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## Investigation of the Blue Oxide of Molybdenum with New Process for the Preparation of Metallic Molybdenum

Allen Rogers

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INVESTIGATION  
of  
THE BLUE OXIDE OF MOLYBDENUM  
with  
NEW PROCESS FOR THE PREPARATION  
of  
METALLIC MOLYBDENUM

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THESIS

Presented to the Trustees and Faculty of the  
UNIVERSITY OF MAINE  
For the Degree of Master of Science.

by

ALLEN ROGERS

HAMPDEN----- MAINE.

June, 1900.

## PREFACE.

The object of this investigation was to ascertain the reason for stannous chloride producing a precipitate, when added to a solution of ammonium molybdate; from this, to get a qualitative test for tin, and if possible, a quantitative process.

This has been accomplished and many interesting facts brought to light. The nature of the above precipitate has been studied, and various methods for the preparation of metallic molybdenum have been investigated. The results of which will be discussed in this thesis and that of of Mr. F. H. Mitchell.

Allen Rogers.

## HISTORICAL.

Molybdenite was for a long time considered to be identical with graphite; it was not until 1778 that the difference was established. <sup>Sheele</sup> showed at that time, that the mineral now called molybdenite gave a white ash on oxidation, while graphite does not. The presence of molybdenum in its oxygen compounds was thus foreseen by him.

It was not however isolated until five years later, when Hjelm obtained it from the sulphide (1783).

The various combining relations which the different members of this group of elements, comprising molybdenum, tungsten and uranium, show toward other elements have been fully understood of recent years.

The admirable work of Berzelius, on molybdenum compounds has been supplemented by that of Kruss

on the sulphides, and Mathman on the oxides, as well as, by the earlier investigations of Blomstrand, Debray and Lichti.

## INVESTIGATION.

Molybdenum occurs in nature mostly in the form of the sulphide, as molybdenite, which as has been noticed, resembles graphite in physical appearance.

It is never found uncombined, In the combined condition it is found in many different forms.

The atomic weight of molybdenum has been a subject of investigation for many years; thus, we find it given from 95.4 to 96.2. In 1897, however, the Belgian Academy of Science awarded a special Stras prize to M. Ad. Vandenberghe, for his determination of its atomic weight. The memoir has recently been published, and the data are now available.

Vandenberghe starts with molybdenum dibromide scrupulously purified. From this he obtains metallic molybdenum, by careful reduction in hydrogen at a

white heat. The atomic weight was determined by the oxidation of molybdenum to molybdenum trioxide, by means of pure nitric acid.

The values are

Molybdenum equals	96.069,	when oxygen is	16.
"	"	95.829,	" 15.96
"	"	95.349,	" 15.88

For all practical purposes the value of molybdenum equals 96 may be assumed.

Molybdenum has a sp. gr. of 8.56. It does not melt in the oxyhydrogen blow-pipe at the temperature at which platinum does. It can, however, be melted readily in the electric furnace.

Wohler prepared molybdenum, by reducing the chloride in a current of hydrogen. By this means he obtained it, <sup>in</sup> as a dull silver colored, somewhat malleable plates. The metal as obtained from molybdenum trioxide, by reducing in a current of hydrogen, at a high

heat, is lustrous. If the reduction is effected at a lower temperature, an ashen grey powder is obtained, which becomes metallic when rubbed. The metal as obtained by Debray was silver white, and hard as topaz. Molybdenum combined with oxygen to form various oxides, the most common of which is the trioxide, or  $\text{MoO}_3$ . By treating this oxide with ammonium hydroxide and making acid with nitric acid, we obtain a solution of ammonium molybdate, as used in the laboratory. By acting upon this solution, diluted with stannous chloride, we obtain a blue precipitate which we are to investigate.

#### PREPARATION OF THE BLUE OXIDE.

To 100 g. of molybdenum trioxide add a sufficient quantity of ammonium hydroxide to dissolve it, add about the same quantity of water, then make slightly acid with nitric acid. The solution should then be made diluted with about five times its volume

of water. To this solution add 15 cc. to 20 cc. of 10 % solution stannous chloride; the very heavy precipitate which forms settles, and is washed several times by syphoning off the supernatant liquid. After washing, the precipitate is thrown upon a plaited filter, and allowed to drain. It is removed from the filter paper, while yet moist, into an evaporating dish, and being placed in an oven, is dried at 100°C.

The first thing which presents itself, is the formula of the precipitate, which we have just prepared. The first method that we used, was to change the precipitate to the metallic condition, by heating <sup>in</sup> a current of hydrogen, for one hour with a Bunsen burner; allowing it to cool, and weighing; repeating the operation until the weight is constant. In this way, the metallic molybdenum corresponded to the oxide,  $Mo_2O_3$ .

The way in which this process was carried out, was to place some of the precipitate in a porcelain

boat, insert into an ignition tube, and heat. This was tried a number of times with the same results. The action did not take place <sup>as</sup> readily, in the blue oxide which had been thoroughly dried, as in the hydrated form. On account of this, we found it advantageous to moisten the oxide after weighing, allowing it to stand to become hydrated, which took place in about an hour. In every case, the action was much hastened.

Having tried the reduction of the blue oxide to the metallic condition, as a method to determine the formula of said oxide, and obtaining uniform results, it seemed well to try some other methods to verify results obtained above.

The second method was, by the oxidation of the blue precipitate to molybdenum trioxide,  $\text{MoO}_3$ , by the use of nitric acid.

Method:- Weigh out from .5 to 1. g. of the blue oxide (which has been thoroughly dried) into a

weighed porcelain evaporating dish, treat with strong nitric acid, heat on the water bath until the blue particles completely disappear, and there remains only a white powder, which is the trioxide of molybdenum. Evaporate to dryness and place in the steam oven for two hours. When dry, place in the dessicator to cool; then weigh, and calculate as  $\text{MoO}_3$ .

Calculation:-  $\text{Mo}_3\text{O}_8 : \text{MoO}_3 :: \text{Weight of Mo}_3\text{O}_8 : x$ ;  
 $x$  equals the amount of  $\text{Mo}_3\text{O}_8$  to be obtained.

Results obtained:-

Wt. of Blue Oxide.	Wt. of $\text{MoO}_3$	Cal.	Wt of $\text{MoO}_3$ .
.100 grams.	.1032 gram.		.1037 gram.
.941 "	.977 "		.977 "
1.0624 "	1.0635 "		1.0635 "

Having noticed the ease with which the blue oxide gives up its oxygen, the question now arises, : can we use this substance to prepare metallic molybdenum? And after investigation, we answer in the affirmative.

#### METHOD OF PREPARING METALLIC MOLYBDENUM.

The first method used has already been explained, that is, by heating the oxide in a porcelain boat in a current of hydrogen. In this the molybdenum was obtained, as an ashen gray powder, which looks metallic in the sunlight.

second method:- Place some of the precipitate in a porcelain boat, and insert into an iron tube, which is heated in a furnace to bright redness, the air first being driven out with a current of carbon dioxide, then with hydrogen.

The boat should remain in the tube for about 15 minutes with a free supply of hydrogen. The product obtained from this process is a bright silver colored mass, which is mixed with a small quantity of molybdenum trioxide. By heating this mass longer, the trioxide is converted into the metallic condition. The heat and reduced molybdenum acted upon the porcelain boat, making it very porous, so that the boat was saturated with the reduced metal and

the trioxide.

Third Method:- In giving this method, I wish to call your attention to a very easy method by which I have been able to reduce a great many substances, where it was not easy to reduce in other ways, and which may be applied <sup>in</sup> any laboratory provided with electricity.

Introduce into the block a twenty ampere fuse, and connect one wire with the resistance. Now arrange the apparatus as in the figure. (A) is a three necked flask. (B & B') are the carbons which are held in position with asbestos plugs. B' has a cavity at the end into which the substance to be reduced is placed. At C is an inlet and outlet tube, through <sup>which</sup> hydrogen is passed.

Introduce the substance to be reduced, and pass in hydrogen until the air is expelled, then connect D with the resistance, and with the tap wire. <sup>on</sup> turn <sup>on</sup> the current and allow it to pass for one minute, let cool and examine the residue. By this pro-

cess the  $\text{Mo}_3\text{O}_7$  was reduced to metallic molybdenum in forty seconds. Thus prepared it is very hard, and dull silver gray in appearance. The current used was twelve amperes.

Fourth Method:- This method consists in the reduction brought about in the electric furnace. The current used in this case was about forty amperes. At this point it may be well to note the manner in which a furnace may be made, easily, in the laboratory, and one which has been found to give very good results. The foundation, fig. 2, is made of fire brick, and placed on a support; B is a block of lime in which three holes are cut as in Fig. 3. D & D' are for the insertion of the carbons C & C'. E is for the introduction of hydrogen through H, which is a common clay pipe. C & C' are connected with the resistance and feed wire, as in the third method. The reduction takes place in about the same time as in the above. The mass is allowed to cool in a current of hydrogen and is the same in appear-

ences in the third method.

The trioxide of molybdenum was acted upon in various ways, as we have noticed for the blue oxide, but in every case the action was much more rapid for the  $\text{Mo}_3\text{O}_8$  than the  $\text{MoO}_3$ . The electric furnace is coming into use very extensively, and by the use of it, many of the metals have been prepared.

Among some of the molybdenum compounds acted upon was molybdenite. This gave off fumes of sulphur, which were converted into sulphur dioxide, the molybdenum was changed to the trioxide, and finally to the metallic condition.

During the investigation, while trying to determine the amount of tin in the mineral cassiterite, which is the oxide of tin,  $\text{SnO}_2$ , a blue color was produced, which proved to be due to the presence of molybdenum; and when, after dissolving the mineral in hydrochloric acid, it was treated with zinc to throw out the tin, the stannous chloride formed acted on the molybdenum present, reducing it

to the blue oxide. This is the only proof that I have been able to get, that molybdenum exists in the cassiterite. This blue color is produced when even a minute quantity of molybdenum is present. I have been able to detect .000012 g. with ease in one cubic centimeter. This action has led to a very delicate test for molybdenum. There are a few substances which produce the blue color, but none so well as the stannous chloride.

#### PROCESS FOR TESTING MOLYBDENUM.

The process used to test for molybdenum was, - to place the substance in a test-tube, add HCl and heat until all has dissolved that will. Add a little water and zinc, heat again, when the acid is nearly neutralized, the blue color begins to show, and continues to intensify, until a deep blue color is produced. The above seems likely to be available as a quantitative test for molybdenum, but I have not as yet, carried out the process sufficiently to determine its desirability for that purpose.

## SUMMARY.

Although this thesis takes up only a part of the work of the investigation carried on, it shows that a few things have been brought to light, which may give us a foundation on which we may be able to erect a valuable structure. The precipitate, and its formula has been determined. The occurrence of the precipitate has given us a delicate test for tin. From this precipitate, we have been able to obtain metallic molybdenum, with very little trouble.

Finally, we have obtained a very delicate qualitative test for molybdenum, and one which may result in a quantitative process for that metal.

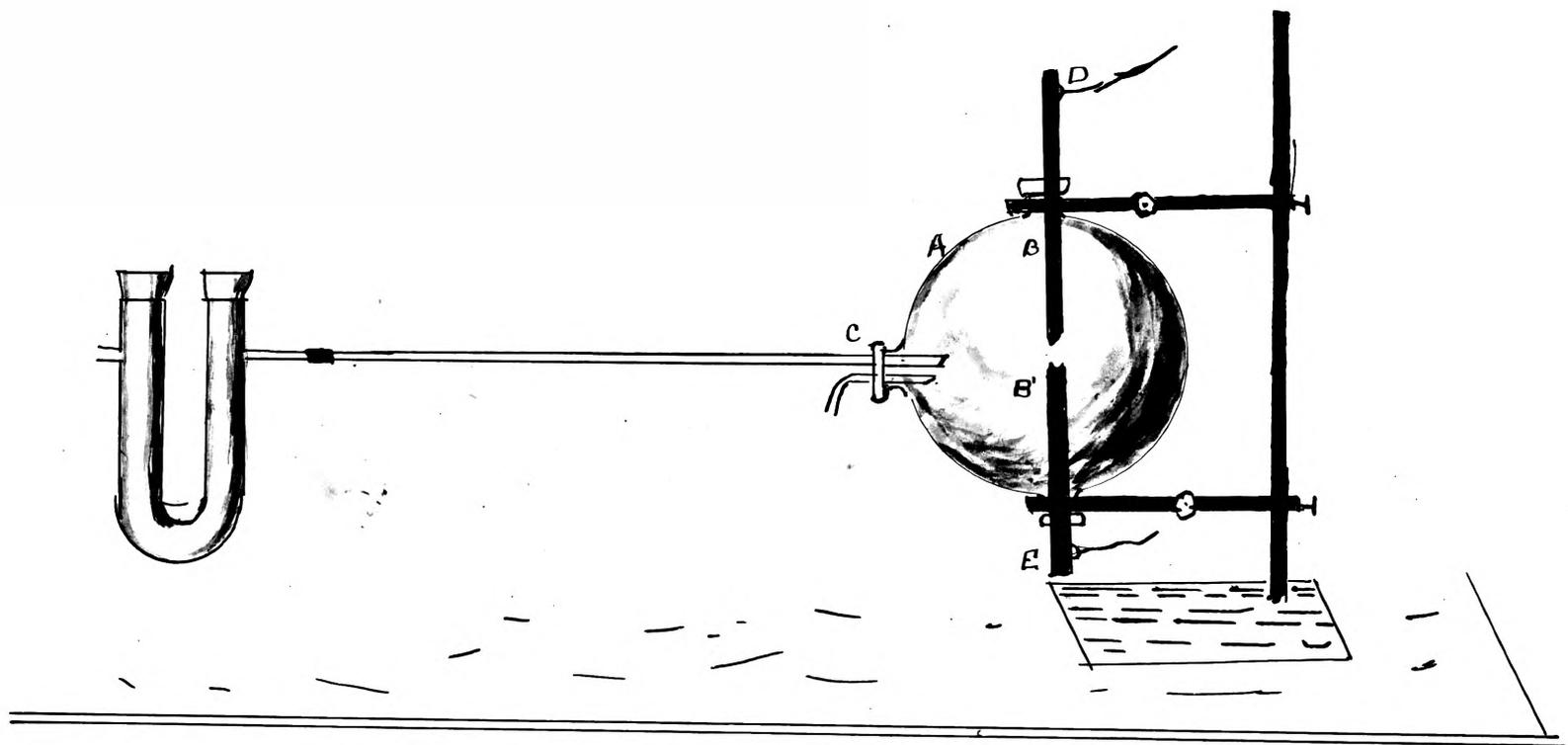


FIG. 1.

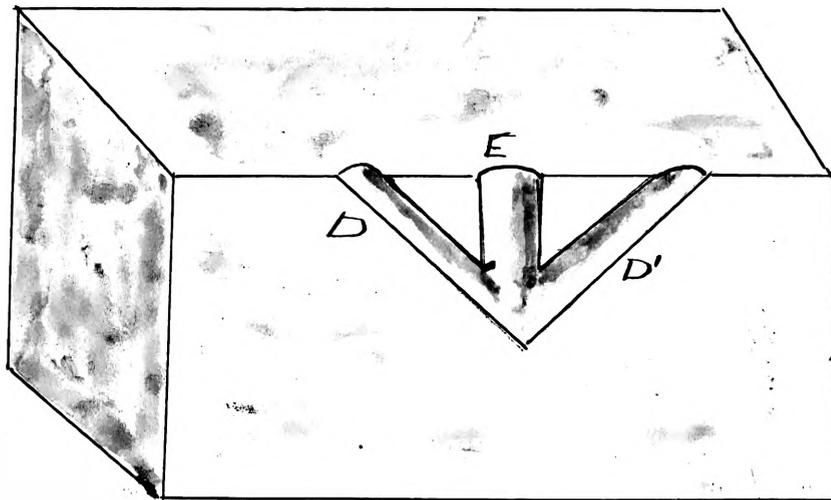


FIG 3

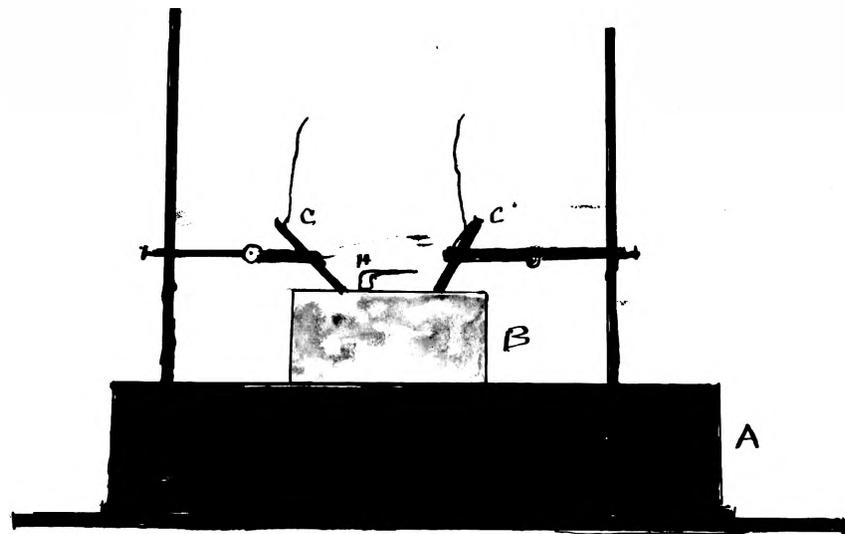


FIG 2

[REPRINTED FROM THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY,  
VOL. XXII, No. 4. APRIL, 1900.]

#### NOTE.

*Test for Tin.*—I have found the blue color produced by the action of stannous chloride upon ammonium molybdate to serve as a very delicate test for tin; and have had my students use it for the last few months with very good results. In working this process one should go through the usual separation, filter off the black flakes, dissolve them in hydrochloric acid, then take a few drops of this solution and add a little water and then some ammonium molybdate. Blue color shows the presence of tin.

To determine the delicacy of the test, I used a standard solution of stannous chloride, and noticed results obtained from the mercuric chloride and ammonium molybdate tests.

Strong solution of  $\text{SnCl}_2$  gives a heavy blue precipitate; with mercuric chloride a heavy white precipitate.

A solution of  $\text{SnCl}_2$  containing 0.000021 gram to 1 cc. gives a deep blue color; with mercuric chloride a faint cloudiness.

A solution of  $\text{SnCl}_2$  containing 0.0000042 gram to 1 cc. gives a faint blue color with ammonium molybdate; with mercuric chloride not even a trace of cloudiness.

I find that the ammonium molybdate as prepared in the laboratory gives the best results.

ALLEN ROGERS.