

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MINNESOTA]

## STUDIES ON THE IGNITION OF PRECIPITATES. II<sup>1</sup> THE CONVERSION OF MOLYBDENUM SULFIDE TO OXIDE, AND THE VOLATILITY OF MOLYBDENUM TRIOXIDE

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There are many contradictions in the literature regarding the temperature at which molybdenum trisulfide can be converted to the trioxide without danger of loss by volatilization of the oxide. Treadwell<sup>2</sup> states that there is no danger of loss if a spacious porcelain crucible is used and it is heated with a free flame not beyond dull red heat. Wolf<sup>3</sup> claims that sufficient volatilization occurs to render the operation inaccurate if the temperature is allowed to rise above 450°. Fischer and Weise<sup>4</sup> maintain that temperatures above 400° are dangerous. Johnson<sup>5</sup> ignites in a large porcelain crucible at 500° to 550°. Scott<sup>6</sup> states that the trioxide sublimes at bright red heat, and Groschuff<sup>7</sup> says it begins to sublime in the neighborhood of the melting point (791°). Bonardi<sup>8</sup> holds that molybdenum trioxide can be completely volatilized at 700°, and that volatilization begins at about 500°. Other authors use such phrases as "Ignite at a low temperature;" "heat with a low flame," etc.

The need for accurate data on the volatilization point of molybdenum trioxide, and the best condition for the quantitative conversion of the sulfide to oxide is apparent.

### Experimental Part

In preparing molybdenum trioxide, the purest ammonium molybdate was recrystallized, finally dissolved in the minimum amount of water, and boiled with a slight excess of redistilled concd. nitric acid to decompose the ammonium salts. The molybdic acid was filtered and well washed with cold water. The dried material was further purified by sublimation. For this purpose the platinum dish containing the oxide was so fitted into a hole in an asbestos plate that the upper edge of the dish extended about 1.2 mm. above the surface of the board. The platinum dish was covered by a large inverted quartz dish, resting on the surface of the asbestos plate. The material in the platinum

<sup>1</sup> The contribution on the oxides of praseodymium by Brinton and Pagel, *THIS JOURNAL*, **45**, 1460 (1923), may be regarded as the first paper of this series.

<sup>2</sup> Treadwell-Hall, "Treatise on Analytical Chemistry," John Wiley and Sons, New York, 1919, vol. II, p. 284.

<sup>3</sup> Wolf, *Z. angew. Chem.*, **31**, 140 (1918).

<sup>4</sup> Fischer and Weise, *Z. anal. Chem.*, **51**, 537 (1912).

<sup>5</sup> Johnson, "Chemical Analysis of Special Steels," John Wiley and Sons, New York, 1920, p. 157.

<sup>6</sup> Scott, "Standard Methods of Chemical Analysis," Van Nostrand Co., New York, 1922, p. 317.

<sup>7</sup> Groschuff, *Z. anorg. Chem.*, **58**, 113 (1908).

<sup>8</sup> Bonardi, *Bur. Mines, Bull.*, **212**, 83 (1923).

dish was heated to fusion over a blast lamp. The light fluffy sublimate had a slight greenish tinge. It was suspended in water and ammonia gas was passed in. All but a trace dissolved on warming. The ammonium molybdate thus obtained was treated as before with nitric acid. The resulting oxide showed traces of ammonium compound by Nessler's test, so it was repeatedly boiled with nitric acid and water, finally filtered and heated to redness in a quartz dish. The ignited mass looked a little grayish, so it was made into a paste with pure nitric acid and heated in a muffle to 200-300°. After grinding finely the slightly yellow greenish powder it was heated for two hours to 400°. The greenish tinge had then disappeared, and it was believed that the molybdenum trioxide was pure.

For heating, a 20cm. tubular electric furnace carrying a 40cm. transparent fused silica tube was used. The temperature could be maintained within a maximum variation of 10° for hours at a time. Temperatures were measured by means of a base-metal thermocouple, which had been calibrated against a standard platinum-metal couple calibrated and certified by the United States Bureau of Standards.

Samples of the pure molybdenum trioxide were placed in porcelain boats and heated under the conditions shown in Table I. To aid in the detection of any sublimate in the cool parts of the tube a slow current of dry, purified air was passed through the tube during the heating, so that any vaporized molybdenum trioxide would be deposited at one end of the tube.

TABLE I

TESTS ON THE VOLATILIZATION OF MOLYBDENUM OXIDE					
Trial No. 1 MoO <sub>3</sub> taken: 0.5913 g.			Trial No. 1 MoO <sub>3</sub> taken: 0.5913 g.		
Time at a given temp. Hours	Temp. ±5°	Loss in weight Mg.	Time at a given temp. Hours	Temp. ±5°	Loss in weight Mg.
4	375-400°	0.1	3	525-565	0.1
10	400	.0	2	585	.2
3	430	.0	10	580	.2
3	450	.0	2.5	610-620	.7
6	470	.0	5	610	1.5
9	490	.0	3	640	1.1
5	505	.1	11	640	4.9
3	535	.0	0.5	745	29.5
3	520	.1	..	...	..
Trial No. 2 MoO <sub>3</sub> taken: 0.9489 g.			Trial No. 3 MoO <sub>3</sub> taken: 0.4991 g.		
		Gain			Loss
3	535	0.2	4	500	0.0
15	550	.2	5	525	.1
11	495	.0	12	490-525	.0
8	505	.1	5	495	.0
12	550	.3	11	555	.2
12	560	.1	3	600	.0
5	590	.5	14	570-590	.4
11	645	4.6	4	650	1.4

In none of the three trials was there visible sublimation until after a temperature of 600° had been exceeded. The weight relations show that there is absolutely no loss of molybdenum trioxide below 500°, while be-

tween 500° and 600° the loss is not greater than 0.1 mg. per hour for precipitates of the size usually encountered. Thus for practical purposes it seems safe to employ any temperature up to 600°. Above 600°, however, the loss becomes appreciable, and this temperature should not be exceeded.

The conversion of precipitated molybdenum trisulfide to the trioxide is the practical problem encountered in analytical work. Various oxidizing agents such as mercuric oxide,<sup>9</sup> lead oxide and ammonium nitrate,<sup>10</sup> and nitric acid<sup>11</sup> have been proposed as an aid to complete oxidation of the sulfur and the carbon of the filter paper. The use of these reagents makes the process more complicated, and in view of our finding that a temperature of 600° was safe for the ignition of the oxide it seemed probable that the use of oxidizing agents could be dispensed with.

A "muffle" was made of a 50cc. porcelain crucible, by covering the bottom (inside) with a disk of asbestos board 4 mm. thick. A support for the crucible containing the precipitate was made from a Nichrome triangle, bent to fit inside the outer crucible, and supported by bending the end wires over the rim of the outer crucible.

To establish the practical working conditions for the ignition, 0.4 g. of pure dry molybdenum trioxide was placed in a porcelain crucible inside the "muffle," and the latter, with its bottom 8 cm. above the top of the burner, was heated with the full flame of a Tirril burner. Igniting for one-hour periods in this way gave losses of about 0.0006 g. per hour. With a more moderate flame, not exceeding 12.5 cm. in height, the maximum loss after one hour's heating was not over 0.0001 g. Without the asbestos shield in the bottom of the crucible the losses were considerable. Portions of a carefully standardized solution of ammonium molybdate, made from the highly purified oxide, were diluted to 150 cc. and 5 cc. of 6 *N* ammonium hydroxide was added. The solutions were saturated with hydrogen sulfide, then acidified with sulfuric acid, and warmed to flocculate the precipitates, after which the molybdenum trisulfide was filtered on paper and well washed with hydrogen sulfide water. The wet precipitates were ignited to constant weight in the "muffle" as before described, using a 12.5cm. flame of a Tirril burner. The results are shown in Table II.

Several of the filtrates were tested for complete removal of molybdenum by evaporating with nitric acid, dissolving the residue in dil. ammonium hydroxide, saturating with hydrogen sulfide, and acidifying with sulfuric acid. The additional precipitate thus obtained never exceeded 0.2 mg., and it was usually unweighable.

<sup>9</sup> Ref. 2, p. 286.

<sup>10</sup> Seligssohn, *J. prakt. Chem.*, [1] 67, 472 (1856).

<sup>11</sup> Hundeshagen, *Z. anal. Chem.*, 28, 142 (1889). Binder, *Chem.-Ztg.*, 42, 255 (1918).

TABLE II

## TESTS ON THE CONVERSION OF MOLYBDENUM SULFIDE TO OXIDE

MoO <sub>3</sub> taken G.	MoO <sub>3</sub> found G.	Difference G.	MoO <sub>3</sub> taken G.	MoO <sub>3</sub> found G.	Difference G.
0.0799	0.0799	0.0000	0.1598	0.1598	0.0000
.0799	.0802	+ .0003	.1598	.1601	+ .0003
.0799	.0798	- .0001	.1598	.1597	- .0001
.0799	.0799	.0000	.1598	.1600	+ .0002
.0799	.0800	+ .0001	.2397	.2393	- .0004
.1598	.1594	- .0004	.2397	.2390	- .0007

In all cases where there was less than 0.1 g. of molybdenum trioxide, constant weight was attained in one hour of heating. For larger amounts as much as two hours was in some cases necessary, but never more. The ignited residues had a very slightly grayish cast. After the filters were once placed in the muffle they required no further attention until they were ready to be cooled and weighed.

An electrically-heated muffle fitted with an armored, high-temperature thermometer, or thermocouple, would of course be ideal; but the arrangement described above can be fitted up in a few minutes with materials to be found in any laboratory.

## Summary

The maximum temperature at which molybdenum trioxide can be safely ignited without fear of appreciable loss by volatilization has been established as approximately 600°.

Conditions and apparatus for accurately and conveniently converting molybdenum trisulfide to trioxide have been described.

The use of oxidizing agents to aid the conversion of the sulfide to oxide is unnecessary.

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## THE CRYSTAL STRUCTURE OF TETRAGONAL LEAD MONOXIDE

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Lead monoxide, PbO, may be prepared in two modifications, a yellow, rhombic form and a red, tetragonal form. Of these the former is the more stable<sup>1,2</sup> at higher, and the latter more stable at ordinary temperatures. It has been suggested<sup>3</sup> that the differences between these forms are due simply to a difference in state of subdivision; but this hypothesis

<sup>1</sup> Geuther, *Ann. Chem.*, **219**, 56 (1883).

<sup>2</sup> Ruer, *Z. anorg. Chem.*, **50**, 265 (1906).

<sup>3</sup> Glasstone, *J. Chem. Soc.*, **119**, 1689, 1914 (1921).