

N.D. <sub>100</sub> .....	0.017 amperes.
Voltage.....	2.45.
Dilution.....	175 cc.
Temperature.....	61° C.
Time .....	5½ hours.

The deposit weighed 0.2370 gram. It was heavier, therefore, than the combined weights of the mercury and uranium. A second trial was made after increasing the volume of phosphoric acid to fifteen cc. The deposit weighed 0.2012 gram. It had a dull lead color. It was strongly ignited to expel the mercury. The scaly residue was boiled with dilute nitric acid and the solution tested with ammonium molybdate. Large amounts of phosphorus were indicated. This would prove that the original deposits of metallic mercury so influenced the uranium salts that they were coprecipitated with that metal. Whatever the composition of the deposit may be it is certainly very variable. It is quite probable that a hydrous uranium phosphate is deposited with the mercury. The filtrates were all free from uranium.

On trying to effect the separation of copper from uranium in acid phosphate solution we experienced the same difficulty as with mercury and uranium. The precipitate consisted of copper, uranium, and phosphorus. The filtrate showed no signs of either copper or uranium. The separation of mercury and manganese was far from satisfactory. The same must be said of nickel and cobalt. They were partially precipitated with the mercury and carried down phosphorus with them. A qualitative test was made to separate uranium in the presence of mercury and phosphoric acid, electrolytically from iron. The deposit contained no iron when a current of  $N.D._{100} = 0.006$  ampere was employed. This separation will receive further study in the immediate future.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 50.]

### OBSERVATIONS UPON TUNGSTEN.

By EDGAR F. SMITH.

Received August 5, 1899.

**T**HIS communication presents fragmentary data upon tungsten collected during a period of years and amply verified by repeated reviews. As tungsten in its various combinations has been an object of great interest to the writer, particularly

the question as to its atomic mass, it need not surprise the reader to find that recourse has been had to so many diverse derivatives in the search for some body which would possess a constitution and properties suitable for an investigation of the problem. In the course of the study numerous observations were made which are not wholly devoid of interest and which are now incorporated in the following paragraphs. The solubility of tungsten trioxide and its derivatives in sulphur chloride deserves consideration; as do the facts that the third oxygen atom defies removal in this way and that pure sulphur chloride does not attack metallic tungsten, hereby enabling us to eliminate the final traces of oxides. The great volatility of the trioxide, on exposure to heat, condemns the ignition of metal in air as a means of deriving the atomic mass. Then, too, the establishment of a crystalline oxide is of some moment. Why the alkyl derivatives failed to appear is difficult to understand. If they could be prepared they would, doubtless, afford a splendid means of determining the atomic mass. Perhaps in the near future we shall find some method of making them. However, it is possible that the more metallic nature of tungsten will prohibit the formation of stable alkyls as seems obvious with the esters of tungstic acid.

For the experimental part of the work the writer is indebted to the several gentlemen whose names are given in the proper places and would here return them his sincere thanks for their kind and indispensable assistance.

## I. THE ACTION OF SULPHUR MONOCHLORIDE UPON TUNGSTEN TRIOXIDE.

BY HERMANN FLECK.

Attention has been directed to the action of sulphur monochloride upon various natural sulphides and oxides.<sup>1</sup> The purpose, primarily, of my study was to ascertain the nature of the body produced when tungsten trioxide, or any of its naturally occurring combinations, *e. g.*, wolframite or scheelite, were heated together with sulphur monochloride to 145° C. On cooling scarlet-red, prismatic needles, one of which measured two and one-half inches, crystallized from the red solution. On exposure to the air they immediately decomposed, evolving hydrochloric

<sup>1</sup> This Journal, 20, 289.

acid, and changing to tungsten trioxide. They dissolved freely in carbon disulphide and sulphur monochloride, but sparingly in benzene. The first crops were impure and gave very unsatisfactory analytical results. To eliminate a yellow powdery substance, admixed with the crystals, the following course was pursued: a tube containing the scarlet crystals, yellow powder, and mother-liquor from which the pressure had been released, was resealed and placed in an upright position in a tall beaker containing boiling water. The sulphur chloride became blood-red in color due to the dissolved crystals. The tube was now carefully inclined and the liquid drained away from the heavy yellow substance into the other end of the tube. The solution cooled instantly and a nest of beautiful crystals separated from it. This procedure was repeated until a complete separation of the two bodies had been achieved. Having finally removed the scarlet crystals from the tube they were further purified by sublimation and recrystallization from suitable solvents. With proper care and exclusion of moisture both courses yielded satisfactory results.

In the sublimation process five to ten grams of the crystals were placed in a wider tube with a three-holed stopper, carrying an inlet and exit tube as usual and a thermometer. The apparatus was filled with perfectly dry carbon dioxide and heat applied. First a ring of condensed mother-liquor made its appearance. The red crystals became dark in color and began to boil at  $215^{\circ}$ . The volatilization was complete at  $225^{\circ}$ . By careful fractional sublimation into bulbs filled with carbon dioxide magnificent scarlet crystals were obtained. These were analyzed. They showed the presence of 53.53 per cent., 53.59 per cent. and 53.94 per cent. of tungsten with 40.99 per cent. of chlorine; no sulphur was found. The oxychloride of tungsten ( $\text{WOCl}_4$ ) required 53.94 per cent. of tungsten and 41.38 per cent. of chlorine.

The product of the interaction of sulphur monochloride and tungsten trioxide is, therefore, tungsten oxytetrachloride— $\text{WOCl}_4$ . Again, a large mass of crystals after removal from the tube was quickly pressed between paper and recrystallized from small quantities of sulphur chloride with which it was boiled and subsequently allowed to cool in an Erlenmeyer flask. After

being freed in this way from the mother-liquor containing sulphur, they were washed with carbon disulphide previously dehydrated by standing over sodium wire. The adhering carbon disulphide was expelled in a current of dry carbon dioxide and the flask was then tightly stoppered. The flask and contents were weighed and a portion of the material removed, after which the flask was reweighed. The quantity of substance for analysis was thus found by difference. The analysis showed the presence of 35.51 per cent. of tungsten and 39.5 per cent. of chlorine. When it is considered that over seven grams of material were used in the estimation of the tungsten, eleven grams for the chlorine and even a larger quantity for the sulphur, the results will not fail to win favor. That the chlorine content is low is not astonishing if we recall how tenaciously moist tungsten trioxide retains hydrochloric and sulphuric acids.

These analytical results and the boiling-point of the scarlet crystals, establish their identity as tungsten oxychloride.

Tungsten dioxide was also changed to the same body on heating it with sulphur monochloride. Even when the oxides were exposed with the sulphur chloride to temperatures as high as  $240^{\circ}$ , the third oxygen atom was not displaced. Tungsten hexachloride and tungsten dioxychloride were never observed.

The action of sulphur chloride upon tungsten metal was also tried. The result of this study showed that pure sulphur chloride, free from chlorine, has no action upon the metal, but when that gas is present in sufficient quantity the metal can be completely changed to the hexachloride, crystallizing in steel-blue needles and forming dark red vapors. With an insufficiency of chlorine, black crystals are produced. These were found to be hexachloride contaminated with metallic tungsten.

Finely divided wolframite and scheelite, as already noted, are also soluble in sulphur monochloride. It may be added that this method affords an excellent means of preparing the red oxychloride. Indeed, it seems to be a superior method in every way for that purpose.

I shall now return to an observation noted in the first section of this communication; *viz.*, that tungsten trioxide used in atomic mass work did not entirely dissolve in sulphur chloride when heated to  $145^{\circ}$  C. Further, it was always necessary to free the

oxychloride from adherent trioxide. Why, if this be pure oxide of tungsten, does it not dissolve completely? Can it be that this insoluble part is the impurity in the oxide which affects the atomic mass? Is it perhaps a nitride, or oxynitride, or some allotropic modification of the trioxide? These questions suggested themselves from time to time and efforts were made to answer them. How this was done will appear in the following paragraphs:

1. Two grams of tungsten trioxide, made from ammonium tungstate, were heated to  $145^{\circ}$  with sulphur monochloride. On cooling the red crystals separated from the solution, leaving, however, much unattacked original material. The crystals were roughly separated from the deposit, pressed between folds of filter-paper, and then allowed to decompose in the air. They were moistened, ignited to the trioxide and reheated in a sealed tube with sulphur monochloride. This trioxide disappeared almost entirely at  $140^{\circ}$ - $170^{\circ}$ , yielding the red crystals as before. The portion remaining unattacked was washed with carbon disulphide, dried, and ignited. It weighed six-tenths gram. When reheated with sulphur monochloride at  $140^{\circ}$ - $170^{\circ}$  it did not dissolve. Larger quantities of ignited tungsten trioxide were treated in this way and thus separated into two distinct parts, each of which was exposed to the action of sulphur chloride until it ceased to dissolve any more. From  $150^{\circ}$ - $180^{\circ}$  there was no further action on the insoluble portion. This point is also indicated by the sulphur chloride no longer assuming a red color due to the oxychloride which it may contain. The oxide from the red crystals, when decomposed and ignited, left a portion of substance insoluble in sulphur monochloride. Could it be that in the ignition of this oxide there was something abstracted from the air that rendered it insoluble in sulphur monochloride? If this were true then it could be readily understood why the oxide prepared by the ignition of ammonium tungstate was so largely insoluble in the sulphur chloride. It would also account for some of the discrepancies noticed in the atomic mass determinations.

2. To demonstrate that the trioxide changes either to an allotropic modification or to some other body, by ignition in air, a sample of it was made by heating moistened oxychloride as gen-

tly as possible. It was then divided into two equal portions (*a* and *b*) of one gram each in weight.

*a* was placed directly into a tube with  $S_2Cl_2$  and heated for eight hours from  $150^\circ$ - $170^\circ$ .

*b* was *not* placed directly into a tube but was heated alone for eight hours in air at a high temperature and then exposed for eight hours to the action of sulphur chloride at  $150^\circ$ - $170^\circ$ .

The contents of *a* were completely dissolved, whereas those of *b* were unattacked. The question remained—what is this insoluble substance?

3. All the material which had previously proved insoluble in sulphur chloride was now collected and heated with this reagent in sealed tubes to  $250^\circ$ . *Its solution was complete.*

4. Possibly the insoluble compound represented an oxynitride. I thought this might be ascertained by analyzing the air in which the trioxide was ignited or by proving the presence of nitrogen in the insoluble material.

5. To demonstrate the falsity or correctness of the idea of an oxynitride having been produced, a portion of tungsten trioxide, soluble in sulphur chloride, was placed in a porcelain tube between two asbestos plugs. At one side was attached a reservoir, consisting of a wide tube, connected by rubber tubing to a second tube of about the same capacity. A regular Hempel burette and leveling tube were joined to the opposite end of the porcelain tube. Mercury was filled into the tubes and a definite volume of air into the burette, the oxygen of which had been accurately determined in another portion of it. Heat was applied to the tube and the air was passed back and forth over the trioxide by raising and lowering the leveling tubes alternately on both sides of the combustion tube. The heating process continued for three hours. After cooling the volume of air had not diminished. Neither nitrogen nor oxygen had been absorbed. *The oxide was not soluble in sulphur chloride.*

6. A portion of the "insoluble" material was placed in a hard glass tube and heated in an air current, which then passed into water, but no reaction for either nitric or nitrous acid was observed.

7. A tube of hard glass, sealed at one end and containing stick caustic potash, was attached to a vacuum pump and heated.

When it had melted and the gas particles enclosed in it had escaped, the tube was cooled and after the introduction of from ten to fifteen grams of the "insoluble" trioxide it was carefully exhausted and sealed. Its contents were heated, when the "insoluble" oxide dissolved. Any nitrogen that might have been present would have been expelled as such or in the form of ammonia. On opening the tube under mercury the latter filled it completely. Gases were not present.

## II. TUNGSTEN ALKYL.

BY E. A. BARNETT.

Riche<sup>1</sup> claims that when he heated metallic tungsten with methyl iodide to 240° in a sealed tube for ten days he obtained a product that upon distillation yielded unaltered methyl iodide and a viscous liquid. The latter only distilled at high temperatures. When it was shaken with a little warm ether-alcohol an oily substance separated, while the ethereal solution contained a compound melting at 110° and crystallizing in colorless plates. To this body he ascribed the formula  $W(CH_3)_3I$ . Cahours,<sup>2</sup> believing that the saturation power of W was  $WX_3$ , repeated the work and obtained the same body. I endeavored to prepare it with the purpose of making other alkyl derivatives in order to use the same in the redetermination of the atomic mass of tungsten. I heated one part of tungsten with four parts of methyl iodide for ten days to 240°. On opening the tubes a sharp, acid, unpleasant odor was noticed. The contents of the tubes were distilled out in a steam-bath. The distillate boiling at 42° proved to be methyl iodide. What remained in the tube was treated with ether-alcohol and filtered. The ether-alcohol solution was allowed to evaporate spontaneously; a greenish black mass remained but colorless crystals were not discernible. The residue was extracted with chloroform and this solution placed aside to crystallize. After standing awhile, plate-like forms appeared. These disclosed the presence of iodine upon applying the test. They also contained tungsten. Thus, 0.2765 gram of material yielded 0.2604 or 93.45 per cent. of tungsten. Two other determinations made with more care gave 94.38 per cent. and 94.31 per cent. of tungsten, respectively. Concentrated nitric acid,

<sup>1</sup> *Jsb. d. Chem.*, p. 373 (1856); *Compt. rend.*, 42, 203 (1856); *J. prakt. Chem.*, 69, 10.

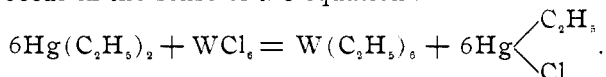
<sup>2</sup> *Ann. Chem. (Liebig)*, 122, 70.

acting on the compound, liberated iodine vapors. The same was observed when heat was applied to the compound. Two determinations of the iodine content were made showing the presence of 1.18 per cent. and 1.58 per cent., respectively.

To ascertain whether the compound contained carbon, portions of it were carefully burnt in an air current, the gases being conducted into lime-water. A precipitate of calcium carbonate was produced. It was filtered out, and from its lime content the corresponding percentage of carbon was calculated. In this way were found 1.99 per cent. and 2.01 per cent. of carbon, respectively.

These results do not indicate a tungsten alkyl, but rather finely divided metal with carbon and adherent methyl iodide.

Tungsten hexachloride and mercury ethide were allowed to interact in ligroin solution. A dark blue mass resulted; this on standing became purplish black in color. I hoped that a change might occur in the sense of the equation :



The reaction product was transferred to a filter and washed with cold ligroin, after which it was introduced into a Soxhlet apparatus and extracted with benzene for three hours. Its color was dark blue or purple. This was dried over sulphuric acid and analyzed :

	Tungsten. Per cent.	Chlorine. Per cent.
Found (in <i>a</i> ) .....	46.33	9.55
" (in <i>b</i> ) .....	46.27	9.21

Carbon was not present. Analyses of other portions revealed the presence of varying amounts of mercury and chlorine.

It is safe to conclude that an alkyl derivative of tungsten cannot be produced in this way. Indeed, I cannot help but doubt the existence of these bodies, for my experiments are not all which have been tried in this laboratory and which have resulted negatively. As little success has been had with molybdenum along similar lines.

### III. TUNGSTEN ALKYL.

BY CLARENCE HALL.

It was my aim to prepare the alkyls of tungsten by the use of



zinc methide and a tungsten chloride. To this end I placed a bulb, containing three and seven-tenths grams of zinc methide, and another containing three and two-tenths grams of tungsten hexachloride in a glass tube sealed at the one end, while its other end was drawn out and through this contracted tube was passed a much smaller tube conveying dry nitrogen. This gas was allowed to pass for more than half an hour through the tube, after which the latter was sealed. By shaking it, the bulbs containing the zinc methide and tungsten hexachloride were broken. When their contents came together heat and light were produced and a black substance separated. After this the tube was heated for a period of six hours at a temperature of  $70^{\circ}$ . A decided pressure was noticed when the tube was opened. The tube contents were treated with ether and the solution examined for tungsten compounds. They were not found present. The residue showed the presence, on analysis, of tungsten, zinc, carbon, and hydrogen. The ratio of these constituents was indefinite. A second trial resulted similarly, so that I gave up all hope of preparing the alkyl body in this manner.

Thinking that possibly in the direct action of the alkylogens upon tungsten metal the character of the latter influenced the reaction, I concluded to act:

1. With methyl iodide upon tungsten obtained by passing sodium vapors in an atmosphere of hydrogen over gently ignited tungsten trioxide. The tube contents after exposure to  $200^{\circ}$  for from eight to ten days were treated and examined as indicated by Riche. The residue, on analysis, showed 1.71 per cent. of carbon, 91.33 per cent. of tungsten, 1.5 per cent. of iodine, and 0.34 per cent. of hydrogen.

2. The metal in this series of experiments was prepared by fusing tungsten hexachloride with metallic sodium. The resulting product was extracted with water and the tungsten was then further purified by alcohol and carefully dried. It was heated as before with methyl iodide. In this instance the alcohol-ether layer on evaporation left a white scaly substance which melted at  $115^{\circ}$ . It revealed the presence, on testing, of iodine, tungsten, and carbon. Had I really found Riche's compound? This I firmly believed until other experiments made in this lab-

oratory proved that this substance was nothing more than sodium iodide mixed with some ethereal tungsten body.

#### IV. ESTERS OF TUNGSTIC ACID.

BY CLAUDE DUGAN.

Several chemists have recorded their experiences in preparing these compounds. Göessmann<sup>1</sup> endeavored to form them by allowing alkyl iodides to act upon silver tungstate, but was unsuccessful. Subsequently, Maly<sup>2</sup> obtained through the action of ethyl alcohol upon tungsten oxychloride ( $WOCl_4$ ) a white flocculent precipitate, which after washing with alcohol was allowed to dry in the air and later over sulphuric acid, when it became a hard, brittle vitreous mass. A single analysis of it gave 85.16 per cent. of tungsten, 5 per cent. of carbon, and 1.64 per cent. of hydrogen, pointing, in the judgment of Maly, to an ester of metatungstic acid,  $W_2O_6.H.C_2H_5 + H_2O$ .

I repeated this experiment, obtaining a body which revealed the presence of 79.6 per cent. of tungsten, 1.06 per cent. of carbon, and 0.84 per cent. of hydrogen.

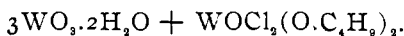
Not doubting in the least the observation of Maly, but thinking probably that the reaction or transposition was not as simple as might be inferred upon reading his paper and that by the action of the hydrochloric acid, evolved in the change, upon the unconsumed alcohol present, water would be produced and this in turn would form varying amounts of tungstic acid which naturally would contaminate the resulting ester, I studied the action of other alcohols in a pure and dry state upon beautifully crystallized and purified tungsten oxychloride.

First, let me present my experience with isobutyl alcohol in the line indicated. When it and the oxychloride were brought together much heat was evolved; a yellow precipitate separated after standing. The filtrate from this was distilled under reduced pressure, when a white starchy mass appeared. This was dried over phosphorus pentoxide and soda-lime. When nearly dry it was dissolved in anhydrous ether. To the ethereal solution pure anhydrous ethyl alcohol was added with the production of a gelatinous white precipitate which was collected and carefully handled until dry and ready for analysis. It was

<sup>1</sup> *Ann. Chem.* (Liebig), 101, 218.

<sup>2</sup> *Ibid.*, 139, 240.

a very brittle powder and contained 7.4 per cent. of carbon, 1.60 per cent. of hydrogen, 65.00 per cent. of tungsten, and 5.76 per cent. of chlorine, which closely approximate the requirements of a compound of the formula



In other words the transposition between the oxychloride and the alcohol was not complete and to the new product there was added hydrated tungstic acid. Whether it is possible to effect a complete transformation and whether the ester can be isolated without contamination with tungstic acid, appears to me rather doubtful. I am led to this view because upon substituting other alcohols and proceeding in the manner of Maly, I invariably obtained products of complex character, containing tungsten, carbon, hydrogen and chlorine. Thus with propyl alcohol a product was isolated which showed the presence of 10.3 per cent. of carbon, 4 per cent. of hydrogen, 6.3 per cent. of tungsten and 5.32 per cent. of chlorine. With amyl alcohol the case was practically the same, and it seems evident that while esters of tungstic acid do perhaps exist they can only be isolated with extreme care and are surrounded by conditions which favor their ready and rapid breaking down. It must be admitted, however, that the tungstic acid in yielding these incomplete esters exhibits the character peculiar to the group in which it is placed by the periodic system and the instability of the desired and expected derivatives must be attributed to the absence of a sufficiently pronounced acid, or non-metallic, nature in the tungsten itself.

## V. THE ATOMIC MASS OF TUNGSTEN.

BY WILLETT L. HARDIN.

In an article published from this laboratory last year<sup>1</sup> it was demonstrated that the method usually employed in the determination of the atomic mass of tungsten is unsatisfactory. The results given in that paper were obtained by the reduction of tungsten trioxide in a current of hydrogen at a white heat, and the subsequent oxidation of the metal in air. Like the determinations of earlier experimenters, these results showed considerable variation; the maximum and minimum values for the atomic

<sup>1</sup> This Journal, 19, 657.

mass of tungsten differed as much as one and a half units. Some of the probable causes of these deviations were also discussed and certain sources of error pointed out.

It was proved, for example, that tungsten trioxide obtained from ammonium tungstate contains nitrogen; that the oxide of tungsten is slightly volatile or that a small portion is carried out mechanically by the water formed in the reduction; and also, that tungsten attacks the vessels in which the atomic mass determinations have been made.

The following experiments were undertaken in the hope of gathering further evidence as to the cause of these variations, and with a view of arriving at a more satisfactory conclusion in regard to the true atomic mass of tungsten.

Tungsten trioxide resulting from experiments made last year was heated to 145° in sulphur monochloride in a sealed tube. About 75 per cent. of the oxide was taken up by the sulphur chloride. When the solution cooled, red crystals separated; these were removed from the unattacked material and after washing with carbon bisulphide were ignited in a current of oxygen, and the oxide thus prepared was reduced in hydrogen.

	Tungsten trioxide. Grams.	Tungsten. Grams.	Atomic mass of tungsten.
1.....	2.42690	1.90610	175.68
2.....	1.62225	1.28195	180.80

The metal from these reductions was reoxidized:

Tungsten. Grams.	Tungsten trioxide. Grams.	Atomic mass of tungsten.
1.24369	1.56691	184.69

On reducing this oxide, the value 183.75 was obtained for the atomic mass of tungsten.

From these experiments it is obvious that the material produced by the ignition of the red crystals is not pure tungsten trioxide. A portion of it was reduced in hydrogen and the volatile products conducted through a solution of copper sulphate. A black precipitate of copper sulphide was thrown down, showing that the substance retained sulphur, even after it had been ignited in a current of oxygen.

When the metal from the red crystals was oxidized and the

product heated in sulphur monochloride in a sealed tube at a temperature of  $145^{\circ}$ , only a portion of it was taken up. This insoluble portion was supposed, at first, to contain nitrogen. A series of observations were made to decide this point.

The first experiment consisted in oxidizing the metal obtained from the red crystals in an atmosphere of commercial oxygen. This was carried out in an asbestos cell, the interior of which was covered with plaster of Paris. The crucible containing the metal was placed in an opening in the bottom of the cell, and a current of oxygen was introduced through a small glass tube which passed through the cover. This arrangement was used for a number of experiments but was unsatisfactory owing to the rapidity with which metallic tungsten oxidizes in an atmosphere of oxygen. The gas was taken up more rapidly than it could be supplied and consequently air passed into the cell around the sides of the crucible. In a second device the metal was oxidized in a combustion tube, the outlet of which was a long narrow tube, immersed at the lower end in mercury or sulphuric acid. This contrivance was very satisfactory in oxidizing the metal away from air.

The oxide obtained in this manner was more insoluble in sulphur monochloride than that obtained by the ignition of the metal in air.

The oxygen employed in these experiments, was then analyzed and found to contain six per cent. of nitrogen. An attempt was, therefore, made to obtain pure oxygen from potassium chlorate and manganese dioxide and from potassium chlorate alone. The gas was collected over recently-boiled distilled water. In every case the oxygen was found to contain about one per cent. of impurity, supposed to be nitrogen, but when tested was discovered to be carbon monoxide. The main object, however, was to get oxygen free from nitrogen; this was accomplished. Metallic tungsten was then oxidized in it, as already described, and the resulting oxide was found to be insoluble in sulphur monochloride at  $145^{\circ}$ .

The soluble and insoluble portions of oxide were next tested for nitrogen by reducing in hydrogen and conducting the resulting vapors into a dilute, standardized solution of hydrochloric acid. The strength of the acid was not perceptibly changed,

showing that not more than a trace of ammonia could have been formed.

The two portions of oxide were further tested for nitrogen by fusing with potassium hydroxide in a sealed glass tube which had been previously exhausted by means of a Geissler pump. The potassium hydroxide was fused before use and allowed to cool in a vacuum. After fusing the oxide with caustic potash, the contracted end of the tube was immersed in mercury and the tip broken off. The mercury completely filled the tube, showing that no gases had been set free in the reaction.

Atomic mass determinations were then made, using first the insoluble and afterward the soluble oxide. The trioxide, resulting from the ignition of the metal in air, was treated with sulphur monochloride at  $145^{\circ}$ . The insoluble portion was removed from the tube and reduced in a current of hydrogen. The resulting metal was oxidized in a current of oxygen and the following result obtained :

Tungsten. Grams.	Tungsten trioxide. Grams.	Atomic mass of tungsten.
2.68250	3.38144	184.20

The red crystals were then removed from the tube, heated in a current of oxygen and reduced in hydrogen. The resulting metal was oxidized as before :

Tungsten. Grams.	Tungsten trioxide. Grams.	Atomic mass of tungsten.
1.90428	2.40021	184.27

The two results are almost identical.

There appears then to be no difference in the composition of the soluble and insoluble oxides. The identity in their composition is also confirmed by the fact that one form can be converted into the other and *vice versa*. If the insoluble portion is converted into ammonium tungstate, the oxide resulting from the ignition of this salt is soluble in sulphur monochloride at  $145^{\circ}$ . When the metal obtained from the red crystals is oxidized in a current of oxygen, the resulting oxide is insoluble in sulphur chloride at  $145^{\circ}$ .

From these observations it seems that tungsten trioxide exists in two forms. To decide this point portions of the oxide were obtained by different methods, and carefully examined. One

portion of the material resulted from the oxidation of metallic tungsten in pure oxygen under a slightly increased pressure. An extremely high temperature was obtained by this procedure. Most of the oxide fused together in an opaque crystalline mass in the bottom of the boat, while a portion of it sublimed in beautiful, shining crystals on the sides of the boat. The fused mass seemed to be striated, indicating a prismatic structure. The sublimed crystals, however, appeared to be of a tetrahedral form. By strongly heating metallic tungsten in the air, Bernoulli<sup>1</sup> and Schafavik<sup>2</sup> obtained microscopic crystals of tungsten trioxide. By fusing the oxide with borax Nordenskjöld<sup>3</sup> also obtained small crystals. This is sufficient evidence to show that tungsten trioxide exists in two forms, the amorphous and crystalline. The latter form is produced from the former at high temperatures.

A sample of the oxide was then prepared by the ignition of ammonium tungstate in air, and another portion by the ignition of metallic tungsten in air. A series of specific gravity determinations were made, using these various samples of oxide. The results were as follows :

## SPECIFIC GRAVITY OF TUNGSTEN TRIOXIDE.

Fused mass .....	7.502
Sublimed crystals .....	7.301
From ignition of tungsten in air .....	7.272
From ammonium tungstate.....	5.804
“ “ “ .....	5.705
“ “ “ (after high heating) .....	6.391
“ “ “ ( “ “ “ ).....	6.820

These results leave no doubt as to the existence of two forms of tungsten trioxide. The specific gravity determinations of earlier experimenters point to the same conclusion :

Hera path.....	5.274
d' Elhujar .....	6.120
Karsten .....	7.130
Nordenskjöld .....	6.30-6.38
Zettnow.....	7.16-7.23

<sup>1</sup> Pogg. *Ann.*, III, 595.

<sup>2</sup> Sitzungsber. d. Akad. d. Wissenschaften in Wien.

<sup>3</sup> Pogg. *Ann.*, III, 246.

The determinations of Nordenskjöld were made with crystals obtained by fusing tungsten trioxide with borax. Under suitable conditions then, it seems that the yellow oxide of tungsten polymerizes.

DETERMINATION OF THE ATOMIC MASS OF TUNGSTEN BY THE  
OXIDATION OF THE METAL IN PURE OXYGEN.

After obtaining oxygen free from nitrogen, it was thought advisable to make use of this gas instead of air, in determining the atomic mass of tungsten by the oxidation method. The metallic tungsten was oxidized in a porcelain boat in a combustion tube. It was noticed in each experiment that a white sublimate was formed in the glass tube. The values obtained varied from 184.1 to 184.8. These results are of little value owing to the volatilization of the material.

An attempt was made to eliminate the error due to the volatilization of the oxide, by placing the boat containing the material in a glass tube, about twenty cm. in length, which had been drawn out to a small opening at one end. This tube together with the boat and contents was carefully weighed and placed in a larger combustion tube in which the oxidation was carried out. A sublimate was formed inside the smaller tube, and also on the walls of the combustion tube near the ends of the weighed tube. The results from these experiments are of no more value than those obtained without the use of the second tube.

A series of observations was next made to determine the amount of volatilization in the oxidation of a definite quantity of metallic tungsten. The same material was oxidized and reduced a number of times without being removed from the porcelain boat. The amount of volatilized oxide was not constant. The following results were obtained :

	Grams.
Weight of $WO_3$ at the beginning of the experiment..	2.36815
“ “ “ after one reduction and reoxidation..	2.36780
“ “ “ “ two reductions and reoxidations	2.36560
“ “ “ “ three “ “ “	2.36430
“ “ “ “ four “ “ “	2.36401

Pure oxygen was used in these experiments. A sublimate was formed, however, when the metal was oxidized in air.

From these trials it is evident that no reliable atomic mass



determinations can be made by the oxidation of metallic tungsten either in air or in pure oxygen. The volatilization of substance would increase the values obtained for the atomic mass. No doubt this will explain why the results obtained by the oxidation method are, in general, higher than those obtained by the reduction method.<sup>1</sup>

#### OCCCLUSION OF HYDROGEN BY METALLIC TUNGSTEN.

The occlusion of hydrogen by metallic tungsten has been suggested by some chemists as a probable source of error in the determination of the atomic mass of this element by the reduction and oxidation methods. Waddell<sup>2</sup> claims that no such occlusion occurs. Derenbach,<sup>3</sup> on the other hand, says that an appreciable quantity of hydrogen is retained by the finely divided metal. In the observations on the atomic mass of tungsten which were published from this laboratory last year, attention was called to the fact that the results obtained were the same whether the metal was cooled in an atmosphere of hydrogen or in a vacuum. In order to definitely settle this question the following experiments were made :

Metallic tungsten which had been allowed to cool in an atmosphere of hydrogen was oxidized in a current of carefully dried oxygen. The vapors resulting from the oxidation were conducted through a U-tube filled with glass wool and phosphorus pentoxide. The results of three experiments are as follows :

	Tungsten. Grams.	Water obtained. Gram.
1 .....	2.5	0.00005
2 .. .....	2.8	0.00070
3 .....	3.0	0.00070

The quantity of hydrogen converted into water in these experiments is inappreciable in quantitative determinations.

In a second series of observations metallic tungsten was oxidized in a current of oxygen and the volatile products were collected over mercury, where they were carefully tested for hydrogen. The results were wholly negative. This precaution was taken owing to the fact that only a minute quantity of hydrogen was converted into water during the oxidation.

<sup>1</sup> See Pennington and Smith: *Ztschr. anorg. Chem.*, (1895).

<sup>2</sup> *Am. Chem. J.*, 8, 280 (1886).

<sup>3</sup> Thesis, Würzburg (1892).

From these and earlier experiments it is evident that no appreciable error in atomic mass determinations is introduced by the occlusion of hydrogen by the metallic tungsten.

#### EXPERIMENTS ON TUNGSTEN OXYCHLORIDE ( $WOCl_4$ ).

The red crystals, resulting upon heating tungsten trioxide with sulphur monochloride in a sealed tube, were found to be the oxychloride. An attempt was made to determine the atomic mass of tungsten from analyses of this compound. The substance was removed from the sealed tube into a larger combustion tube, filled with carbon dioxide. It was then sublimed, in a current of carbon dioxide, into small glass bulbs which were afterward sealed off. The analysis was carried out in the following manner :

One of the bulbs containing a portion of the sublimed material was carefully weighed. The tip was then broken off and the bulb quickly introduced into a glass-stoppered distilling flask containing strong nitric acid. When the acid was heated the chlorine content of the crystals was changed to oxychlorides of nitrogen and free chlorine. These gases were expelled from the flask and collected over an aqueous solution of silver nitrate, previously saturated with silver chloride. The solution was contained in a long-necked, inverted flask. The vapors were allowed to remain in contact with the liquid until the chlorine was completely changed to silver chloride. The quantity of silver chloride formed was determined in the usual manner, using a Gooch crucible. All the washings were made with water containing a little nitric acid and saturated with silver chloride. The tungstic acid, which remained in the flask, was ignited and weighed as the trioxide.

A large series of analyses were made but the results were too discordant to establish anything with certainty. Upon careful examination it was discovered that the red crystals, even after sublimation, contained varying quantities of sulphur as an impurity. It was also found that the tungstic acid in the distilling flask retained chlorine. Traces of the latter could be detected in the oxide after ignition. In view of these difficulties the method was given up as valueless for atomic mass determinations.

## PRECIPITATION OF SILVER BY MEANS OF METALLIC TUNGSTEN.

Smith<sup>1</sup> showed that silver could be precipitated as metal from an ammoniacal solution of the nitrate by means of metallic tungsten. The results proved that six atoms of silver were precipitated for each atom of tungsten added. Thinking that this method might prove of value in determining the atomic mass of tungsten quite a number of observations were made.

The silver used in the experiments was purified by the Stas method. The nitrate obtained from this metal was dissolved in pure water in a platinum dish; a slight excess of ammonium hydroxide was then added to the solution. Finely divided metallic tungsten was next added in sufficient quantity to precipitate about one-half of the silver present. The solution was digested for some time in the cold, and the quantity of silver, which had been precipitated, was then determined. Many of the results for the atomic mass of tungsten were close to the theoretical while others showed considerable variation. The quantity of ammonia in the solution was varied and experiments were made at different temperatures but the results were too variable to establish anything with certainty. The precipitated metallic silver was then carefully examined and found to contain small quantities of silver tungstate. Notwithstanding the presence of this substance, the results in many instances were close to the theoretical. The method, however, will not answer for atomic mass determinations.

## EXPERIMENTS ON BARIUM METATUNGSTATE.

By estimating the water of crystallization in barium metatungstate, Scheibler<sup>2</sup> endeavored to determine the atomic mass of tungsten. His results varied more than one unit. The values from the determinations of barium and tungsten were rejected by him. In reviewing the work on tungsten, it was thought advisable to repeat these experiments.

The material was prepared in a manner similar to that described by Scheibler; sodium metatungstate was formed by boiling a solution of the normal salt with tungstic acid. The salt, which was obtained with difficulty by this method, was recryst-

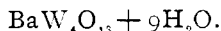
<sup>1</sup>*Ztschr. anorg. Chem.*, 1, 360 (1892).

<sup>2</sup>*J. prakt. Chem.*, 83, 324 (1861).

tallized. Pure barium chloride was prepared by recrystallizing the commercial C. P. salt several times. Sodium metatungstate and barium chloride were then dissolved in water, heated to boiling and mixed in equivalent quantities. A portion of the tungsten and barium came down as a white precipitate; this was filtered out and the solution allowed to cool. During the cooling more of the white precipitate separated, and in many cases the whole tungsten content changed to the insoluble barium salt. In some instances, however, only a portion of the substance sustained this change. It was filtered out, and on further evaporation of the solution, crystals of barium metatungstate separated. In some of the preparations, the sodium metatungstate was made by the action of the electric current on the normal sodium salt. This material was furnished by Dr. Geo. E. Thomas.

The water content of the crystals was determined by heating the powdered salt in a porcelain crucible for one hour at a dull red heat. The results were varied. The salt appeared to be slightly efflorescent. The values obtained for the atomic mass of tungsten are more discordant than those obtained by Scheibler, and hence are of no particular value.

After decomposing the salt with aqua regia, the barium was determined as sulphate and the tungsten as trioxide. These results also varied too greatly for atomic mass determinations; they, however, approximated the generally accepted formula,



THE MOST PROBABLE VALUE OF THE ATOMIC MASS OF  
TUNGSTEN.

It would appear that all of the preceding methods for the determination of the atomic mass of tungsten are unsatisfactory. So far as known, there is no perfectly reliable method for the determination of this constant. The method of reduction and oxidation is probably more accurate than any of the other methods which have been employed. The results obtained by it vary about one unit, and even more in exceptional cases. The high values published by some experimenters are undoubtedly due to the volatilization of oxide. The mean of all the determinations is approximately 184. Until a more accurate means

has been devised for determining the atomic mass of tungsten, it will perhaps be better to accept the result 184, as the most probable value of this constant.

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ON  $\beta$ -HEPTYLAMINE.<sup>1, 2</sup>

[FIRST PAPER.]

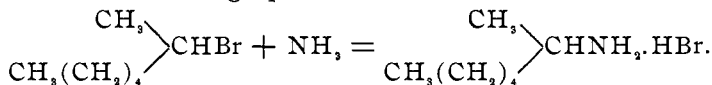
BY THOMAS CLARKE.

Received August 2, 1899.

ALTHOUGH  $\beta$ -heptylamine has been prepared by Cahours and Pelouse<sup>3</sup> and later by Schorlemmer,<sup>4</sup> the description of it was so meager, that it was considered worth while to study this base more thoroughly.

$\beta$ -Heptyl bromide, prepared according to the method of Venable<sup>5</sup> from heptane of the *Pinus sabiniana*, was heated in a sealed tube at 100° with an excess of an alcoholic solution of ammonia. The resulting products were primary  $\beta$ -heptylamine hydrobromide, ammonium bromide, heptylene, and unchanged  $\beta$ -heptyl bromide. There was no evidence of the formation of a base other than primary  $\beta$ -heptylamine, which accords with the observations of Jahn,<sup>6</sup> that by the action of ammonia on isopropyl iodide,  $\beta$ -hexyl iodide or  $\beta$ -octyl iodide, only amide bases are formed. The formation of unsaturated hydrocarbons of the series  $C_nH_{2n}$  was observed by Jahn,<sup>7</sup> in the action of ammonia on isopropyl iodide and  $\beta$ -hexyl iodide.

The results show that, similar to the examples cited from Jahn, two separate reactions take place in the action of ammonia on  $\beta$ -heptyl bromide. One is the condensation of the ammonia with the bromide to form the primary amine hydrobromide as shown in the following equation :



<sup>1</sup> I name those compounds which have the group or element characterizing them attached to the second carbon atom in the normal hydrocarbon chain,  $\beta$ -derivatives; thus  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHNH}_2\text{CH}_3$  is called  $\beta$ -heptylamine.

<sup>2</sup> Read at the Columbus meeting of the American Association for the Advancement of Science.

<sup>3</sup> *Jsb. d. Chem.* (1863), 528.

<sup>4</sup> *Ann. Chem.* (Liebig), 127, 318.

<sup>5</sup> *Ber. d. chem. Ges.*, 13, 1650.

<sup>6</sup> *Monatsh. Chem.*, 3, 165.

<sup>7</sup> *Ibid.*, 3, 166 and 170.