribution to our knowledge upon the atomic mass of tungsten (*Amer. Chem. Journ.*, 8, 280). He experi-

enced much difficulty in obtaining pure tungsten trioxide. He found by considerable investigation that Rose's method for the separation of molybdenum and tungsten was the most convenient. Traube (*Jahr. für Mineralogie*, etc., Beilageband, 7, 232) and more recently Friedheim (*Z. für anorg. Chemie*, 1, 76) has shown that this procedure does not entirely eliminate the molybdenum. Recent investigations, in this as well as in other laboratories, upon artificial and supposedly pure, as well as natural tungstates have proved that these all contain molybdenum in appreciable amounts, and it may well be questioned whether the earlier determinations of the atomic mass of tungsten were not affected by the presence of traces of molybdenum. Its complete and absolute removal would tend to raise the value of this constant of tungsten. An effort to this end appeared to be desirable.

An attempt was first made to free the trioxide from impurities through the sodium salts. This course was abandoned inasmuch as traces of alkali persistently adhered to the tungsten. This fact is not new; Schneider was fully aware of it, and in consequence he had recourse to another method, which was also adopted in this investigation with some modifications.

A quantity of tungsten trioxide, derived from wolframite, was heated in a porcelain dish for three days with concentrated nitric acid. The latter was then decanted and the yellow oxide was well washed with water. It was next subjected to the action of boiling *aqua regia* for the same length of time, the acid solution, however, being removed from time to time. The washings and acid liquor were tested for iron. When this was no longer detected the washed trioxide was dissolved in yellow ammonium sulphide, air being excluded as much as possible. The solution was filtered from insoluble material, and concentrated almost to the point of crystallization, when hydrochloric acid was added. The liquid was removed from the resulting precipitate, which was ignited, then boiled with nitric acid, and later with *aqua regia*. The resulting trioxide no longer showed the presence of iron and manganese. It was then washed, brought into a porcelain dish, covered with distilled water and ammonia gas conducted over the liquid until it was saturated. Several days were required for this purpose. Only a very small residue remained undissolved. It contained a trace of silica and a little greenish-yellow oxide. Hydrogen sulphide gas was next introduced into the ammoniacal solution, which was then digested at 80° C., for several hours. On the addition of pure dilute hydrochloric acid to this solution tungsten trisulphide was precipitated. This was filtered out, washed and roasted in a large porcelain crucible with air access. The trioxide prepared in this manner no longer contained silica, iron or manganese. If tin had been originally present it would have gone out with the *aqua regia*, and any columbic acid would have remained when the trioxide was subjected to the ammonium sulphide treatment. The next step was to prove the presence or absence of molybdenum. A portion of the purified tungsten trioxide was converted into the ammonium salt and the sulphocyanide test

(Braun, *Zeit. f. Analyt. Chemie*, 2, 36) for molybdenum applied to its aqueous solution. The presence of molybdenum was very evident. The ignition of the tungsten trioxide in the earlier stages of purification had not eliminated this constituent. Instead of adopting Rose's method as was done by Waddell, and thus introducing the possible contamination from a fixed alkali, recourse was had to the reaction of Debray—the volatilization of the molybdic acid as oxychloride— $\text{MoO}_3 \cdot 2\text{HCl}$ (*Compt. rend.*, 46, 1098, and Liebig's *Annalen*, 108, 250). The experiments of Péchard (*Compt. rend.*, 114, 173, and *Zeit. f. anorg. Chemie*, 1, 262), as well as those more recently made by Smith and Oberholtzer (*Journ. Am. Chem. Soc.*, 15, 18, and *Zeit. f. anorg. Chemie*, 4, 236), and by Smith and Maas (*Journ. Am. Soc.*, 15, 397, and *Zeit. f. anorg. Chemie*, 5, 280), give evidence that by this means molybdenum can be expelled from tungsten derivatives. To this end the remainder of the tungsten trioxide was placed, in portions, in a porcelain boat and exposed to the action of hydrochloric acid gas, aided by a gentle heat ($150\text{--}200^\circ\text{C.}$), until a volatile sublimate of $\text{MoO}_3 \cdot 2\text{HCl}$ was no longer noticed. Upon reoxidizing the residual tungsten trioxide in open porcelain crucibles and then subjecting portions of the same to the sulphocyanide test the presence of molybdic acid was no longer observed. This was taken as an evidence of its complete removal.

The trioxide subjected to the treatment described in the last paragraph was suspended in water into which ammonia gas was conducted. The oxide dissolved without leaving a trace of foreign matter. The salt obtained upon evaporation was crystallized three times; it was then dried and ignited with careful exclusion of dust. This material was now regarded as sufficiently pure for the experiments projected. As it was not intended to attempt any determinations by reduction of the oxide, the latter was reduced in a current of hydrogen, carefully purified, to the metallic state. The reductions were made in a large platinum crucible after the manner of Von Pfordten (*Ber. d. deutsch. Chem. Gesell.*, 17, 731). Inasmuch as the reduced metal slowly alloys with the platinum the resulting metallic powder was in all instances gently shaken from the crucible after it had cooled in a current of hydrogen. The reduction of trioxide proceeds quite rapidly in the above manner and is always complete. The product is dark gray in color. Its specific gravity was found to be 18.64 at 0° . It was carefully preserved from dust and moisture in drying bottles.

The amount of oxygen absorbed by the conversion of tungsten into its trioxide was made the basis of the determinations recorded in this paper.

The oxidations were made in porcelain crucibles. These were supported in close-fitting asbestos rings so that reducing gases could not gain access to the hot oxide. To avoid loss from particles being carried out mechanically a porcelain lid wider than the crucible was placed over it, at the height of one-half inch. A careful examination of this lid from time to time showed no traces of tungstic oxide. Dust particles were also excluded in this manner. No other work was done in the room in

which these oxidations were performed. All draughts were avoided. The crucibles were handled with nickel crucible tongs. They were allowed to cool in vacuum desiccators over sulphuric acid. Calcium chloride cannot apparently be used for this purpose, at least a superficial greenish tinge was always noticed on the oxide cooled in this way. Direct sunlight also causes a reduction of the trioxide, therefore the desiccators were kept covered with a black cloth.

At the beginning of each oxidation the flame applied was quite small. The metal increased in bulk as it oxidized, and in five minutes had assumed a light yellowish-green color. At the expiration of half an hour the heat was increased. Later a stronger heat was allowed to act and continued until the oxidation was finished. The first period of each oxidation continued through five hours. The crucible and contents were cooled and weighed. The second period lasted three hours additional, after which the crucible was allowed to cool. It was again weighed, and even if there was no change in weight from that first recorded, the ignition was continued for two hours more. The third weight, if constant, was taken as final. Each oxidation, therefore, was not considered finished until it had been continued through a period of at least ten hours.

The weighings were made upon a Becker balance with weights, which had been adjusted for this work. The vacuum standard was observed, and oxygen taken equal to sixteen in all the calculations. The results were as follows :

	WEIGHT OF TUNGSTEN IN GRAMS.	WEIGHT OF OXYGEN IN GRAMS.	ATOMIC MASS OF W.
1.	0.862871	0.223952	184.942
2.	0.650700	0.168900	184.923
3.	0.597654	0.155143	184.909
4.	0.666820	0.173103	184.902
5.	0.428228	0.111168	184.900
6.	0.671920	0.174406	184.925
7.	0.590220	0.153193	184.933
8.	0.568654	0.147588	184.943
9.	1.080973	0.280600	184.913
	Mean.....		184.921
Maximum.....			184.943
Minimum.....			184.900
			.043

Clarke (*Recalculation of the Atomic Weights*, 1882, Washington) and Becker (*Atomic Weight Determinations*, 1880, Washington) in their recalculations of this constant of tungsten both arrive at the figures 184.02

(O=16), while Ostwald (*Outlines of General Chemistry*, translated by Walker, 1890, p. 30) says, "the mean of the good determinations is $W=184$ " Waddell (*Amer. Chem. Jr.*, 8, 280) gives as the mean of his determinations 184.5 (O=16). The results presented in this communication show, therefore, a wide difference from those usually looked upon as most correct.

The evidence in earlier papers of the absence of molybdenum from the tungsten is far from satisfactory. Waddell recognizes this; hence he employs Rose's method for the removal of molybdenum from his starting-out material. Since the publication of his research other experimenters have declared and proved the insufficiency of this method (Traube, Friedheim, *loc. cit.*) for the purpose to which Waddell applied it. For this reason the Rose method was not followed in this present investigation, as well as from fear that it might introduce alkali, difficult to eliminate. As a substitute for it the method of Debray was adopted.

In considering the factors that possibly could have caused a rise in the atomic value other than that occasioned by the complete removal of molybdenum, two suggest themselves. First, the occlusion of hydrogen by the finely divided metallic tungsten, upon cooling in that gas, would produce such a result. Waddell (*loc. cit.*) by one experiment is satisfied that such gas occlusion does not occur. Derenbach (*Inaug. Dissertation*, Würzburg, 1892) claims that there is an appreciable retention of hydrogen by the finely divided metal. The question is therefore one of importance, and while this communication contains no data on this point, yet if an occlusion equal to that claimed by Derenbach (*Dissertation*, p. 43) be granted to have occurred in each experiment recorded in this investigation the final result would not be equal to that actually obtained. We must therefore look further for the cause of the rise in the atomic value. The reductions of the trioxide were made in a platinum vessel. An examination of the metallic tungsten for platinum did not show its presence.

Again, tungsten trioxide volatilizes slightly at elevated temperatures; its escape would operate to augment the final value of the tungsten constant. There is, however, no evidence that loss in this way did occur, for the porcelain lid suspended over the crucible during the long ignition period never showed the presence of trioxide. Even if such a volatilization had taken place, it is not at all probable that three weighings could have been made with no change in the same. Furthermore, the remarkable concordance of the individual results among themselves precludes the idea that the rise in the found atomic mass is attributable to volatilization of trioxide. In the end it seems most reasonable to assume that the new value is due to a full and complete elimination of the last traces of molybdenum from the tungsten prior to its oxidation.

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