A STUDY OF THE CHEMICAL BEHAVIOR OF TUNGSTEN AND MOLYBDENUM AND THEIR TRIOXIDES[1]

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INTRODUCTION.

Group VI of the Periodic System contains a sub-group of more metallic elements—chromium, molybdenum, tungsten, uranium—among the derivatives of which many interesting analogies manifest themselves. Upon comparing the metals themselves, numerous points of interest appear. Thus, beginning with chromium, possessing the lowest atomic mass as well as the highest specific heat, we observe that it oxidizes but slowly when heated in ordinary air. Molybdenum gradually changes under like conditions through its brown and blue oxides until finally it reaches its most stable form, molybdenum trioxide. The same may be remarked of tungsten, although it burns only at elevated temperatures. Uranium, on the contrary, oxidizes at relatively low temperatures. Considering this sub-group as a whole, we can probably detect greater similarities in chemical deportment and analogies in derivatives between molybdenum and tungsten than between the remaining members. To learn more of the behavior of these two metals, to disclose, if possible, differences of conduct while exposed to the influence of the same reagents, is the chief aim of the present investigation. Prefacing the actual study of the metals are some observations upon the deportment of their trioxides which are not devoid of interest, especially as they, in a measure, confirm some earlier observations. The results of this research, while largely of a qualitative character, yet demonstrate quantitative differences between tungsten and molybdenum which serve to define more clearly their position in the Periodic System.

I. *Action of Phosphorus Pentachloride upon Tungsten and Molybdenum Trioxides.*—Persoz and Bloch (*Compt. rend.*, **28**, 86, 389) assert that if the anhydrides of inorganic acids be heated

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[1] From author's thesis presented to the Faculty of the Department of Philosophy of the Univ. of Pa. for the degree of Ph.D., 1894.

together with phosphorus pentachloride, the products of the reaction will consist of the anhydride and phosphorus pentachloride. They say, for example, that under this treatment tungsten trioxide yields the derivative $WO_3.PCl_5$. Hugo Schiff (*Annalen der Chemie*, 102, Heft I) expresses the opinion that in the reaction described, the final products are compounds of equivalent amounts of phosphorus oxychloride with the chlorides of the acids; that tungsten trioxide and phosphorus pentachloride yield a reddish-brown liquid, from which phosphorus oxychloride can readily be distilled, leaving at the same time a reddish-brown residue. The latter, Schiff believes to be tungstyl (or wolframyl) chloride, WO_2Cl_2.

Teclu has made a more recent investigation of this reaction (*Annalen der Chemie*, **187**, 255). He finds that as a result of heating tungsten trioxide together with phosphorus pentachloride to 170° in a sealed tube, he obtained tungsten *hexachloride*. Its solution in phosphorus oxychloride was brown in color.

It seemed to me while engaged in a study of the behavior of tungsten trioxide in vapors of various gaseous compounds, that a repetition of this experiment of Teclu was quite desirable. To this end, equivalent weights of tungsten trioxide and phosphorus pentachloride were intimately mixed, introduced into a porcelain boat, and the latter placed in a hard glass tube contracted at intervals. The air in the tube was expelled by conducting carbon dioxide through it. On applying heat to the boat a white and very volatile crystalline sublimate made its appearance. This was caught at the extreme anterior portion of the tube. Vapors of phosphorus oxychloride were given off, recognizable by their characteristic sharp smell. A brown sublimate next formed beyond the boat. The contents of the boat were red-brown in color, melted to a dark red liquid, and gave off red-brown vapors resembling those of bromine in color. They condensed to steel-blue colored isometric forms. In every respect they indicated the tungsten hexachlóride. A careful examination with a magnifying glass revealed brown needles of the pentachloride distributed around them. These could not be removed, hence the analysis made gave a result that ranges between the theoretical requirements of the penta- and hexachloride. In order to weigh the product and prevent decomposition by contact with air, the tube was sealed at the contracted parts, allowed to cool, and then weighed, after which it was cracked by a hot rod, the contents dissolved out, and the tube refilled with carbon dioxide and reweighed.

0.2562 gram = material.
0.1559 gram = WO_3 obtained by ignition.
0.1236 gram = W equivalent.

48.25 = per cent. of tungsten obtained.
46.34 = per cent. of tungsten in WCl_6.
50.89 = per cent. of tungsten in WCl_5.

It may also be observed that the intensity of the heat applied, as well as its duration, had much to do with the quantity of brown material produced. This is not surprising, if the fact be recalled that the hexachloride passes into the pentachloride by ignition in carbon dioxide or hydrogen.

The analysis of another, bright red and more volatile product, showed it to be tungsten oxytetrachloride, $WOCl_4$.

0.0632 gram = material.
0.0423 gram = WO_3 obtained by ignition.
0.03352 gram = W equivalent.

53.05 = per cent. of tungsten obtained.
53.86 = theoretical per cent. of W in $WOCl_4$.

These experiments were repeated with essentially the same results so that I feel Teclu is justified in asserting that $1WO_3 + 5PCl_5$ give, as direct products, tungsten hexachloride and phosphorus oxychloride. My mode of procedure being somewhat different from that of Teclu will at once explain why in addition to phosphorus oxychloride and tungsten hexachloride, I also got the tungsten pentachloride and oxychloride.

An atmosphere of nitrogen instead of carbon dioxide was tried and gave the same result, but to a less satisfactory degree.

The same method of treatment was also applied to a mixture of equivalent quantities of molybdenum trioxide and phosphorus pentachloride. The reaction took place at lower temperature and was more rapid and energetic than in the case of tungsten trioxide. At first a very volatile white sublimate was deposited in the forward part of the tube, followed by copious brown vapors. On driving these over gently, a black liquid residue was left in the boat. This solidified, on cooling, forming shining needle crystals which, on examination, proved to be molybdenum pentachloride. Owing to the immediate oxidation in contact with air it was not possible to remove other adhering lower chlorides from the boat, but the latter was at once put into a tube filled with carbon dioxide and thus weighed. The contents of the boat were then dissolved in water and nitric acid and the chlorine determined by titration with tenth normal silver nitrate, potassium chromate being used as an indicator.

0.8296 gram = material.
0.51475 gram = chlorine by silver nitrate.
63.25 = per cent. chlorine found.
64.83 = theoretical per cent. Cl in $MoCl_5$.

The low result is accounted for by the presence of lower chlorides which could not be separated.

II. *Action of Silicon Tetrachloride upon the Tungsten and Molybdenum Trioxides.*—Vapors of silicon tetrachloride were passed over tungsten trioxide while the latter was subjected to the heat of a combustion furnace. It was hoped that tungsten hexachloride might be formed according to the equation:

$$2WO_3 + 3SiCl_4 = 2WCl_6 + 3SiO_2.$$

The air was first expelled from the tube by a current of carbon dioxide and then the latter was passed through the small flask containing silicon tetrachloride which was subjected to the heat of a water-bath. No action took place, however, although the operation was continued for about two hours. When a small quantity of air was admitted, tungsten oxytetrachloride and tungstyl chloride were formed.

Silicon tetrachloride was likewise without action on molybdenum trioxide. Rauter (Dissertation, Tübingen, 1893), heated the trioxides together with silicon tetrachloride in sealed tubes. His products were oxychlorides, perhaps in great part due to the presence of air.

III. *Action of Various Gases upon Metallic Tungsten and Molybdenum.* (*a*) *Action of Nitric Oxide.*—As it was not known whether nitric oxide would have a reducing or oxidizing action it was passed over the metals as well as their trioxides, heat being applied at the same time. The gas was generated by the action of nitric acid on copper and dried by passing through sulphuric acid. Tungsten trioxide was put into a porcelain boat and the latter into a piece of hard combustion tubing to which heat was applied with one or more Bunsen burners. Nitric oxide gas was passed through the tube and strong heat applied to the boat for half an hour or more. No change was produced on the tungsten trioxide. Molybdenum trioxide treated in a similar way was also unchanged.

Then finely powdered metallic tungsten was placed in the tube, all the air carefully expelled by the current of nitric oxide, and heat applied gradually. At a moderately high temperature (below red heat) action between the metal and nitric oxide began and then proceeded rapidly by means of the heat generated by the reaction, the contents of the boat becoming almost white hot. The product of the reaction was tungsten trioxide.

Metallic molybdenum was subjected to the same treatment. The reaction began only at red heat and proceeded rapidly but with less energy than in the case of tungsten. After continued strong ignition the result of the reaction was not the trioxide but the dioxide of molybdenum.

(*b*) *Action of Nitrous Oxide.*—Metallic tungsten was placed in the tube and the air carefully driven out of the latter before heat was applied. The action on the tungsten began just as the glass tube began to show signs of redness. The reaction was rapid, with evolution of light and heat, but less energetic than with nitric oxide. Tungsten trioxide was the final product.

Metallic molybdenum, treated in the same manner, required full red heat before any reaction took place. The product was again molybdenum dioxide.

(*c*) *Action of Nitrogen Peroxide.*—With tungsten, the action began at low temperature, hardly more than 300°–350°, and proceeded rapidly, but not with the evolution of as much light as with nitric oxide, probably for the reason that the reaction began at lower temperature. Tungsten trioxide was again the product.

With molybdenum the action began at incipient red heat, proceeded with more energy than in the preceding instances, and at once formed molybdenum trioxide.

Considering that nitrous oxide (N_2O) shows in its heat of formation (—17,740 Cal.) that it is an endothermic body, and that nitric oxide (NO) and nitrogen peroxide (NO_2 = —2,045 Cal.) are members of the same class, it is not surprising that the trioxides of the metals are not in any manner affected by them.

(*d*) *Action of Sulphur Dioxide.*—Tungsten began to be oxidized at moderately high temperature, but no evolution of light occurred. On continued application of high red heat, only lower tungsten oxides (blue, greenish, and brown) were formed and no trioxide was apparent. A deposit of sulphur was formed on the anterior part of the tube.

With molybdenum, action took place only at the highest temperature, no light being evolved. The oxidation proceeded slowly, and the final product was molybdenum dioxide. Sulphur was deposited on the walls of the tube.

In sulphur dioxide the oxygen is more firmly bound than in any other derivative of these two elements, and yet these metals, molybdenum and tungsten, are capable of withdrawing it.

(*e*) *Action of Methylamine.*—A current of this gas was generated by heating, in a small flask, a mixture of quicklime and methylamine hydrochloride, the gas being dried by passing over quicklime. The escaping gas was finally conducted into dilute hydrochloric acid. The metals, tungsten and molybdenum, were each heated in this gas. It was thought that a reaction might take place similar to that when metallic potassium is heated in methylamine, namely, the production of the cyanide of the metal. No change, however, took place with the metals, but the dilute hydrochloric acid into which the escaping gas was conducted became charged with hydrocyanic acid. This was undoubtedly produced by the methylamine becoming decomposed in passing through the red hot tube.

IV. *Action of Various Gases on the Tungsten and Molybdenum Trioxides.* (*a*) *Action of Ethylene.*—Tungsten trioxide heated in a stream of this gas began to be reduced at red heat, the reduction proceeding slowly. Water was condensed on the forward part of the tube, and a mirror of carbon was deposited near the boat. The fact of its being carbon was proved by afterward burning it, no residue being left. After applying heat for about an hour, a gentle stream of ethylene being maintained, the tungsten trioxide was found to be reduced to a deep blue oxide, quite homogeneous. This oxide was put into an ammoniacal solution of silver nitrate, but after standing more than an hour no metallic silver was precipitated.

Molybdenum trioxide was treated in a similar manner; reduction took place more promptly and readily. A beautiful bronze-brown colored crystalline oxide was left. This was weighed and put into an ammoniacal solution of silver nitrate and digested for some time. The oxide went into solution and metallic silver was precipitated and afterward weighed.

0.0994 gram = weight of material.
0.1538 gram = weight of silver precipitated.
0.0686 gram = corresponding amount of molybdenum, according to the proportion :
2Ag : Mo : : 0.1538 : 0.0686.
69.02 = per cent. Mo in bronze-brown oxide.
70.58 = per cent. Mo in Mo_2O_5.

This result, although not as accurate as could be desired, indicates the brown oxide to be Mo_2O_5.

(*b*) *Action of Acetylene.*—In a stream of this gas tungsten trioxide was slowly reduced at red heat, a mixture of blue and brown oxides being the result, the latter underlying the former. It may be remarked that in all the reductions and oxidations noticed, the part of the substance near the bottom, or closest to the heat, was most readily acted on, and the reaction most completely carried out.

Molybdenum trioxide was reduced more readily and promptly than tungsten trioxide, and the same bronze-brown oxide was obtained as that from ethylene. Underlying this oxide there was a shining, crystalline, metallic-looking product. In its physical properties it resembled ordinary coke, being light and porous, and easily crushed. A portion of it was put into a silver nitrate solution previously rendered ammoniacal. Metallic silver was precipitated, but there remained black particles undissolved; dilute nitric acid was added and the solution warmed till the silver was dissolved; a black residue was left undissolved. This was filtered out, dried, and ignited on platinum foil; it was completely burned, no ash being left, thus indicating its composition to be pure carbon. This being the case, it would indicate the probable formation of a *molybdenum carbide*. A quantitative analysis of this material was made as follows: a weighed quantity was put into an ammoniacal silver nitrate solution and gently warmed till metallic silver had separated out. It was then filtered through a weighed filter and dried at 100°–110°. After weighing, the precipitate was separated, as far as possible, from the filter, and treated with moderately dilute nitric acid and warmed. The silver was dissolved, leaving a black residue of carbon. This was brought upon a dried filter and weighed. Results as follows:

0.1312 gram = weight of "carbide."
0.9059 gram = weight of silver and carbon.
0.0083 gram = weight of carbon.
0.8976 gram = weight of silver by difference.

Calculating the equivalent amount of molybdenum

6 Ag : Mo : : 0.8976 : x
x = 0.1329 gram molybdenum.

This gives more molybdenum than the original weight of material, but disregarding this and taking the weights of molybdenum and carbon as found, and dividing by their atomic weights it gives 0.001384 molybdenum to 0.000691 carbon, or two parts molybdenum to one part carbon.

This would indicate a formula, Mo_2C.

Two other analyses were made, only the carbon being determined as above, the molybdenum being taken by difference. Results of second analysis are as follows:

0.0642 gram = weight of " carbide."
0.0026 gram = weight of carbon.

0.0616 gram = weight of molybdenum.

These results indicate the formula, Mo_3C.

The third analysis was as follows:

0.1255 gram = weight of "carbide."
0.0081 gram = weight of carbon.

0.1174 gram = weight of molybdenum.

This approximates the formula, Mo_2C, as found in the first analysis. It may be that it is not a definite chemical compound but only a mixture, though the yields obtained at different times for the foregoing analyses had all the same appearance and physical properties. A further investigation of this compound will be made.

(*c*) *Action of Methane.*—Tungsten trioxide was heated in methane at the highest heat of a Bunsen burner for nearly an hour with no apparent reduction. The full heat of a blast-lamp was then applied which caused the reduction of tungsten trioxide to the blue oxide, W_2O_5.

Molybdenum trioxide began to be reduced at the ordinary heat of a Bunsen flame. After heating thus to redness for about half an hour the boat was found to contain both metallic molybdenum and the dioxide, the former being underneath the latter.

(*d*) *Action of Ethane.*—Neither of the trioxides was affected by this gas, though heated for upwards of half an hour.

(*e*) *Action of Phosphine.*—Tungsten trioxide was first placed in the tube. Reduction began when the flame had been played under the boat only a few times, so that the temperature could not have been above 125°–150°. Even before any reducing effect was noticed, a faint white vapor rose from the boat but soon disappeared. The reaction proceeded rapidly, leaving a deep-blue colored product in the boat. A sublimate of phosphorus was formed on the sides of the tube. A portion of the blue oxide was weighed off and ignited to the trioxide in order to determine the percentage of tungsten.

0.0563 gram = weight of material.
0.05645 gram = WO_3 obtained by ignition.
0.04477 gram = corresponding weight of W.
79.52 = per cent. tungsten.

This result seems to correspond to the theoretical 79.70 per cent. of tungsten in the oxide W_3O_8. In another portion of the blue oxide, phosphorus was determined by digesting with nitric acid, thus converting any phosphorus into phosphoric acid, neutralizing with ammonia, and precipitating with "magnesia mixture." The amount of phosphorus found was only between one and two per cent., indicating that it was probably only mechanically admixed with the oxide. A further confirmation of this is the fact that the sides and edges of the boat were observed to be moist after brief standing in air.

Molybdenum trioxide began to show signs of reduction without any application of heat, and when heat was applied in the gentlest way the reduction proceeded rapidly. As in the case of tungsten a faint white vapor was first formed. There was left a beautiful, lustrous, crystalline product with royal-purple color. A yellow film of phosphorus was formed on the sides of the tube. A portion of the purple oxide was ignited to trioxide with the following result:

0.0452 gram = weight of material.
0.0476 gram = MoO_3 obtained by ignition.
0.03173 gram = corresponding weight of Mo.
70.20 = per cent. molybdenum.

This corresponds to the theoretical 70.58 per cent. molybdenum in the oxide Mo_2O_5.

Another portion, treated with nitric acid, was completely dissolved; only 1.99 per cent. of phosphorus was found, hence it could not have been chemically combined, but came from phosphorus that had been deposited on the boat.

Ammonia acts upon both tungsten and molybdenum trioxides more energetically, and the products of the reaction are far more complicated than in the above instances. The less basic character of phosphine compared with ammonia explains the difference.

(*f*) *Action of Arsine.*—The products were the same blue and purple oxides that were obtained with phosphine, but the reduction took place much more sluggishly. As usual, molybdenum trioxide was the more readily reduced. Much metallic arsenic was formed on the sides of the tube. Only a comparatively gentle heat was applied, owing to the ready decomposability of arsine.

A commonly occurring statement made in regard to the hydrides of nitrogen, phosphorus, and arsenic, is that basicity diminishes with rise of atomic mass; hence it is not surprising that arsine should show the sluggish behavior noted above.

V. *Reduction of the Tungsten and Molybdenum Trioxides by Magnesium, Zinc, and Aluminum.*—(*a*) *Action of Magnesium.*—Tungsten trioxide and powdered magnesium in molecular proportions were mixed and heated in a small glass tube drawn out to a point. At a low temperature the magnesium was oxidized with a little puff, light being evolved. A gray to black residue was left. This was digested with dilute hydrochloric acid which left a black or slightly grayish residue. A portion of this was weighed off and ignited to tungsten trioxide in order to determine the percentage of tungsten.

0.0858 gram = weight of material.
0.0928 gram = WO_3 obtained by ignition.
0.0736 gram = W corresponding.
85.76 = per cent. tungsten.

This corresponds to the theoretical 85.18 per cent. tungsten in tungsten dioxide, thus showing that the trioxide is reduced to dioxide by magnesium.

The reduction of molybdenum trioxide took place in a similar manner, a black residue being left. This was digested with dilute hydrochloric acid and the molybdenum determined by ignition to the trioxide.

0.0386 gram = weight of material.
0.0466 gram = MoO_3 obtained by ignition.
0.03106 gram = Mo corresponding.
80.48 = per cent. Mo.

This corresponds to the theoretical 80.00 per cent. molybdenum in the sesquioxide, and seems to indicate that magnesium reduces molybdenum trioxide to sesquioxide.

These reductions were also carried out in an atmosphere of hydrogen. At a comparatively low temperature, hardly above 350°, the action between magnesium and tungsten trioxide took place with a little flash of light and the evolution of sufficient heat to crack the combustion tube in which the operation was being performed. The residue was dark gray to black, and looked somewhat metallic. The percentage of tungsten was determined as before.

0.10085 gram = weight of material.
0.1114 gram = WO_3 obtained by ignition.
0.08835 gram = W corresponding.
87.60 = per cent. tungsten.

This seems to indicate the formation of the sesquioxide which contains 88.46 per cent. of tungsten.

Molybdenum trioxide was reduced at even lower temperature, with formation of the dioxide as shown by the following analysis:

0.1050 gram = weight of material.
0.1214 gram = MoO_3 obtained by ignition.
0.08093 gram = Mo corresponding.
77.07 = per cent. Mo.
75.00 = per cent. Mo in MoO_2.

The trioxide obtained by ignition was apparently not homogeneous; this fact taken together with the above variation from the theoretical per cent. makes the above result more than doubtful. Besides, it is hardly likely that a lower oxide would be obtained by reduction in air than in hydrogen.

(*b*) *Action of Zinc.*—The experiments with metallic zinc were carried out in the same manner as those with magnesium. Heated in air, in a drawn out tube, the mixture of tungsten trioxide and zinc dust began to react at a moderate heat (300°–400°), the reduction proceeding slowly throughout the mass without the evolution of light. The residue was a gray to brown mixture, which the estimation of tungsten indicated to be the oxide W_2O_5.

0.1169 gram = weight of material.
0.12064 gram = WO_3 obtained by ignition.
0.09568 gram = W corresponding.
81.84 = per cent. tungsten.
82.12 = per cent. W in W_2O_5.

Molybdenum trioxide mixed with zinc dust and heated was reduced more readily and at lower temperature than tungsten trioxide. The action was also more energetic, being concluded with a little explosive puff. Examination of the residue indicated it to be probably Mo_2O_5.

0.1028 gram = weight of material.
0.1109 gram = MoO_3 obtained by ignition.
0.07393 gram = Mo corresponding.
71.91 = per cent. Mo.
70.58 = per cent. Mo in Mo_2O_5.

These two experiments with zinc were then repeated in a current of hydrogen. Tungsten trioxide was easily and gradually reduced at about the same temperature as before. The product was brownish; analysis showed it to be the dioxide.

0.11295 gram = weight of material.
0.1202 gram = WO_3 obtained by ignition.
0.09533 gram = W corresponding.
84.40 = per cent. tungsten.
85.18 = per cent. W in WO_2.

Molybdenum trioxide was easily reduced at low temperature, the reaction taking place with a slight puff. The product was brownish in color. Analysis as follows:

0.1070 gram = weight of material.
0.1164 gram = MoO_3 obtained by ignition.
0.0776 gram = Mo corresponding.
72.52 = per cent. Mo obtained.
70.58 = per cent. Mo in Mo_2O_5; 75.00 = per cent. Mo in MoO_2.

Thus the product seems to be an intermediate one, but this was doubtless caused by impurities. The brownish color of the product suggests, perhaps, that it is the dioxide. If there were an oxide with the composition Mo_4O_9, it would have 72.72 per cent. of molybdenum, which is quite close to the percentage actually obtained.

(*c*) *Action of Aluminum.*—The trioxides were intimately mixed with molecular quantities of powdered aluminum, placed in a glass tube three or four inches long, sealed at one end, and heated.

With tungsten trioxide there was no action till full red heat was reached when there was a flash and slight report, cracking the tube and scattering its contents. There was not enough material left for analysis, but the walls of the tube were coated with a brownish oxide, probably the dioxide.

With molybdenum trioxide the action was similar, but took place at somewhat lower temperature and was not quite so violent. The sides of the tube were covered with dark blue oxide, probably Mo_2O_5.

These experiments were repeated in an atmosphere of hydrogen but were not successful as no reaction took place. This is undoubtedly for the reason that the temperature required is so high that the trioxides were reduced by the hydrogen before action with aluminum could take place.

At least one interesting fact is brought out by these experiments on oxidation and reduction, and that is that there is a considerably stronger affinity between tungsten and oxygen than there is between molybdenum and oxygen. This is proved by the fact that in every case the former metal was more readily oxidized while its trioxide was reduced with more difficulty. This is also further illustrated by the experiments with ferric chloride next to be described.

VI. *Reduction of Ferric Chloride by the Metals, Tungsten and Molybdenum.*—A solution of ferric chloride of known strength was made by dissolving piano wire in hydrochloric acid, oxidizing with nitric acid, and evaporating on the water-bath with addition of hydrochloric acid. It was then taken up with water, a few drops of hydrochloric acid added to dissolve basic salts, and the solution, containing 1.11293 grams iron, diluted to one liter.

First a general experiment was made by putting a small indefinite quantity of each metal, in a finely divided state, into an indefinite quantity of ferric chloride solution and a few drops of hydrochloric acid added. The solution containing molybdenum, after standing an hour or so with frequent stirring, lost the yellow color of the ferric salt, hence more was added. The liquid was then largely diluted, a little sulphuric acid added, and a titration made with potassium permanganate to ascertain if reduction of the ferric salt had taken place. A very considerable quantity of ferrous salt was found to be present. The solution containing tungsten stood for several hours but no discharge of color of the ferric salt was noticed. Titration with permanganate however showed a small amount of ferrous salt to be present.

Quantitative experiments were then made to ascertain the relation between the amounts of molybdenum and tungsten and the quantity of ferrous chloride produced. Very small quantities of the metals were taken, as the qualitative experiments showed that the amounts taken for those tests would require a very large amount of ferric solution.

(*a*) *Molybdenum.*

First Experiment:

0.0040 gram = weight of molybdenum taken.
0.01321 gram = metallic iron found by titration.
0.01382 gram = metallic iron equivalent to 0.0040 gram Mo.

according to the proportion:

Mo : 6Fe : : 0.0040 : 0.01382.
Error = 0.00061 gram.

Twenty-five cc. of the ferric solution were used containing 0.02782 gram metallic iron. The molybdenum was completely dissolved. Time of experiment one to two hours. The experiment shows also that 1Mo is equivalent to 6Fe according to the equation,

$$6FeCl_3 + Mo = MoCl_6 + 6FeCl_2.$$

Second Experiment:

0.00445 gram = molybdenum taken.
0.01566 gram = iron found by titration.
0.01557 gram = iron equivalent to 0.00445 gram Mo.
Error = 0.00009 gram.

All the molybdenum was completely dissolved.

Time, one to two hours.

Twenty-five cc. of ferric solution used.

Third Experiment:

0.0867 gram = molybdenum taken.

The action with this larger quantity of metal was very slow, and after standing for about forty hours there was still a considerable amount of metal not dissolved.

Fourth Experiment:

In this experiment a more concentrated solution of ferric chloride was used containing 11.4022 grams metallic iron to one liter.

0.07857 gram = molybdenum taken.
0.26702 gram = iron found by titration.
0.27499 gram = iron equivalent to 0.07857 gram Mo.
Error = 0.00797.

That is, only 97.10 per cent. of the molybdenum had gone into solution. This solution stood forty-eight hours and there were still small solid particles to be noticed suspended in the solution.

It seems from the foregoing experiments that complete solution and reduction do not take place in a reasonable length of time, except with small quantities of the metal. The results of the first two experiments are interesting as throwing further light on the valency of molybdenum, and in suggesting an excellent method for the accurate determination of the atomic mass of this metal as compared with iron.

(*b*) *Tungsten.*

First Experiment:

0.0042 gram = tungsten taken.
0.0007345 gram = iron found by titration.
0.00767 gram = iron equivalent to 0.0042 gram tungsten.

according to the proportion :

W : 6Fe : : 0.0042 : 0.00767
9.57 = per cent. of tungsten dissolved.

Time, two hours.

Second Experiment:

0.00446 gram = tungsten taken.
0.001958 gram = iron found by titration.
0.00814 gram = iron equivalent to 0.00446 gram tungsten.
24.05 = per cent. of tungsten dissolved.

Time, four hours.

Third Experiment:

0.00516 gram = tungsten taken.
0.002692 gram = iron found by titration.
0.009422 gram = iron equivalent to 0.00516 gram tungsten.
28.57 = per cent. of tungsten dissolved.

Time, six hours.

Fourth Experiment:

0.00475 gram = tungsten taken.
0.005237 gram = iron found by titration.
0.00863 gram = iron equivalent to 0.00475 gram tungsten.
60.69 = per cent. of tungsten dissolved.

Time, eight hours.

These experiments were made with the more concentrated ferric chloride solution. There is seen to be a gradual increase in the amount of iron reduced, roughly proportional to the time ; but complete solution of tungsten could not be obtained, although small portions were allowed to remain over forty-eight hours in the ferric solution.

This reducing power of molybdenum and tungsten, indicated in the preceding experiments, is further corroboration of the experiments made by Smith (*Ztschr. anorg. Chem.*, **1**, 360), with these metals and solutions of silver, gold, and mercury salts. It is further additional comparative evidence of the conduct of the metals of this subdivision of group VI. Of the behavior of chromium in this direction we have no experimental evidence, but of uranium it is known that it reduces salts of tin, platinum, gold, copper, mercury, and silver to the metallic condition. With molybdenum the reduction with these metals proceeds quite rapidly, but the speed diminishes with rise in atomic mass, so that the sluggish action of tungsten in ferric salts is not surprising.

THE DETERMINATION OF SULPHUR IN PYRITES.

A REPLY TO DR. LUNGE.

BY THOMAS S. GLADDING.

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IN this JOURNAL (June *1894*) I published an investigation of the several methods of estimating sulphur in pyrites. As a result of that investigation I rejected all other methods and recommended, in the strongest terms, the general scheme published by Dr. Lunge in his "Alkali-makers' Handbook." At the same time I advised a few minor modifications as conducive to greater certainty and ,accuracy. In this JOURNAL (March *1895*) Dr. Lunge makes a vigorous attack upon each and every one of these modifications. An examination of his paper brings out the important fact that he admits that every modification proposed is accurate in its nature with one single exception. Unfortunately for Dr. Lunge, the single feature selected for condemnation is the one most easily capable of rigid and positive proof as to its absolute accuracy. I shall reserve the consideration of this point and take up in order the modifications to which such strenuous objection is made.

He objects to the use of one gram instead of half a gram. In reply I have found that by my method one gram is as easily handled as one-half gram and double the accuracy is attained in consequence. He objects to the use of a bromine solution instead of aqua regia as a solvent for pyrites. This substitution was made for the reason that quite often when using aqua regia I was annoyed by the separation of free sulphur. Since adopt-