

THE ATOMIC WEIGHT OF TUNGSTEN.*

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When we examine Clarke's Recalculations of the Atomic Weights, or Becker's Atomic Weight Determinations, we will find various figures representing the atomic mass of tungsten, which differ greatly from each other.

The method pursued by most of the experimenters was the reduction of tungstic acid and weighing of the reduced metallic tungsten; some oxidized the metal to tungstic acid, and Bernouilli also reduced the trioxide of tungsten and calculated the atomic weight from the amount of water formed.

The cause of these great differences is due not so much to the methods employed as to the impurities contained in the material used for the experiments. All have recognized this, and their principal aim was to obtain a chemically pure tungstic acid. It is comparatively easy to rid the substance from iron, manganese, aluminum, etc. But some difficulty is encountered in removing the last traces of silicic acid, and in separating molybdenum, which was not eliminated in most determinations. The analogy of the compounds of these two metals makes their separation more difficult, and the importance of the influence of the presence of molybdic acid (MoO_3) upon the results of the atomic weight determination of tungsten was recognized by Schneider (*Journal für praktische Chemie*, 50). He took the greatest pains in preparing a pure material, and removed the molybdic acid by strong ignition. Later investigators, however, have shown that it is not possible to completely separate tungsten from molybdenum by mere ignition.

Waddell more recently (*American Chemical Journal*, 8, 280), after considerable and careful work, obtained probably purer material than previous investigators. He found many difficulties in separating molybdenum from tungsten, and con-

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sidered Rose's method of separation as the most convenient; but Traube (*Jahrbuch für Mineralogie*, etc. *Beilageband*, VII., p. 232), and more recently Friedheim and Meyer (*Zeitschrift für anorganische Chemie*, **1**, 76), have shown that by Rose's method the elimination of molybdenum is not complete.

It is safe to admit that all former investigators had a tungstic acid contaminated with more or less molybdic acid, which tended to lower the atomic weight of tungsten, and the proof of it is the latest work on this subject by Pennington and Smith (*Proc. Amer. Philos. Soc.*, **33**, 332), who obtained a value (184.90), that differs quite appreciably from that usually accepted as representing the atomic mass of the element under consideration.

We have undertaken, in this present investigation, to determine the atomic weight of tungsten from the quantity of water formed by the reduction of tungsten trioxide. Bernouilli (*Poggendorff's Annalen*, **111**, 599) attempted to determine this constant in the same way, but the value which he obtained (186) we must consider as too high.

The greatest care was taken to obtain a really chemically pure tungstic acid, for the purpose of ascertaining whether the elimination of the last traces of molybdenum would be likely to produce a rise in the atomic mass.

We obtained our tungstic trioxide by digesting the finely-powdered mineral wolframite from Zinnwald (Bohemia), in aqua regia, for several days; the trioxide thus obtained was boiled in a porcelain dish for five days in aqua regia, decanting from time to time the exhausted acid, washing the yellow oxide thoroughly with water. This operation was continued until the acid and washings showed complete absence of iron. The well-washed trioxide was then brought in a porcelain dish, covered with water, and ammonia-gas conducted into the liquid until saturated, dissolving the tungstic acid to ammonium metatungstate [$W_4O_{13}(NH_4)_2 + 8H_2O$]. Several days were required for this operation, and only a little greenish residue remained undissolved, containing traces of iron and probably columbic acid. The clear ammoniacal solution, after filtration, was concentrated in a porcelain dish almost to the point of crystallization. During

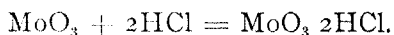
this operation it was necessary to filter several times, an amorphous brown precipitate being formed, as well as a gelatinous one, probably traces of silica. The concentrated solution was left standing to crystallize out the metatungstate of ammonium. The white crystalline needles were thoroughly washed with water, dried and ignited in a porcelain crucible to tungstic acid, excluding the entrance of dust by a large, suspended porcelain cover, admitting the air freely. This tungsten trioxide was twice re-crystallized and ignited and finally digested with yellow ammonium sulphide, excluding the air as much as possible, heating gently until the solution had a reddish-brown color. A little black residue was filtered off and tungsten trisulphide (WS_3) was precipitated from the clear solution of ammonium sulphotungstate [$WS_4(NH_4)_2$], by additions of small quantities of pure hydrochloric acid. After washing the precipitate by decantation and on the filter, it was dried and ignited in an open porcelain crucible to tungstic acid. After boiling this tungstic acid for two days in aqua regia, frequently renewing the acid and washing thoroughly with water, the trioxide was dissolved once more in yellow ammonium sulphide, no residue whatever being left behind. This solution was treated as above and the resulting tungstic sulphide ignited to the trioxide.

So far, we were perfectly sure that we had no iron, manganese, aluminum, silica, etc., contaminating our tungstic acid.

Now one more element remained to be separated from tungsten, and this is molybdenum. The presence of molybdenum was proved by converting a small quantity of the purified trioxide into the ammonium salt, and applying the sulphocyanide test, Braun (*Zeitschrift für analytische Chemie*, **2**, 36), which showed plainly the presence of this element. This demonstrated that the many previous operations of purification did not eliminate molybdenum, and strengthens our opinion that the tungstic trioxide used in all former investigations, except that of Pennington and Smith (*loc. cit*), was contaminated with molybdenum. To separate these two elements we had recourse to the vola-

tility of molybdenum oxychloride ($\text{MoO}_3 \cdot 2\text{HCl}$) Debray (*Comptes Rendus*, **46**, 1098, 1850) (*Liebig's Annalen*, **108**, 250).

The experiments of Pechard (*Comptes Rendus*, **114**, 173, and *Zeitschrift für anorg. Chemie*, **1**, 262), and those more recently made by Smith and Oberholtzer (*Jour. Amer. Chem. Soc.*, **15**, 18, and *Zeitschr. für anorg. Chemie*, **4**, 236), and by Smith and Maas (*Jour. Amer. Chem. Soc.*, **15**, 397, and *Zeitschr. für anorg. Chemie*, **5**, 280), prove beyond doubt the quantitative separation of molybdenum from tungsten by heating and passing dry hydrochloric acid gas over the mixture, the following reaction taking place:



Small portions of the purified tungstic acid were placed in porcelain boats and exposed to the action of pure hydrochloric acid gas, prepared from salt and pure sulphuric acid. The gas escaping from the generating flask passed through a bottle with sulphuric acid and a tower filled with calcium chloride, and then entered the combustion tube, where it came in contact with the tungsten trioxide. A gentle heat was applied and gradually increased to about 200°C ., until the white volatile sublimate of molybdenum oxychloride was no longer observed. The residue in the boat always showed some traces of reduction, so that it was re-oxidized in open porcelain crucibles. To determine complete absence of molybdenum small portions of it were subjected to the sulphocyanide test; no trace of the molybdic reaction was observed.

Only now we considered that we had a chemically pure tungstic acid, and proceeded to the actual determination of the atomic weight. This was done by conducting a current of pure and dry hydrogen over a carefully-weighed quantity of tungstic acid, collecting the water formed in a U-tube filled with freshly calcined calcium chloride.

The hydrogen used by us in the reductions was prepared from pure sulphuric acid and the purest obtainable zinc. To purify the gas it was conducted through a series of bottles containing potassium permanganate, an alkaline solution of

lead nitrate, silver nitrate, sulphuric acid, caustic potash, calcium chloride, and finally through a nine-inches-long glass tube, filled with bright, polished iron wire, the latter being gently heated. After this, the gas was admitted to the tube, where it came in contact with the ignited tungstic acid contained in a platinum boat. The water produced in the reduction was collected in a weighed, glass-stoppered U-tube, filled with anhydrous calcium chloride. A similar tube was attached to this, to prevent absorption of moisture from the surrounding atmosphere. Before beginning the reduction, the tube was dried thoroughly, until constant weight of the U-tube was obtained.

The reduction of tungstic acid is not very easy, requiring a very high temperature and long time; in our experiments we ignited for about eight hours. After displacing the hydrogen in the U-tube, it was hung in the balance-case for half an hour, and then weighed; a second weighing was made after twenty minutes, but no difference was observed. The balance and the weights were perfectly adjusted, and all weighings reduced to the vacuum standard, and in the calculations, oxygen was taken as 16 and hydrogen as 1.008 (Clarke).

The results of six experiments were as follows:

	<i>Weight of Tungstic Acid in grams.</i>	<i>Weight of Water in grams.</i>	<i>Atomic Mass of Tungsten.</i>
(1)	0.983024	0.22834	184.683
(2)	0.998424	0.23189	184.709
(3)	1.008074	0.23409	184.749
(4)	0.911974	0.21184	184.678
(5)	0.997974	0.23179	184.704
(6)	1.007024	0.23389	184.706
Mean,			184.704
Maximum,			184.749
Minimum,			184.678
Difference,			0.071

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