very long story short, the point I was trying to reach was to get a softer, tougher steel for rails than the steel maker wanted to make. The final answer to me was, "We cannot make a soft, tough steel as fast as we can make a hard or more brittle steel." Part of this result was due to mechanical characteristics, that is to say, the rolling of a harder, higher carbon steel is easier, since its melting-point is lower, and it softens more under heat. But, and the point I want to bring out is, the amount of the final additions, as they are called in the steel trade, that is of the spiegel and ferromanganese added at the end of the blow to remove the oxides that are formed, is considerably greater when you make a hard steel than when you make a soft steel. Now, I think it is perfectly clear that if you add to a bath of metal, after the blow is finished—which is in reality a substance containing a good deal of metallic iron and a good deal of oxide of iron—if you add say, in one case, 500 pounds of melted spiegel, and in another case 1000 pounds, the reaction will take place more rapidly in the second case. In reality therefore, the question of the speed of the reaction, which results in freeing the bath of metal from the oxide, is a very live and important question commercially, and I am only sorry to have to tell you that the steel people were a little stronger than I was, and consequently they are making steel about as they have a mind to, and getting out the oxide, we hope, but fear that they do not.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. No. 21.]

THE OXIDES OF TUNGSTEN.[1]

BY EN. D. DESI.

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WHILE engaged in re-determining the atomic mass of tungsten, by reduction of its trioxide in a current of hydrogen, the writer carefully observed the color changes taking place in the oxide as the temperature varied.

When studying the literature of this metal, no precise information was found about the bodies formed during the reduction, as was expected. Although a great many compounds of tungsten have been investigated, those of the metal with oxygen have

[1] From author's thesis presented to the University of Geneva, Switzerland, for the degree of Doctor in Science.

been entirely neglected. The few recorded observations relate solely to the results of qualitative experiments.

As most of the oxides of the other elements of group VI of the periodic system, as CrO, Cr_3O_4, Cr_2O_3, CrO_2, CrO_3; MoO, Mo_2O_6, Mo_3O_8, Mo_5O_{12}, Mo_5O_7, MoO_3; UO, U_3O_2, U_4O_5, U_3O_4, U_2O_3, U_3O_8, are well known and defined, the study of the oxides of tungsten was important.

The well-determined oxides of the metal are:

1. *Tungstic Acid*, WO_3, obtained by treating one of the minerals with aqua regia, or by treating a tungstate with an acid, or by igniting the metal in the presence of air.

2. *The Blue Oxide*, $W_2O_5 = WO_3.WO_2$, obtained by reducing the trioxide at a low temperature with hydrogen. Care must be taken not to heat above the formation of traces of water. In this way Malagutti[1] obtained a body of constant composition. It is also prepared by treating a soluble tungstate with hydrochloric acid and tin. The liquid takes on a beautiful deep blue color, due probably to the solution of the blue oxide in the hydrochloric acid.

3. *Tungsten Dioxide*, WO_2, a brown substance obtained by heating the trioxide to a red heat in a current of hydrogen, or by treating a soluble tungstate with hydrochloric acid and zinc. The dioxide formed in this way is very unstable; it rapidly oxidizes to tungstic acid.

As tungsten has many properties in common with the other elements of group VI, and especially with molybdenum, it should also form intermediary oxides.

Muthmann[2] has made interesting observations upon the oxides of molybdenum. He succeeded in finding definite methods for preparing them, as well as for determining their composition. In the course of the present work the writer will return to this subject.

PREPARATION OF TUNGSTIC ACID.

Commercial tungstic acid is a product of very dubious purity, even that of the leading manufacturers, marked C. P., invariably contains molybdic acid.

It seemed to me to be of the utmost importance to use in my

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[1] *Ann. Chem.* (Liebig), 9, 273.

[2] *Ann. Chem.* (Liebig), 228, 108.

researches the purest possible material, so as to be perfectly sure that the reactions obtained are due solely to tungsten.

The preparation of chemically pure tungstic acid is a long and tedious operation which need not be described here, as it has already been outlined in detail by Smith and Desi.[1]

OXIDES OF TUNGSTEN.

I.

Muthmann[2] obtained molybdenum dioxide (MoO_2) in beautiful violet crystals by heating the following mixture for several hours:

	Grams.
Ammonium molybdate	8
Boric acid	7
Molybdic acid	7
Fused potassium carbonate	24

On account of the great analogy between tungsten and molybdenum, it was thought that tungsten dioxide could be obtained by using the same method. A similar mixture was accordingly made, taking tungsten salts instead of molybdenum, and fusing in a covered platinum crucible for three hours. The result was a porous, white mass, and at the bottom of the crucible a very small quantity of a brown substance, insoluble in water or acids. When this was ignited in a porcelain crucible, with access of air, it did not change in appearance nor in weight.

The platinum crucible was badly corroded and a second experiment resulted in several holes; a nickel crucible did not fare better.

The quantity of the brown substance was too small to allow of investigating its composition.

As satisfactory results could not be obtained with metal crucibles, the experiment was tried in a smooth Battersea crucible, using the following mixture:

	Grams.
Ammonium tungstate	9
Tungstic acid	7
Fused potassium carbonate	21
Boric acid	7

This mixture was heated in a wind furnace until a quiet fusion

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[1] *J. Franklin Inst.*, **139**, 290.

[2] *Ann. Chem.* (Liebig), **228**, 116.

set in. After thorough cooling the crucible was broken in halves; beautiful light green crystals were found, resembling ammonium chloride in structure. After a few hours exposure to the air they became white.

Treated with water they broke down into an insoluble, amorphous, white substance free from boron, and into a soluble body. The latter, when acted upon with hydrochloric acid, became yellow in color, but when heated regained its former white color. The aqueous solution was concentrated on the water-bath; during this operation a point was reached, when a very viscous liquid was obtained, which could not be evaporated to dryness. This is one of the properties of a large number of double salts of boric and tungstic acids.

Diluting this viscous liquid with a few drops of water, it was placed in a vacuum desiccator, over sulphuric acid. After a week small crystals appeared, and a little later beautiful, hexagonal, perfectly developed prisms, soluble with difficulty in water. Besides these well-developed crystals, a white, amorphous powder separated, very soluble in water. The crystals were separated from the amorphous substance, dissolved in water and the solution placed in a vacuum desiccator. This operation was repeated several times, but the white, amorphous substance appeared every time, showing that the crystalline substance had broken down into two bodies, both containing tungsten, boron, and potassium.

The object being to investigate the oxides of tungsten, the study of these two bodies was not continued any further.

II.

ACTION OF SULPHURIC ACID UPON METALLIC TUNGSTEN AT THE ORDINARY ATMOSPHERIC PRESSURE.

In most of our chemical treatises the statement is made that metallic tungsten is not acted upon by sulphuric acid, or at least very slightly. The writer's experience demonstrates the contrary, for metallic tungsten is readily attacked by concentrated sulphuric acid at a temperature of 200° C. It is not possible, however, to dissolve it completely, even in the boiling acid. In this respect it differs from molybdenum, which is readily dissolved in concentrated sulphuric acid far below 200° C.

Metallic tungsten and thirty-five cc. of concentrated sulphuric acid were introduced into a small flask. Sufficient heat was applied to maintain a quiet evolution of sulphurous acid, showing thus, that a reduction took place and a blue substance was formed. As soon as sulphurous acid ceased to be evolved, heating was stopped.

Part of the blue substance was suspended in the liquid, subsiding after two or three days and then beginning to oxidize to tungstic acid. The clear, colorless, supernatant acid liquid, when treated with water, gave a precipitate of pure, yellow tungsten trioxide. On this account the dark blue substance in the flask was not washed with water but with alcohol and then ether, preventing, as much as possible, contact with the air as long as it was not perfectly dry.

In the subsequent experiments the heating, washing, and drying were made in an atmosphere of carbon dioxide.

The blue substance, once dried, is very stable. It precipitates metallic silver from a solution of silver nitrate and is readily oxidized to tungsten trioxide when ignited. Treated with ammonia, a gray metallic powder is formed which, according to analyses, is metallic tungsten.

0.1265 gram gray substance gave 0.1588 gram tungsten trioxide, equal to 0.1259 gram tungsten, or 99.53 per cent. tungsten.

The ammoniacal liquid, treated with hydrochloric acid, deposited yellow tungstic acid.

Several ignitions of the blue substance to tungsten trioxide, gave an average of 92.08 per cent. tungsten, corresponding well with the requirements of the formula of the monoxide of tungsten, WO, containing theoretically ninety-two per cent. tungsten.

Experiment 1.—0.0957 gram blue substance gave 0.1114 gram tungsten trioxide, or 0.0883 gram tungsten, or 92.25 per cent. tungsten.

Experiment 2.—0.1923 gram blue substance gave 0.2232 gram tungsten trioxide, or 0.1770 gram tungsten, or 92.03 per cent. tungsten.

Experiment 3.—0.2835 gram blue substance gave 0.3292 gram tungsten trioxide, or 0.2611 gram tungsten, or 92.02 per cent. tungsten.

Having determined the percentages of the tungsten, it was thought that a determination of the oxygen would be still more convincing. A weighed quantity of the blue substance was accordingly reduced in a current of hydrogen, the water from the reduction being collected in a weighed U-tube filled with freshly calcined calcium chloride.

Experiment 1.—0.5588 gram blue substance gave 0.0498 gram water, or 0.0437 gram oxygen, or 7.02 per cent. oxygen, thus proving conclusively that the blue substance is the *monoxide of tungsten.*

When we consider the decomposition of the monoxide of tungsten by ammonia into metallic tungsten and a soluble tungstate, we must come to the conclusion that tungsten monoxide, WO, is not formed by the union of only one atom of tungsten and one atom of oxygen, but must be more complicated, perhaps $W_2O.WO_2$, which would correspond to tungstous acid.

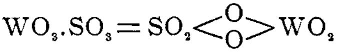
The clear, colorless sulphuric acid solution obtained from the treatment of metallic tungsten with concentrated sulphuric acid, upon addition of water, precipitates yellow tungstic acid without passing first through the green and blue stages of oxidation. Evaporated in a platinum dish, it soon takes a dark brown color, almost black, and becomes very viscous; if water is added, a brown flocculent, very rapidly oxidizable precipitate is formed. On trying to filter, it oxidized very rapidly, so that it was impossible to obtain a homogeneous mass.

The color and behavior of this precipitate leads me to the supposition that it is *tungsten dioxide*, which shows the same properties when prepared in the wet way.

If we continue to evaporate to dryness, a brilliant, black, amorphous, very hygroscopic residue is left, which can be quite strongly heated, without any apparent change.

Several attempts were made to prepare a larger quantity of this black substance, but being very light, the greatest part is carried off by the heavy sulphuric acid fumes, very little remaining in the dish, not enough to make an analysis.

To determine the state of oxidation of the tungsten in the sulphuric acid solution, ten cc. of it were added to 190 cc. of standard potassium permanganate. Tungstic acid was precipitated; and titrating with a ferrous salt, almost no change was observed in the standard of the permanganate, the difference being due only to the dilution. This means that the tungsten is in the sulphuric acid solution in its highest state of oxidation, and that it forms with sulphuric acid, like molybdenum, the anhydride of the sulphotungstic acid



$$WO_3.SO_3 = SO_2{<}\genfrac{}{}{0pt}{}{O}{O}{>}WO_2$$

which differs from that of molybdenum by its stability; that of molybdenum soon begins to take on a greenish color, indicating a reduction.

The formation of the sulphotungstic anhydride is also analogous to the combination of uranyl (UO_2) with acid radicals, as $UO_2.SO_4$, etc.

If instead of treating tungsten with concentrated sulphuric acid at a low temperature, it be heated to the boiling-point of the acid, the evolution of sulphurous acid is violent, and two different substances will be seen floating in the liquid, one blue and the other white, settling down when the reaction is completed. These two substances were separated with great difficulty by an operation similar to "panning" with alcohol, then washing with ether and drying in an atmosphere of carbon dioxide.

Tungsten was determined in the greenish-blue substance by ignition and weighing of the resulting tungstic acid.

Experiment 1.—0.4796 gram greenish-blue substance gave 0.5688 gram tungsten trioxide, or 0.4511 gram tungsten, or 94.02 per cent. tungsten.

Experiment 2.—0.2239 gram greenish-blue substance gave 0.2644 gram tungsten trioxide, or 0.2096 gram tungsten, or 93.61 per cent. tungsten. From this the formula W_4O_3 is deduced, containing theoretically 93.87 per cent. tungsten.

In group VI of the elements we do not find another similar oxide, with the exception of that of uranium, U_4O_3, prepared by Peligot, by treating a solution of U_4Cl_8 with ammonia. It is a light green-colored, rather unstable compound.

The quantity of oxygen in W_4O_3 was determined by reducing it in a current of hydrogen, as in a former experiment.

Experiment.—0.5321 gram greenish-blue substance gave 0.0358 gram water, or 0.0318 gram water, or 5.97 per cent. oxygen, corresponding to the theoretical requirement of the formula, 6.13 per cent. oxygen.

W_4O_8 is decomposed by ammonia into metallic tungsten and tungstic acid ; it precipitates silver from a solution of silver nitrate, insoluble in acids. The sulphuric acid solution, from the treatment of metallic tungsten with concentrated sulphuric acid, has the same properties as that obtained at a low temperature.

III.

ACTION OF SULPHURIC ACID UPON METALLIC TUNGSTEN IN SEALED TUBES.

Sulphuric acid being so easily reduced by metallic tungsten at the ordinary atmospheric pressure, it was necessary to see what results would be obtained by allowing these two substances to act upon each other in sealed tubes and at different temperatures.

One gram of pure metallic tungsten and forty cc. of concentrated sulphuric acid were heated in a sealed tube for five hours at 105° C. At this temperature almost no reaction took place, so I increased the temperature to 150° C. for seven hours.

The contents of the tube had an entirely different appearance; there was a beautiful, clear, dark blue liquid, and a solid body of the same color, strongly adhering to the sides of the tube. Opening the tube, a very large quantity of sulphurous acid escaped with great violence.

The blue substance was well washed with alcohol and then ether, and dried at 100° C., in an atmosphere of carbon dioxide. It is a homogeneous, dark blue mass, that precipitates metallic silver in brilliant scales, from a solution of silver nitrate ; ammonia and alkalies decompose it into metallic tungsten and a soluble tungstate ; the metallic tungsten proved to be very pure.

0.2115 gram gray substance gave 0.2667 gram tungsten trioxide, or 0.2115 gram tungsten, or 100 per cent. tungsten.

On adding water to the blue sulphuric acid solution, a green precipitate is formed, which in time becomes yellow from the oxidation to tungstic acid.

The blue substance, when ignited, is immediately transformed into yellow tungsten trioxide, from which the percentage of tungsten was calculated :

Experiment 1.—0.2512 gram blue substance gave 0.2802 gram tungsten trioxide, or 0.2221 gram tungsten, or 88.41 per cent. tungsten.

Experiment 2.—0.2136 gram blue substance gave 0.2493 gram tungsten trioxide, or 0.1977 gram tungsten, or 88.41 per cent. tungsten.

Experiment 3.—0.2555 gram blue substance gave 0.2848 gram tungsten trioxide, or 0.2258 gram tungsten, or 88.38 per cent. tungsten.

These three analyses were made with the product of three different tubes and correspond very well with the requirements of the formula of the tungsten sesquioxide :

$$\mathrm{W_2O_3 = WO.WO_2},$$

containing theoretically 88.46 per cent. tungsten.

The quantity of oxygen was also determined by reduction in a current of hydrogen. The metallic tungsten remaining in the boat also corresponds to the formula of the sesquioxide.

0.4111 gram blue substance gave 0.0530 gram water, or 0.0473 gram oxygen, or 41.52 per cent. oxygen.

0.3577 gram tungsten equals 88.44 per cent. tungsten.

This oxide has a great similarity to the sulphur sesquioxide (S_2O_3), which element belongs to the same group of the periodic system as tungsten. The sesquioxide of sulphur is decomposed by water into sulphur, sulphurous acid, and sulphuric anhydride (SO_3) and dissolves with a blue color in concentrated sulphuric acid. The difference between tungsten sesquioxide and sulphur sesquioxide is that the former is decomposed by ammonia, instead of by water, into metallic tungsten and tungsten trioxide ; probably tungsten dioxide is also formed but, being very unstable, it oxidizes very rapidly to tungsten trioxide.

The analogy between tungsten and sulphur is further shown by the property of silver sulphite to be decomposed by water into metallic silver and sulphuric acid.

The two equations demonstrate the analogy:

$$\mathrm{Ag_2O.SO_2 + O\genfrac{}{}{0pt}{}{H}{H} = 2Ag + SO_2{<}\genfrac{}{}{0pt}{}{OH}{OH}};$$

$$\mathrm{WO.WO_2 + \genfrac{}{}{0pt}{}{OHNH_4}{OHNH_4} = W + WO_2{<}\genfrac{}{}{0pt}{}{O(NH_4)}{O(NH_4)} + H_2O},$$

so we can consider W_2O_3 to be the tungstite of tungsten.

Molybdenum sesquioxide differs from that of tungsten, by not being decomposed by ammonia or the alkalies. Chromium sesquioxide (Cr_2O_3) differs by not being reduced by hydrogen, is not affected by heat, and is insoluble in acids.

To investigate the influence of heat in the reaction of sulphuric acid upon metallic tungsten, in sealed tubes, one gram of metallic tungsten was introduced into several tubes with varying quantities of concentrated sulphuric acid, and heated between 170° and 180° C., for seven hours. The tubes contained a blue liquid and a homogeneous blue substance. Upon opening them, sulphurous acid escaped. The blue substance was washed with alcohol and ether and then dried at 100° C. in an atmosphere of carbon dioxide.

This blue substance is of a lighter shade than the sesquioxide, is soluble in concentrated sulphuric acid, precipitates metallic silver from a solution of silver nitrate, and is decomposed by ammonia into metallic tungsten and tungstic acid.

Addition of water to the blue, sulphuric acid solution will precipitate a greenish-blue body, which becomes yellow (WO_3) when it stands for some time. A certain quantity of this blue solution which had stood for three weeks in a small flask not well corked, changed its blue color to dark green, remaining perfectly clear. The sulphurous acid which it contained was driven off by passing a current of carbon dioxide until it was perfectly odorless; five cc. were then added to 190 cc. of standard potassium permanganate so as to find the state of oxidation of the tungsten. The quantity of tungsten was determined by precipitating the tungstic acid in ten cc. of the green solution, by addition of water. From different experiments the writer concluded that the green substance in solution must be W_5O_{12}. Muthmann[1] has obtained the same oxide of molybdenum (Mo_5O_{12}), by treating, in a flask, metallic molybdenum with concentrated sulphuric acid, at a low temperature.

This experiment was repeated several times between 170° and 180° C., always obtaining the same blue compound:

Experiment 1.—0.3651 gram blue substance gave 0.3992 gram tungsten trioxide, or 0.3166 gram tungsten, or 86.71 per cent. tungsten.

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[1] *Loc. cit.*

Experiment 2.—0.2644 gram blue substance gave 0.2881 gram tungsten trioxide, or 0.2285 gram tungsten, or 86.43 per cent. tungsten.

Experiment 3.—0.3272 gram blue substance gave 0.3575 gram tungsten trioxide, or 0.2835 gram tungsten, or 86.70 per cent. tungsten.

Experiment 4.—0.2837 gram blue substance gave 0.3096 gram tungsten trioxide, or 0.2455 gram tungsten, or 86.53 per cent. tungsten.

From these results is deduced the following formula:

$$W_5O_9 = WO_3.2W_2O_3,$$

containing theoretically 86.47 per cent. tungsten.

Oxygen was determined by reducing the blue substance in a current of hydrogen gas, as in former experiments.

0.4561 gram blue substance gave 0.0690 gram water, or 0.0614 gram oxygen, or 13.46 per cent. oxygen, corresponding well to the formula W_5O_9 with 13.53 per cent. oxygen.

A third series of experiments in sealed tubes was made at temperatures varying from 200°–250° C.

These results were not satisfactory, no homogeneous compounds, but mixtures of various colors, being obtained.

In tubes heated at 250° C. it was possible to see some yellow tungstic acid and, contrary to all former experiments, the sulphuric acid was perfectly colorless; probably higher oxides were formed, which are insoluble in sulphuric acid, whereas the lower oxides are soluble.

These traces of tungstic acid led to the hope that by increasing the temperature and heating for a long time, the metallic tungsten could be completely oxidized to tungstic acid; but all attempts were fruitless, probably on account of not being able to obtain a temperature sufficiently high.

IV.

ACTION OF SULPHUROUS ACID UPON METALLIC TUNGSTEN.

In one of the former experiments, where metallic tungsten was treated with concentrated sulphuric acid in an open flask at the ordinary atmospheric pressure, a few grains of the metal adhered to the neck of the flask far above the sulphuric acid.

When the reaction began by evolving sulphurous acid, those grains of metallic tungsten slowly changed their color, becoming first green and then blue. As the temperature was low the tungsten could not have been oxidized by the oxygen from the air, as in ignition, and, as the reaction in the flask took place very gently, no sulphuric acid was thrown on the grains, so that the only explanation for this oxidation is that the sulphurous acid was readily reduced by tungsten.

This observation suggested the examination of the action of sulphurous acid upon tungsten under different conditions.

A small quantity of metallic tungsten was spread out in a hard glass tube, so as to offer a large surface for the action of the sulphur dioxide prepared by reducing sulphuric acid with copper. When all the air from the apparatus was driven out I began to heat the tungsten gently, but no reaction took place. Heating stronger to dull red, the gray color of the metal slowly began to become blue. When the whole mass appeared to be homogeneous, heating was discontinued, and the mass allowed to cool in the current of sulphur dioxide. Examining this blue substance carefully under the microscope a brown body seemed to be mixed with it, which was probably tungsten dioxide.

This experiment was repeated at various temperatures and for varying periods of time, but always more or less brown substance was formed. To prevent some parts of the metal being heated more than others, the tube was slowly turned, constantly exposing in this way new parts of the tungsten to the action of heat and of the sulphurous acid.

Obtaining no satisfactory results, the action of sulphurous acid upon metallic tungsten in sealed tubes was tried.

I first prepared a concentrated solution of sulphurous acid. The gas, after passing through three wash-bottles, entered a flask filled with distilled water, imbedded in a mixture of ice and salt; after complete saturation the contents of the flask, of a gelatinous consistency, was poured into a tube sealed at one end, containing metallic tungsten. During the sealing of the open end of the tube the sealed end was kept in the refrigerating mixture, so as not to lose any gas.

After the tube acquired the temperature of the surrounding air it was heated at 110° C. for ten hours. A green body was formed and a large quantity of free sulphur floated in the liquid.

Another tube was heated at 90° C. for the same length of time, when its contents had exactly the same appearance as that of the first tube.

On opening the tubes, the sulphurous acid escaped with great violence. Separation of the green substance from the free sulphur was tried by different mechanical means, amorphous sulphur being insoluble in carbon bisulphide; being unsuccessful in my attempts, I treated the green substance with carbon disulphide in a sealed tube for about half an hour, at 100° C. This operation succeeded very well, all the sulphur being dissolved. The green substance did not change in appearance; it was washed with water, alcohol, and ether, and dried in an atmosphere of carbon dioxide. The tungsten was determined by ignition.

Experiment 1.—0.2625 gram green substance gave 0.2649 gram tungsten trioxide, or 0.2100 gram tungsten, or 80.09 per cent. tungsten.

Experiment 2.—0.5012 gram green substance gave 0.5065 gram tungsten trioxide, or 0.4017 gram tungsten, or 80.14 per cent. tungsten.

Experiment 3.—0.3267 gram green substance gave 0.3305 gram tungsten trioxide, or 0.2621 gram tungsten, or 80.22 per cent. tungsten.

From these results is calculated the following formula:

$$W_5O_{14} = 4WO_3.WO_2,$$

containing theoretically 80.44 per cent. tungsten.

Knowing now that sulphurous acid will oxidize metallic tungsten, it was interesting to examine how far it would reduce tungstic acid.

The sealed tubes were prepared in exactly the same way as in the former experiments, taking tungstic acid instead of metallic tungsten. At 100° and 125° C. no change took place. At 150° C. the tungsten trioxide began to take a green color and free sulphur was liberated. The liquid was colorless and clear. I repeated this experiment at different temperatures, but did not succeed in obtaining a homogeneous compound.

Two of these tubes were lying on my desk for several months, exposed to the light and the direct rays of the sun. It was observed that the green substance darkened until it had a very dark green color, which apparently did not change any more and was homogeneous. One end of the tube was opened, sulphurous acid escaped, and the green substance was rapidly washed with water, but it changed its dark green color to light green again. The free sulphur was separated by dissolving it in carbon disulphide, in a sealed tube; the result was a still lighter green substance, not homogeneous.

These experiments show that tungstic acid is reduced by sulphurous acid, but the resulting lower oxides are not stable. The action of light in this case is very interesting and might be the starting point of some important investigations.

The second tube was kept sealed over one year longer. During this time the dark green color of the substance gradually changed to light green, and on opening the tube no trace of sulphurous acid was perceptible, but instead a very strong odor of hydrogen sulphide. The liquid had a yellow color.

V.

ACTION OF HEAT UPON AMMONIUM METATUNGSTATE.

$$W_4O_{13}(NH_4)_2 + 8H_2O.$$

Berlin,[1] obtained an oxide of molybdenum, which, according to his analyses, has the formula $Mo_3O_8 = 2MoO_3.MoO_2$, a molybdate of molybdenum. He prepared it by heating strongly over a blast lamp, in a platinum crucible, a mixture of two parts of molybdenum trioxide and one part of ammonium molybdate. After cooling, the sides of the crucible were found to be covered with beautiful purple crystals, soluble in ammonia.

Later Muthmann[2] found that this oxide contained a considerable amount of nitrogen, which naturally lowered the percentage of molybdenum in it. He freed it of nitrogen by repeated boiling with hydrochloric acid and determined its formula to be

$$Mo_5O_{12} = 2MoO_3.3MoO_2.$$

On account of the great analogy between tungsten and molybdenum, the same experiment was tried with ammonium metatungstate (one part) and tungstic acid (two parts), heated strongly for one hour over the blast lamp in a covered platinum crucible. The result was a mixture of blue and green oxides and undecomposed tungsten trioxide.

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[1] *J. prakt. Chem.*, 49, 447.

[2] *Loc. cit.*

This mode of operating is very unsatisfactory, it being impossible to keep the air away from the contents of the crucible. The same mixture was introduced into a well-covered porcelain crucible and then into a large Battersea crucible, completely imbedded in powdered charcoal, the whole closed with refractory clay; in this way no air could possibly reach the hot contents of the crucible. It was heated for ten hours to white heat, in a wind furnace, and allowed to cool slowly over night. Opening the small crucible the sides were found, covered with a beautiful crystalline substance of all possible colors.

Evidently, a reduction took place, but probably an inadequate quantity of the reducing agent was present to complete the reduction. As in this case, the hydrogen of ammonium metatungstate is the reducing agent, the experiment was repeated, taking the metatungstate alone and heating it for ten hours to a white heat.

The porcelain lid was fused to the crucible so that it had to be broken to reach its contents, which consisted of a perfectly homogeneous, gray, crystalline metallic substance, with a yellow reflex like brass filings, according to the exposure to the light. These crystals were carefully collected, a weighed quantity ignited and, from the tungstic acid obtained, it was concluded that it was metallic tungsten.

Experiment 1.—0.2429 gram gray crystals gave 0.3068 gram tungsten trioxide, or 0.2426 gram tungsten, or 99.87 per cent. tungsten.

Experiment 2.—0.1138 gram gray crystals gave 0.1434 gram tungsten trioxide, or 0.1137 gram tungsten, or 99.91 per cent. tungsten.

The temperature has a great influence in all these experiments upon the final result. Another experiment was performed by heating ammonium metatungstate for one and a half hours, only to bright red instead of to a white heat. The crucibles were prepared as in the foregoing experiments.

The small crucible, after the operation, contained a beautiful purple substance, with a yellow metallic reflex, insoluble in water, acids, and alkalies. It precipitated metallic silver from an ammoniacal solution of silver nitrate and easily burned to tungsten trioxide.

Experiment 1.—0.4075 gram purple substance gave 0.4181 gram tungsten trioxide, or 0.3315 gram tungsten, or 81.35 per cent. tungsten.

Experiment 2.—0.3112 gram purple substance gave 0.3183 gram tungsten trioxide, or 0.2524 gram tungsten, or 81.09 per cent. tungsten.

Experiment 3.—0.3626 gram purple substance gave 0.3713 gram tungsten trioxide, or 0.2945 gram tungsten, or 81.21 per cent. tungsten.

Experiment 4.—0.3874 gram purple substance gave 0.0819 gram water, or 0.0727 gram oxygen, or 18.78 per cent. oxygen.

0.3146 gram tungsten, or 81.20 per cent. tungsten.

From this was calculated the formula,

$$W_3O_8 = 2WO_3.WO_2,$$

which would be the tungstate of the tungsten dioxide containing theoretically 81.17 per cent. tungsten and 18.83 per cent. oxygen.

In Roscoe and Schorlemmer's treatise, Vol. 2, p. 208, mention is made of a blue oxide, to which the formula W_3O_8 is given. It was obtained by reducing tungstic acid in a current of hydrogen at 250° C. No properties of the oxide are given.

As small quantities of nitrogen could be occluded by the purple substance or even chemically combined, a small quantity of it was ignited in a current of hydrogen and the escaping gas conducted into a dilute cochineal solution. After one hour of this treatment the reduction was complete, but the cochineal solution had not changed in the least, demonstrating the complete absence of nitrogen.

Cochineal is a very delicate test for ammonia, the least trace changing its color to purple.

The substance remaining in the boat corresponds well with the requirements of the formula W_3O_8 (81.17 per cent. tungsten).

0.3462 gram purple substance gave 0.2813 gram tungsten, or 81.25 per cent. tungsten.

VI.

ACTION OF ETHYLENE UPON TUNGSTIC ACID.

The well known property of ethylene of decomposing by heat into acetylene and methane, which in turn is decomposed into acetylene and hydrogen, afforded a new method of reducing tungstic acid by nascent hydrogen, and not by the wet way, which necessarily must lead to new results.

A small quantity of tungsten trioxide was spread out in a hard glass tube and a rapid current of ethylene (C_2H_4) passed through to expel all the air from the apparatus.

The ethylene gas was prepared by introducing drop by drop from a separating funnel a mixture of one part of alcohol and two parts of sulphuric acid into a flask containing twenty-five grams of absolute alcohol and 550 grams of sulphuric acid, heating very gently on a sand-bath. Ethylene gas prepared in this way always contains sulphurous acid and carbon dioxide; to free it from these admixtures it was conducted through three wash-bottles containing a concentrated solution of caustic potash, then through two towers, one filled with pieces of caustic potash, the other with calcined calcium chloride. The gas thus purified and dried, entered the tube containing the strongly heated tungstic acid. From time to time, the tube was turned, so as to offer fresh surfaces to the action of the heat and ethylene gas.

Soon the yellow color of the trioxide began to change and in a short time the whole quantity was transformed into a dark blue, homogeneous substance, retaining the crystalline form of the trioxide used. In the cold part of the tube minute drops of water were condensed.

After cooling in the current of ethylene, a weighed quantity of the blue substance was ignited in an open porcelain crucible. It oxidized very rapidly to yellow tungstic acid, but great was my astonishment, when weighing, to find that the weight of the tungstic acid *did not differ from that of the blue substance before the ignition.*

Experiment 1.—0.4037 gram blue substance gave 0.4037 gram tungsten trioxide.

Experiment 2.—0.4462 gram blue substance gave 0.4461 gram tungsten trioxide.

Experiment 3.—0.1152 gram blue substance gave 0.1150 gram tungsten trioxide.

Experiment 4.—0.1150 gram blue substance gave 0.1150 gram tungsten trioxide.

The presence of carbon being possible in this substance, a combustion was made as with an organic substance. After heating strongly for five hours, the U-tube and potash bulbs were weighed, but there was no appreciable change of weight, showing complete absence of carbon and hydrogen.

Only in two ways can the writer explain this phenomenon. Either the substance is a new modification of tungstic acid, which is not probable on account of the formation of traces of water when treating tungstic acid with ethylene, or it is an oxide coming very near the limit of tungstic acid, and its molecular weight being so high that the small increase of weight when igniting it to tungstic acid cannot be determined.

The blue substance is insoluble in acids and alkalies, and does not precipitate silver from a solution of silver nitrate.

The action of acetylene (C_2H_2) upon tungstic acid at different temperature was also tried, but in no case could any change be found in the appearance of the trioxide.

Only a very small deposit of carbon could be seen, due to the decomposition of acetylene by the heat.

VII.

ACTION OF THE OXIDES OF CARBON UPON TUNGSTIC ACID.

Muthmann[1] studied the action of carbon monoxide upon molybdic acid and succeeded in reducing it to metallic molybdenum.

The same reduction was tried with the tungstic acid, heating it strongly in a current of carbon monoxide, prepared by treating oxalic acid with sulphuric acid, conducting the escaping gas through two wash-bottles containing a strong solution of caustic potash, to retain any carbon dioxide, and then through two towers filled with calcium chloride. After five hours of intense heating in the boat, three distinct, differently colored layers were found; at the bottom the substance was brown, the second layer was blue, and the top layer was almost unaffected tungstic acid. The same portion was heated for five hours more, the brown substance increasing in quantity. It was then heated for over twenty hours, but no homogeneous substance could be obtained.

This shows the great affinity of tungsten for oxygen. Muthmann obtained metallic molybdenum after ten hours of the same

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[1] *Loc. cit.*

treatment, whereas tungsten after thirty hours was still in the form of oxides.

When U_3O_8 is heated for a long time in a current of carbon dioxide it is decomposed to U_2O_2.

Tungsten trioxide was subjected to the same treatment, heating a weighed quantity in a platinum crucible and introducing into it a current of dry carbon dioxide. Two hours of heating over the blast-lamp produced no change.

VIII.

ACTION OF ALKALI METALS AND HALOID SALTS UPON TUNGSTIC ACID.

A. Action of Potassium Bromide.—It was found that if tungstic acid is heated with a solution of potassium bromide and a few drops of hydrochloric acid, a reaction takes place. The solution takes on a green color which, upon continued heating, again becomes yellow. This reduction led to the idea that by fusing a mixture of potassium bromide and tungstic acid, well-defined bodies could be obtained.

Three grams of tungstic acid and ten grams of potassium bromide, thoroughly mixed, were introduced into a well-covered porcelain crucible and then imbedded in powdered charcoal in a larger crucible, as in former experiments, and the whole heated to white heat for six hours in a wind furnace. After thorough cooling the small crucible was opened and a gray, crystalline metallic powder was found. After washing it with water and drying at 110° C., a weighed quantity was ignited; it burned rapidly to yellow tungstic acid.

Experiment 1.—0.0987 gram gray substance gave 0.1238 gram tungsten trioxide, or 0.0982 gram tungsten, or 99.5 per cent. tungsten.

Experiment 2.—0.3384 gram gray substance, gave 0.4266 gram tungsten trioxide, or 0.3383 gram tungsten, or 99.97 per cent. tungsten.

This gray substance is consequently metallic tungsten.

The same mixture was treated at different temperatures and for varying periods, but no well-defined bodies were obtained; probably by varying the proportions of the two substances, other well-defined compounds would result.

B. Action of Potassium Iodide.—Schulze[1] fused potassium iodide and tungstic acid, but does not seem to have obtained any well-defined bodies, as he does not give any analytical results.

Two grams of potassium iodide and one gram of tungstic acid were treated as in the experiments under *A*.

The small crucible contained a beautiful purple, crystalline substance, precipitating metallic silver from an ammoniacal solution of silver nitrate, insoluble in acids and alkalies. This substance has all the characteristics of that obtained from the action of heat upon metatungstate of ammonium. The amount of tungsten calculated from the tungstic acid obtained by ignition of a weighed quantity of the purple substance, corresponds well with the requirements of the formula W_3O_8, with 81.17 per cent. tungsten.

Experiment 1.—0.2131 gram purple substance gave 0.2181 gram tungsten trioxide, or 0.1729 gram tungsten, or 81.14 per cent. tungsten.

Experiment 2.—0.3127 gram purple substance gave 0.3202 gram tungsten trioxide, or 0.2539 gram tungsten, or 81.19 per cent. tungsten.

Another mixture of one gram tungstic acid and four grams potassium iodide, after the same treatment as above, gave quite a different result. Metallic tungsten was obtained.

0.1225 gram gray powder gave 0.1544 gram tungsten trioxide, or 0.1224 gram tungsten, or 99.98 per cent. tungsten.

C. Action of Potassium Chloride.—One gram tungstic acid and two grams potassium chloride, were treated as under *B*, for five hours. The sides of the crucible were covered with beautiful, glittering, gray crystals, which were metallic tungsten.

0.1066 gram gray powder gave 0.1340 gram tungsten trioxide, or 0.1065 gram tungsten, or 99.90 per cent. tungsten.

The action of the haloid salts of the other alkali metals was also studied, and it was found that the reducing power diminishes with the lower atomic weight; the temperature must be higher and the action of heat longer.

D. Action of Metallic Potassium.—The remarkable reducing action of the haloid salts of the alkali metals cannot be explained otherwise than that at a very high temperature they are dissocia-

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[1] *J. prakt. Chem.*, 21, 439.

ted into their component parts. The alkali metal being, so to say, in the nascent state, combines with eagerness with the oxygen of the tungstic acid and sets free metallic tungsten.

The bottom of a porcelain boat was covered with small, bright pieces of metallic potassium, and on top of it tungstic acid. The whole was introduced into a hard, glass tube, through which a current of dry nitrogen passed; the nitrogen was prepared by dropping a concentrated solution of sodium nitrite into a hot, concentrated solution of ammonium chloride, the gas passing through two calcium chloride towers, before entering the tube. After all the air was expelled from the apparatus, the tube was gently heated under the boat, increasing the temperature slowly, until the potassium began to melt. Soon white vapors began to rise from the boat, condensing to a white powder in the cooler parts of the tube. Increasing the temperature a little, blue and purple fumes of the different oxides of potassium were formed. The reduction began to be violent, when suddenly a deflagration took place, and all action ceased immediately.

The boat was allowed to cool in the atmosphere of nitrogen. It contained a gray, spongy mass, fused to the side of the boat and covered with a white coating (K_2O). After washing with water, a gray metallic, very finely divided powder was left, which was metallic tungsten.

0.1892 gram gray powder gave 0.2385 gram tungsten trioxide, or 0.1891 gram tungsten, or 99.91 per cent. tungsten.

If, instead of washing the contents of the boat with water, hydrochloric acid is used, a clear, dark blue solution is obtained, which oxidizes very rapidly to a green-colored liquid and then a yellow-greenish precipitate is formed, which in time becomes entirely yellow. The supernatant liquid is colorless and clear. The undissolved residue in the boat is gray metallic tungsten.

0.1965 gram gray powder gave 0.2477 gram tungsten trioxide, or 0.1964 gram tungsten, or 99.95 per cent. tungsten.

E. Action of Metallic Sodium—The previous experiment was repeated, but instead of potassium, metallic sodium was used.

The reaction takes place at a higher temperature, is not so violent, and the deflagration liberates less heat. The contents of the boat were much darker in color after being washed. The substance is almost black and flocculent, burning rapidly to tungstic acid when ignited. It proved to be metallic tungsten.

0.1190 gram black substance gave 0.1500 gram tungsten trioxide, or 0.1189 gram tungsten, or 99.91 per cent. tungsten.

IX.

ACTION OF METALLIC MAGNESIUM UPON TUNGSTIC ACID.

As magnesium is a much less active element than the alkali metals, the writer thought that perhaps it would enable him to obtain new oxides.

In a porcelain boat was placed a mixture of one gram tungstic acid and 0.75 gram metallic magnesium powder, the whole introduced into a hard glass tube and a current of dry nitrogen passed over it. The tube was gently heated under the boat until it was dull red in color, when a violent deflagration took place, generating so much heat that the tube became quite red, and broke in several places.

After cooling in the atmosphere of nitrogen the boat was taken out; it contained a very hard, gray substance, firmly adhering to the sides of the boat. It was covered with magnesium oxide and emitted a peculiar, garlic-like odor. After detaching this gray mass from the sides of the boat, it was ground in a mortar to a fine powder. On adding a little water, it began to effervesce strongly. The escaping gas was collected in a test-tube, and in bringing it to a flame, a little puff was heard, showing the decomposition of water.

Neither magnesium nor tungsten decompose water at the ordinary temperature. Then this powder must be an alloy of the two metals.

A certain quantity of the gray substance was left on the sides of the boat, to which was added a drop of hydrochloric acid; a little explosion occurred, with a blue flame. This explosion is due to a magnesium silicide, formed by heating magnesium strongly in contact with the silicon of the porcelain boat,

$$Si_3Mg_5 = Mg_3Si_2 + SiMg_2,$$

which is easily decomposed by hydrochloric acid, the free silicon forming with hydrogen, siliconhydride, SiH_4, an inflammable gas at the ordinary temperature.

This experiment of the reduction of the tungstic acid with magnesium in an *iron* boat was repeated, to prevent the formation of the magnesium silicide. The result was a gray mass as before, decomposing water and generating hydrogen when treated with hydrochloric acid; the residue is then insoluble in acids, except in aqua regia, and is an alloy of magnesium and tungsten.

Filtering off the hydrochloric acid from the gray mass, the drops toward the end of the funnel were seen to take on a dark blue color, which during the fall to the bottom of the flask changed to yellow without forming any precipitate. If water is added to this filtrate yellow tungstic acid is precipitated.

A portion of the gray mass was treated with hydrochloric acid in an atmosphere of carbon dioxide, filtered in the same gas into a flask also filled with it. In this case the hydrochloric acid solution did not take first a blue color, but it immediately became yellow, and water did not precipitate tungstic acid in the cold, but only upon heating.

To determine the state of oxidation of the tungsten in this solution, ten cc. were added to 190 cc. of potassium bichromate solution (tenth-normal), but its standard did not change, showing that the tungsten is at its highest state of oxidation and must form like molybdenum, an oxychloride of tungsten,

$$WO_3.2HCl.$$

This oxychloride of tungsten is probably analogous to chlorochromic acid, $CrO_2 < {Cl \atop OH} = CrO_3.HCl$, and to chlorosulphonic acid, $SO_2 < {Cl \atop OH} = SO_3.HCl$, being decomposed when heated into anhydride.

The gray substance precipitates metallic silver from a solution of silver nitrate. As it dissolves with difficulty even in aqua regia, I fused it with potassium bisulphate, obtaining soluble magnesium sulphate and insoluble tungstic acid, which were separated by filtration. In the filtrate magnesium was precipitated as magnesium-ammonium phosphate.

0.4598 gram gray substance gave 0.4179 gram tungsten trioxide, or 0.3314 gram tungsten, or 72.08 per cent. tungsten.

0.5916 gram gave 0.1279 gram magnesium pyrophosphate or 27.81 per cent. magnesium.

Different experiments gave about the same results, with slight variations.

Instead of reducing the tungstic acid with magnesium in a current of nitrogen, carbon dioxide was used. The reduction took place very slowly, at a very high temperature, and without deflagration. The resulting product had the color of steel, decomposed in water, and apparently also absolute alcohol when hot.

THE OXYNITRIDES OF TUNGSTEN.

I.

ACTION OF AMMONIUM CHLORIDE UPON TUNGSTIC ACID.

Continuing the experiments of the reduction of tungstic acid by various reducing agents, a large number of bodies containing tungsten, nitrogen, and oxygen were the result.

No suboxides or true nitrides of tungsten could be obtained, the affinity of tungsten to oxygen being so great that it was impossible to substitute the last traces of oxygen by nitrogen.

A long series of experiments was made under varying conditions, and the conclusion was drawn that nitrides of tungsten can be obtained only by treating the chlorides of tungsten.

Ammonium chloride being easily dissociated by heat, a mixture was made of tungstic acid and ammonium chloride in excess and heated in a covered porcelain crucible over the blast lamp, until no more fumes were evolved. Opening the crucible, there was found on the top some slightly decomposed tungstic acid, underneath a mixture of blue and green oxides, and at the bottom a black crystalline substance. Some of the crystals reflected the light so strongly that they were first taken to be some small pieces of glass that had accidentally found their way into one of the reagents used.

This black substance was again twice treated with ammonium chloride, succeeding in this way in obtaining a homogeneous, black, very light substance, insoluble in acids and alkalies.

The sides of the crucible were covered with a black, metallic deposit, which suggested the presence of nitrogen on account of its similarity with nitrides of chromium and uranium.

To ascertain the presence or absence of nitrogen, the well washed and dried black substance was treated in a hard glass tube with hydrogen, the gas escaping from the tube being conducted into a cochineal solution, which changed its color very soon to purple, thus showing the formation of ammonia, and consequently the presence of nitrogen in the black substance. A nitride was obtained instead of a lower oxide. The nitrogen was estimated by Dumas' method.

It was also important to know whether this substance contained hydrogen. A weighed quantity was ignited in a current of oxygen, taking all precautions to prevent the formation of nitrogen oxides. Any water formed was absorbed in a U-tube, filled with freshly calcined calcium chloride. After five hours heating, the increase of weight of the U-tube was only 0.0002 gram, corresponding to 0.08 per cent. hydrogen, so that hydrogen is absent.

If the black substance is ignited in a current of hydrogen abundant water vapors are condensed in the cooler parts of the tube, showing the presence of oxygen.

The tungsten was estimated by igniting a weighed quantity of the black substance in an open crucible. Even prolonged and very strong heating will not oxidize it completely to yellow tungstic acid. In one experiment the substance was ignited for two days, taking every precaution to prevent the combustion gases from the burner entering the crucible; but pure yellow tungsten trioxide was not obtainable, a large quantity remaining black, some being dark and some light green. To complete the oxidation I had to use aqua regia repeatedly and obtained in this way an almost complete oxidation; the tungstic acid still had a greenish tint.

All the oxynitrides, obtained by different methods, are oxidized with difficulty, showing a great affinity between tungsten and nitrogen; even aqua regia breaks down this intimate union of the two elements only after long action.

Experiment 1.—0.2837 gram black substance gave 0.3188 gram tungsten trioxide, or 0.2528 gram tungsten, or 89.10 per cent. tungsten.

0.2047 gram black substance gave 0.0192 gram nitrogen, or 9.41 per cent. nitrogen.

0.4518 gram black substance gave 0.0077 gram water, or 0.0068 gram oxygen, or 1.51 per cent. oxygen.

From this is deduced the formula $W_{20}N_{27}O_4$.

	Calculated.	Found.
Tungsten	89.28	89.10
Nitrogen	9.16	9.41
Oxygen	1.55	1.51

Experiment 2.—0.1293 gram black substance gave 0.1366 gram tungsten trioxide, or 0.1083 gram tungsten, or 83.75 per cent. tungsten.

0.2718 gram black substance gave 0.03493 gram nitrogen, or 12.85 per cent. nitrogen.

0.5006 gram black substance gave 0.0182 gram water, or 0.0162 gram oxygen, or 3.23 per cent. oxygen.

From this the following formula is derived: W_2N_4O.

	Calculated.	Found.
Tungsten	83.63	83.75
Nitrogen	12.72	12.85
Oxygen	3.63	3.23

Experiment 3.—0.3247 gram black substance gave 0.3539 gram tungsten trioxide, or 0.2806 gram tungsten, or 86.44 per cent. tungsten.

0.3192 gram black substance gave 0.02432 gram nitrogen, or 7.61 per cent. nitrogen.

0.4758 gram black substance gave 0.0311 gram water, or 0.0276 gram oxygen, or 5.80 per cent. oxygen.

From this the following formula is calculated: $W_5N_6O_4$.

	Calculated.	Found.
Tungsten	86.14	86.44
Nitrogen	7.86	7.61
Oxygen	5.99	5.81

Experiment 4.—0.1997 gram black substance gave 0.2213 gram tungsten trioxide, or 0.1755 gram tungsten, or 87.88 per cent. tungsten.

0.3125 gram black substance gave 0.02176 gram nitrogen, or 6.96 per cent. nitrogen.

0.3894 gram black substance gave 0.0222 gram water, or 0.0198 gram oxygen, or 5.08 per cent. oxygen.

From this the following formula is derived: $W_3N_3O_2$.

	Calculated.	Found.
Tungsten	88.17	87.88
Nitrogen	6.71	6.96
Oxygen	5.11	5.08

Hoping to obtain better results by increasing the temperature, a mixture of ten grams tungstic acid and twenty grams of ammonium chloride was made in a well-covered, smooth crucible, the whole placed in a large crucible, then filled with powdered charcoal and closed with a lid and fire-clay, so that no air could possibly affect the reduction. It was heated in a wind furnace to bright redness for five hours. After thorough cooling, the small crucible was opened and several crystalline substances of different colors were found.

Different proportions of the mixture and different temperatures were tried, but a homogeneous substance could not be obtained. Finally a mixture was made of ten grams of tungstic acid and sixty grams ammonium chloride, heated to white heat for twelve hours and a black, amorphous powder obtained, insoluble in acids and alkalies, and attacked with difficulty by aqua regia.

0.3278 gram black powder gave 0.4099 gram tungsten trioxide, or 0.3250 gram tungsten, or 99.14 per cent. tungsten.

Consequently it is metallic tungsten. As it must contain some impurity, probably nitrogen, it was boiled for several hours with hydrochloric acid, frequently changing the acid; after washing it with water and drying at 105° C., a weighed quantity was ignited; the hydrochloric acid had removed most of the impurities.

0.2867 gram black powder gave 0.3609 gram tungsten trioxide, or 0.2863 gram tungsten, or 99.85 per cent. tungsten.

After a great many experiments I came to the conclusion that it is impossible to obtain a nitride by means of ammonium chloride, and that it is also impossible to obtain at will and every time the same well-defined body, the result depending entirely upon the temperature, which cannot be regulated nor controlled in this case.

II.

ACTION OF POTASSIUM CYANIDE UPON TUNGSTIC ACID.

If tungstic acid is added to potassium cyanide in fusion it will be completely dissolved without changing the color of the fused cyanide. If we continue the addition of tungstic acid a point will be reached when it will no more be dissolved, but instead a black mass will be formed.

Tungsten trioxide will also be dissolved in an aqueous solution of potassium cyanide. If alcohol is added to this solution, and then ether, a heavy yellow, sometimes brown liquid will separate, which after a few weeks will deposit a black substance insoluble in acids or alkalies.

The black substance obtained by fusing tungstic acid and potassium cyanide, was well washed with water, a difficult operation. Being very light, it takes considerable time to settle, and even the densest filter paper will not retain it.

A qualitative test for nitrogen and oxygen proved the presence of both elements. As potassium cyanide contains carbon, the possibility of its presence in the black substance suggested itself; a combustion, as for organic compounds, showed complete absence of carbon.

A weighed quantity was ignited in an open porcelain crucible, for several hours, adding from time to time a few drops of aqua regia, but it was not possible to obtain a pure yellow tungstic acid, as it persistently retained a greenish color.

Nitrogen was determined as before according to Dumas' method.

0.3744 gram black substance gave 0.3913 gram tungsten trioxide, or 0.3103 gram tungsten, or 82.87 per cent. tungsten.

0.2040 gram black substance gave 0.02027 gram nitrogen, or 9.03 per cent. nitrogen.

0.4001 gram black substance gave 0.0324 gram water, or 0.0288 gram oxygen, or 7.21 per cent. oxygen.

From this the following formula is derived: $W_5N_8O_5$.

	Calculated.	Found.
Tungsten	82.82	82.86
Nitrogen	10.07	9.93
Oxygen	7.19	7.21

An interesting point remained to be determined: whether the reducing power of the potassium cyanide would increase with the temperature.

To this end a crucible containing ten grams of tungstic acid and fifteen grams potassium cyanide was imbedded in charcoal inside of a large crucible, as in former experiments, and heated to white heat for twelve hours, in a wind furnace. After thorough cooling the small crucible was twisted out of shape, showing that the temperature must have been very high; its sides were incrusted with small, perfectly round, ***bright***, *silver-white metallic globules*, very brittle, insoluble in acids, and attacked with difficulty even by aqua regia. An ignition showed that these globules were very pure metallic tungsten.

0.1752 gram crushed globules gave 0.2209 gram tungsten trioxide, or 0.1752 gram tungsten, or 99.97 per cent. tungsten.

In the literature of tungsten no mention is found of its preparation in this form.

The same mixture of ten grams tungsten trioxide and fifteen grams potassium cyanide was similarly treated as before, but instead of heating to white heat, it was heated to bright red. The result was a black oxynitride.

0.2431 gram black substance gave 0.2612 gram tungsten trioxide, or 0.2071 gram tungsten, or 85.21 per cent. tungsten.

0.3081 gram black substance gave 0.02295 gram nitrogen, or 7.45 per cent. nitrogen.

0.3724 gram black substance gave 0.0307 gram water, or 0.0272 gram oxygen, or 7.32 per cent. oxygen.

The following formula is derived : $W_7N_8O_7$.

	Calculated.	Found.
Tungsten	85.18	85.21
Nitrogen	7.40	7.45
Oxygen	7.40	7.32

A thorough mixture of ten grams tungstic acid, ten grams potassium cyanide, and ten grams finely powdered charcoal was treated under the same conditions as before, heating to bright red. A black powder was the result, mixed with the charcoal, which could not be separated, both substances having about the same density.

III.

ACTION OF CYANOGEN UPON TUNGSTIC ACID.

As potassium cyanide reduces tungstic acid to metallic tungsten at a very high temperature, it was thought that cyanogen would have perhaps a greater reducing power, and that metallic tungsten could be obtained at a lower temperature.

A porcelain boat containing tungsten trioxide was introduced into a hard glass tube ; after driving out the air from the apparatus with dry cyanogen, prepared by dropping a concentrated solution of potassium cyanide into a hot concentrated solution of copper sulphate, the boat was gently heated. At a red heat the trioxide began to change its color to brown, which soon became darker, and with the increase of temperature finally black. It is a very beautiful, glossy substance, like velvet, with a bluish tint. Like all the other oxynitrides it is oxidized with difficulty by ignition and aqua regia.

1.1140 gram black substance gave 1.1323 gram tungsten trioxide, or 0.0898 gram tungsten, or 80.61 per cent. tungsten.

0.3814 gram black substance gave 0.1473 gram nitrogen, or 3.86 per cent. nitrogen.

0.3227 gram black substance gave 0.0564 gram water, or 0.0502 gram oxygen, or 15.55 per cent. oxygen.

The following formula is derived: $W_5N_3O_{11}$.

	Calculated.	Found.
Tungsten	80.84	80.61
Nitrogen	3.69	3.86
Oxygen	15.46	15.55

This experiment was repeated several times, heating as long as twenty hours. The hard glass tube became soft, but no metallic tungsten could be obtained. The result was always an oxynitride.

SEPARATION OF MOLYBDENUM FROM TUNGSTEN.

When these two metals are together in the form of their trioxides they can be quantitatively separated by Debray's method.[1]

If molybdenum and tungsten are in solution they can be separated by Rose's method. To their solution tartaric acid is added and then a current of hydrogen sulphide is passed in, precipitating the molybdenum as sulphide (MoS_3), while tungsten remains in solution.

Friedheim and Meyer[2] found that this method is not quite satisfactory, a certain quantity of molybdenum always escaping the action of the hydrogen sulphide and thus remaining in solution.

Tungstic acid is found to be entirely insoluble in concentrated or dilute sulphuric acid, hot or cold, whereas molybdenum trioxide is very easily and rapidly dissolved, so that we have in this deportment a very simple and exact method for the separation of the two elements.

UNIVERSITY OF PENNSYLVANIA.

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[1] *Loc. cit.*

[2] *Ztschr. anorg. Chem.*, 1, 76.