

Another point has occurred to us: our results by permanganate have led us to suspect that all the copper may not be present in the precipitate as cuprous oxide. We are satisfied that after precipitation, and until acted upon by the ferric sulphate solution, no oxidation of the precipitate takes place, yet we find more copper by the electrolytic method than by the permanganate. The ratio is 1 : 0.9905. It may be urged that this represents the error due to the determination of the cuprous oxide by the permanganate method, but we are unwilling to concede this.

However, even were this granted, the admission would not affect the accuracy of the method we offer, for correct results depend only upon the permanganate factor, and not upon the absolute amount of copper.

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[CONTRIBUTIONS FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 36.]

## THE ATOMIC MASS OF TUNGSTEN AND THE PREPARATION OF SODIUM PERTUNGSTATE BY MEANS OF THE ELECTRIC CURRENT.<sup>1</sup>

BY GEORGE EDWARD THOMAS.

Received January 5, 1899.

### I. THE ATOMIC MASS OF TUNGSTEN.

THERE have been numerous determinations of the atomic mass of tungsten made in this laboratory; but as there were noted discrepancies in the results obtained, it was deemed advisable to pursue further investigation, as there appeared to be a probability that an examination of the trioxide of tungsten from different sources might reveal the cause of the disagreement mentioned.

Scheelite from Schlackenwald, Bohemia, and wolframite from Monroe county, Connecticut, were treated independently as follows: The finely divided minerals were digested for several days with *aqua regia*, and the insoluble residue washed repeatedly with water, and subsequently treated with ammonium hydroxide. These solutions were then evaporated and the crystals obtained were ignited, and to remove any molybdenum which might be

<sup>1</sup> From the author's thesis for the degree of Doctor of Philosophy.

present, the trioxides were exposed in a porcelain boat to the action of hydrochloric acid gas at a gentle heat in a tube of hard glass.

After the reignition of the oxides, they were placed in a porcelain dish, covered with distilled water, and ammonia gas introduced until complete saturation was attained. These salts were repeatedly crystallized until perfectly white.

It appeared desirable, before further work was undertaken, to submit portions of the two oxides to Dr. W. L. Hardin, for examination, as he was, at the time of this research, determining by means of elaborate apparatus the atomic mass of tungsten by reduction of the trioxide in hydrogen gas and subsequent reoxidation of the metal.<sup>1</sup>

Reduction of tungsten trioxide obtained from wolframite from Connecticut :

|         | Weight of WO <sub>3</sub> .<br>Grams. | Weight of W.<br>Grams. | Atomic mass<br>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 :

|         | Weight of W.<br>Grams. | Weight of WO <sub>3</sub> .<br>Grams. | Atomic mass<br>of tungsten. |
|---------|------------------------|---------------------------------------|-----------------------------|
| 1 ..... | 2.48088                | 3.12790                               | 184.05                      |
| 2 ..... | 2.44588                | 3.08318                               | 184.22                      |
| 3 ..... | 3.29370                | 4.15260                               | 184.06                      |

Experiments on material from scheelite from Bohemia. Two reductions were as follows :

|         | Weight of WO <sub>3</sub> .<br>Grams. | Weight of W.<br>Grams. | Atomic mass<br>of tungsten. |
|---------|---------------------------------------|------------------------|-----------------------------|
| 1 ..... | 2.77363                               | 2.19950                | 183.89                      |
| 2 ..... | 2.13327                               | 1.69120                | 183.63                      |

The oxidation gave :

|         | Weight of W.<br>Grams. | Weight of WO <sub>3</sub> .<br>Grams. | Atomic mass<br>of tungsten. |
|---------|------------------------|---------------------------------------|-----------------------------|
| 1 ..... | 2.18985                | 2.76060                               | 184.17                      |
| 2 ..... | 1.68208                | 2.12070                               | 184.08                      |

These investigations prove conclusively that the trioxides from both minerals were identical, and that the errors alluded to were not to be attributed to the difference in the sources of the minerals examined, and as it was evidently unnecessary to

<sup>1</sup> This Journal, 19, 657 (1897).

confirm his observations, further study in this particular direction was discontinued.

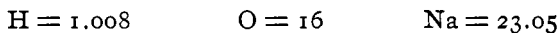
In the belief that there was something present in the mineral, or in the method for obtaining the material for analysis, which caused the lack of concordance in the results, another line of procedure was adopted.

1648 grams of finely pulverized wolframite, from Zinnwald, Bohemia, were fused with four times their weight of sodium carbonate in a wind furnace. Iron crucibles were employed, but the intense heat melted the crucibles, with an incidental loss of material, requiring the use of fire-clay vessels.

The fusion of unattacked oxides, sodium tungstate, and sodium carbonate, was lixiviated with water, and the solution of the sodium salts siphoned off. A purification by means of fractional crystallization was attempted; at least sixty crystallizations were made covering a period of about two months. Large quantities of silica were separated, which was introduced partly by the use of fire-clay crucibles. After this prolonged treatment the sodium tungstate, although perfectly white and apparently pure, contained a trace of sodium carbonate and silica.

However, the results from the water of crystallization, by heating the salt in an air-bath at temperatures varying between 180° and 200° C., were so concordant that it appeared probable that this might prove to be a reliable method for ascertaining the atomic mass of tungsten.\*

Preliminary investigation:



In this series of experiments calibrated weights were not employed and a Troemner balance was used, suited for ordinary analytical work.

|         | Weight of salt.<br>Grams. | Weight of<br>water.<br>Grams. | Per cent.<br>water. | Atomic mass. |
|---------|---------------------------|-------------------------------|---------------------|--------------|
| 1.....  | 1.4267                    | 0.1558                        | 10.92               | 183.82       |
| 2.....  | 2.1275                    | 0.2323                        | 10.91               | 183.86       |
| 3.....  | 2.3599                    | 0.2582                        | 10.94               | 183.19       |
| 4.....  | 6.8925                    | 0.7534                        | 10.93               | 183.50       |
| 5.....  | 3.2494                    | 0.3554                        | 10.94               | 183.30       |
| 6.....  | 4.4651                    | 0.4880                        | 10.93               | 183.55       |
| 7.....  | 7.1011                    | 0.7759                        | 10.93               | 183.63       |
| 8.....  | 11.0159                   | 1.2057                        | 10.94               | 183.07       |
| 9.....  | 9.3313                    | 1.0194                        | 10.92               | 183.69       |
| 10..... | 8.1501                    | 0.8912                        | 10.93               | 183.38       |

The difficulty encountered in the separation of sodium tungstate from sodium silicate indicated the necessity of abandoning this material for further use for atomic mass determinations.

Therefore, to test the accuracy of this method, ammonium tungstate from scheelite, from Bohemia, and wolframite, from Connecticut, purified as already described, were ignited, and the trioxide obtained was dissolved in sodium hydroxide prepared by dissolving metallic sodium in distilled water in a platinum dish. This solution was evaporated to crystallization; after repeating this operation three times the salt was found to contain sodium carbonate, due to absorption of carbon dioxide from the air, caused by the excess of sodium hydroxide. It was dissolved in distilled water and decomposed by electrolysis in an apparatus described on page 378. The greater portion of the sodium hydroxide in the outer compartment was added to the contents of the bulb; the remainder was rejected in order that there might be no excess of sodium hydroxide present. This solution was evaporated to crystallization, the salt dissolved, filtered and recrystallized. The product was examined for silica, carbon dioxide, and ozone, with negative results.

These crystals of sodium tungstate were white, and upon analysis yielded 70.274 per cent. of tungsten trioxide, the theoretical value, on a basis of 184 as the atomic mass of tungsten, being 70.303 per cent. Varying the conditions of temperature produced different results, indicating that all of the water was not eliminated at 200° C., and at much higher temperatures volatilization ensues. Therefore 0.7903 gram of the salt was heated for one-half hour at 220°, allowed to cool, and weighed, the loss indicating 10.85 per cent. water. Repeated experiments were made with a corresponding increase in temperature and loss, until between 264°–294° C., when no loss in weight was observed, and the percentage of water found equaled 10.907, the theoretical on a basis of 184 for the atomic mass of tungsten being 10.909. Upon sintering the salt in a platinum crucible there was a loss of 11.03 per cent. in weight, and when the covered crucible is kept at a red heat for some time, a white substance is noticed on the lid. There were also four determinations made by heating the salt in a tube of glass, and collecting the water in a U-tube containing sulphuric acid and pumice

stone, the results confirming the belief that volatilization accompanied an increase of temperature. The following atomic mass determinations were made by heating the normal salt between 268° and 295° C. A Troemner balance (sensitive to the fortieth of a milligram) and weights previously calibrated were employed.

FIRST SERIES.

|         | Weight of Na <sub>2</sub> WO <sub>4</sub> .2H <sub>2</sub> O.<br>Grams. | Weight of water.<br>Gram. | Atomic mass. |
|---------|---|---------------------------|--------------|
| 1 ..... | 1.36222   | 0.14842                   | 184.507      |
| 2 ..... | 1.06905   | 0.11638                   | 184.852      |
| 3 ..... | 1.40966   | 0.15366                   | 184.421      |
| 4 ..... | 2.34595   | 0.25556                   | 184.628      |
| 5 ..... | 1.00236   | 0.10913                   | 184.822      |
| 6 ..... | 1.12350   | 0.12236                   | 184.710      |
| 7 ..... | 1.19171   | 0.12963                   | 185.116      |
|         | Mean,   |                           | 184.722      |
|         | Maximum difference,   |                           | 0.695        |

SECOND SERIES.

|          |           |         |            |
|----------|-----------|---------|------------|
| 8 .....  | 1.04092   | 0.11365 | 183.884    |
| 9 .....  | 1.34561   | 0.14763 | 182.290    |
| 10 ..... | 1.01077   | 0.10916 | 187.507    |
| 11 ..... | 1.01065   | 0.11042 | 183.668    |
| 12 ..... | 1.03371   | 0.11226 | 185.657    |
|          | H = 1.008 | O = 16  | Na = 23.05 |

The results are not recorded in the order in which they were obtained. Those from one to seven inclusive are grouped together as indicating those which are most concordant, and consequently believed to most nearly approach the true atomic mass.

The marked discrepancies appear to have been incident to the difficulty of obtaining a uniform temperature in all parts of the air-bath. It was thought that a slight error might have been introduced by the presence of hygroscopic moisture in the air-dried salt. Upon allowing a portion to remain in a desiccator over calcium chloride for some hours, no appreciable loss in weight was observed.

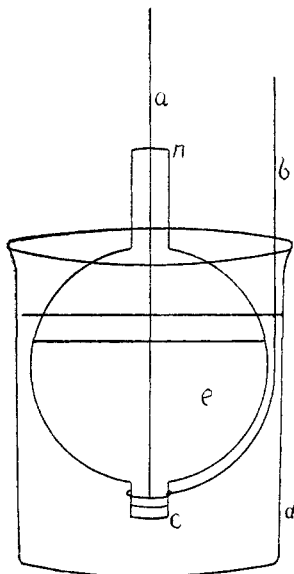
The great difference between the molecular weight of water and the atomic mass of tungsten causes the slightest errors of analysis to seriously affect the results; which, in addition to the danger of volatilizing a portion of the material, appears to

render the method unsuited for the determination of the atomic mass of tungsten.

## II. SODIUM PERTUNGSTATE.

When sodium tungstate was electrolyzed in a platinum crucible, and the solution subsequently acidulated with hydrochloric acid, a gas was evolved which liberated iodine from a solution of potassium iodide. To further the investigation of this phenomenon, an apparatus was constructed to facilitate more complete oxidation, as this was believed to be the cause of the reaction observed upon the addition of the acid.

The figure represents the apparatus, one half actual size. The outer vessel, *d*, is a beaker glass; the inner compartment consists of a bulb with two openings, the lower aperture being covered with parchment, which is employed to prevent the solution of



sodium tungstate from flowing into the beaker, *d*. By placing the finger over the opening, *n*, all of the solution subjected to the oxidizing action about the anode, *a*, may be separated without loss or contamination. The anode consists of platinum wire, while the cathode may be platinum, nickel, or iron, as it is not corroded.

E. Pechard<sup>1</sup> describes the preparation of a new oxygen compound of tungsten by the boiling of paratungstate of sodium with hydrogen peroxide, the solution acquiring, during the operation, a yellowish tint and yielding no precipitate upon the addition of nitric acid; the crystals obtained, to which he ascribed the formula  $\text{Na}_2\text{O} \cdot \text{W}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , liberated chlorine from hydrochloric acid and iodine from potassium iodide. Experiments were first made with solutions containing an excess of alkali; but as acid solutions are more favorable to oxidation, varying quantities of acid were subsequently added to the solution of the sodium tungstate.

After numerous experiments extending over a long period, the best results were attained by employing a current which showed before the introduction of the electrolyte into the circuit, an amperage of one and four-tenths, and a voltage of 107. The electrolyte consisted of a solution of fifteen grams of sodium tungstate dissolved in fifty cc. water and one-half cc. acetic acid (twenty-five per cent.), a corresponding quantity of acid being added to the water in the beaker to facilitate the conduction, and a further addition of one-quarter cc. acetic acid, after four hours' contact, to the contents of the bulb.

During the operation much heat is generated, due to the resistance offered by the electrolyte; and the solution in the bulb as the salt approaches the para condition, caused by the alkali permeating the membrane and collecting about the cathode, acquires a yellow color. After six hours' treatment it will yield no precipitate upon the addition of nitric acid. The solution should then be removed from the bulb, as prolonged contact with the current will affect a complete decomposition with a subsequent separation of tungstic acid. The solution after this treatment is acid in reaction.

The yellow solution when evaporated on a water-bath below  $100^\circ \text{C}$ . becomes sirupy, retains its yellow color, possesses a very high specific gravity, and when allowed to crystallize, yields yellowish-white crystals. These were thought from their appearance and their reactions, namely, the liberation of chlorine from hydrochloric acid and ozone upon the addition of sulphuric and nitric acids, to be perfectly pure sodium pertungstate; but upon

<sup>1</sup> *Compt. rend.*, 112, 1060-1062.

making determinations of oxygen in different samples, by the use of Bunsen's apparatus, collecting the chlorine liberated by boiling with hydrochloric acid, in a solution of potassium iodide, and titrating with a standardized solution of sodium hyposulphite, it was found that less than four-tenths of a per cent. of oxygen was present.

The work of Pechard indicated the presence of 2.82 per cent. to 2.93 per cent. of oxygen. These experiments gave positive proof that the oxidation in the diaphragm cell was not complete, due in all probability to the short interval that the current could act while the salt was in the para condition, as the composition of the contents of the inner bulb is constantly changing. Fractional crystallization was not applicable, owing to the readiness with which the oxygen compound and the other sodium tungstates dissolve in water. Attempts were made to affect its solution in various solvents; but chloroform, benzene, carbon disulphide, ether, and ethyl alcohol were without action. It was found that a ninety per cent. solution of methyl alcohol would dissolve the sodium pertungstate, but a portion of the contaminating salt was also soluble; however, this was largely eliminated.

Upon subsequent crystallization over calcium chloride, the yellow crystals liberated ozone while in the desiccator, indicating a partial decomposition; and upon experimenting, it was found that the method was inoperative as a means of separation. The possible oxidation of the alcohol would also render this treatment unsatisfactory. Before this knowledge was acquired attempts were made to prepare other pertungstates by double decomposition with salts of the metal; this, however, was abandoned after the impurities were discovered, and the efforts for their removal proved unsuccessful. After this work was completed an experiment was made using a more concentrated solution, and subjecting it to the action of a current of less intensity at a temperature below 20° C. Large quantities of ozone were evolved, and the solution, after subjecting it to the action of hydrochloric acid, only gave a faint test for chlorine, indicating that a higher temperature in this instance is more favorable to oxidation.

It may be noted that the oxygen in this compound is present



as ozone, for upon ignition of the salt a gas was evolved which liberated iodine from potassium iodide. Hence, there is no doubt whatever that pertungstate of sodium was formed, and although the isolation of this substance was not accomplished, the preparation of the compound by this method is of great importance, as it shows an additional analogy to exist between tungsten and sulphur, the second member of this group.

While pursuing this work, a modification of this process suggested itself as an admirable means of preparing meta- or paratungstate of potassium or sodium. The only change necessary for the accomplishment of this result appears to be the elimination of the acid, and the use of a graduated beaker for the outer vessel. A definite quantity of the normal salt is introduced into the bulb. The diaphragm prevents the contamination of the outer liquid with sodium tungstate, as it was found that it did not permeate the membrane. Definite portions of the solution of the alkali may be removed from time to time, and titrated with normal acid until the requisite amount of alkali has been separated. The ozone present may be removed by heating from 200° to 400°. The crystals are dissolved and transformed into barium meta- or paratungstate by the addition of barium chloride.

The accuracy of this theory will be determined in the near future. From a theoretical standpoint, it appears to be better suited for the preparation of the salts mentioned than the methods now employed.

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### OBSERVATIONS ON DERIVATIVES OF ACONITIC ACID.

BY D. C. HANNA AND EDGAR F. SMITH.

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#### I. ACTION OF PHOSPHORUS TRISULPHIDE UPON ACONITIC ACID.

**A** CONITIC acid was prepared by the method of Hentschel.<sup>1</sup> One hundred and sixty-eight grams of it were then converted into the sodium salt, and portions of forty grams of this salt and eighty grams of phosphorus sulphide were intimately

<sup>1</sup> *J. prakt. Chem.* [2], 35, 205.