This work was carried out under the direction of Professor Edmund H. Miller, and it is with great pleasure that I take this opportunity of thanking him for the counsel and kind encouragement which he extended to me throughout the research.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 85.]

ON THE REDUCTION OF MOLYBDENUM BY ZINC AND THE RATIO OF BISMUTH TO MOLYBDENUM IN BISMUTH AMMONIUM MOLYBDATE.

BY EDMUND H. MILLER AND HENRY FRANK.

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NUMEROUS investigations have been made on the reduction of molybdenum by zinc in a reductor. W. A. Noyes[1] and Frohman came to the conclusion that the reduction corresponded to a salt of the oxide Mo_2O_3, provided that the air is displaced by carbon dioxide in the titrating flask. Blair[2] and Whitfield, however, although they followed Noyes and Frohman's conditions, could never attain a reduction equivalent to the oxide Mo_2O_3, but almost invariably obtained reduction equivalent to an oxide, $Mo_{24}O_{37}$. Other investigators have either confirmed the results of Blair and Whitfield or come to the conclusion that the reduction did not proceed even as far as $Mo_{24}O_{37}$, but to a point corresponding to an oxide of the formula $Mo_{12}O_{19}$. Drown,[3] however, by the use of 100-mesh zinc in a closed flask, has obtained a reduction corresponding to the oxide Mo_2O_3.

It was the object of this work to study the extent of the reduction produced in a reductor when the conditions, such as the length of the column of zinc, the acidity, the temperature and the atmosphere were varied, and to see whether the oxide Mo_2O_3 could be reached (Part I). And also, when the conditions for a definite degree of reduction were obtained, to apply these to the confirmation of the ratio of bismuth to molybdenum in the new bismuth

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[1] This Journal, **16**, 553.

[2] *Ibid.*, **17**, 747.

[3] Blair's "Chemical Analysis of Iron," 4th edition, p. 99.

ammonium molybdate described by Riederer in the preceding article (Part II).

PART I.

About 6 liters of ammonium molybdate solution were made containing 10 grams of $(NH_4)_6Mo_7O_{24}.2H_2O$ per liter. This was standardized by precipitating as lead molybdate, giving the following values per cubic centimeter in grams of molybdic oxide, 0.008032 : 0.008034 : 0.008037 : 0.008026 : 0.008024; average, 0.008031.

Neither conversion of the sulphide to oxide nor evaporation of the solution with nitric acid gave concordant results, so, to obtain a check by another method, Smith's electrolytic method was followed exactly, which gave for two determinations 0.008020 and 0.008035 gram of molybdic oxide per cubic centimeter, thus confirming the accuracy of the lead molybdate determinations.

A sufficient quantity of potassium permanganate solution was prepared and standardized both against ferrous ammonium sulphate and oxalic acid. The value was 0.004546 gram of iron per cubic centimeter.

According to the reactions

$$5Mo_{12}O_{19} + 34KMnO_4 = 60MoO_3 + 17K_2O + 34MnO, \tag{1}$$

$$5Mo_{24}O_{37} + 70KMnO_4 = 120MoO_3 + 35K_2O + 70MnO, \tag{2}$$

$$5Mo_2O_3 + 6KMnO_4 = 10MoO_3 + 3K_2O + 6MnO, \tag{3}$$

the value of this permanganate solution in grams of MoO_3 is

0.004133. $12Mo = 34Fe$. $Mo_{12}O_{19}$ to MoO_3, (1)
0.004015. $12Mo = 35Fe$. $Mo_{24}O_{37}$ to MoO_3, (2)
0.003903. $12Mo = 36Fe$. Mo_2O_3 to MoO_3, (3)

using the atomic weights of 1903, Fe, 55.9 and Mo, 96.

Experiment I.—An ordinary reductor was used with a 10-inch column of unamalgamated zinc (20-30 mesh); the bulk of the solution was 200 cc.; the acidity, 10 cc. concentrated sulphuric acid; the temperature, 75° C. The molybdate solution was followed immediately by 100 cc. of hot water and titrated at once in the reductor flask. The permanganate required for the iron in the zinc was deducted throughout. The time required for the solution to pass through the reductor was two minutes in this case.

The results were:

Ammonium molybdate. cc.	$KMnO_4$. cc.	MoO_3. Gram.	Value of $KMnO_4$ per cc. in grams of MoO_3.
20	40.0	0.1606	0.004015
25	49.8	0.2007	0.004030
21	41.8	0.1687	0.004027

The results of this first experiment, though not very concordant, show an approximation to the value 0.004015 which corresponds to reduction equivalent to $Mo_{24}O_{37}$.

Experiment II.—Here and throughout the rest of the work a long glass tube, provided with a glass stop-cock, was used as a reductor. In this set of experiments, the length of the column of zinc was 15 inches; the time of passage 5-7 minutes; the temperature, 75° C.; the bulk of solution, 200 cc.; of wash water, 100 cc.; the acidity, 10 cc. of concentrated sulphuric acid.

The results were as follows:

Ammonium molybdate solution. cc.	$KMnO_4$. cc.	MoO_3. Gram.	Value of $KMnO_4$ in grams of MoO_3.
20	40.00	0.1606	0.004015
22	44.10	0.1767	0.004007
12	24.28	0.0964	0.003970
21	42.20	0.1687	0.003998
20	40.00	0.1606	0.004015
20	40.20	0.1606	0.003995
20	40.12	0.1606	0.004003
		Average,	0.0040004

With the longer time and the longer column of zinc, the results show a satisfactory agreement and that the reduction has proceeded slightly beyond $Mo_{24}O_{37}$. The factor for the MoO_3 standard calculated from these results is 0.88, the factor for phosphorus in the yellow precipitate 0.01579.

Similar experiments were made at a temperature of 25° C., with both a long and a short reductor, but the results were unreliable.

Experiment III. Reduction and Titration in an Atmosphere of Carbon Dioxide.—The apparatus consisted of a 500 cc. wide-mouthed bottle, fitted with a three-hole, rubber stopper. Through one hole the end of the reductor was passed, through the second the long tip of a burette, while the third was provided with a tube connecting with the suction. The procedure was as follows: The air in the reductor was first displaced by sucking a stream of carbon dioxide through it and then filled with air-free water to a height of 3 inches above the level of the zinc. Five grams of sodium bicarbonate were placed in the bottom of the bottle and then all the air replaced by carbon dioxide from a generator; then 5 cc.

of dilute sulphuric acid were poured in the bottle and the cork, containing the burette filled with permanganate and the reductor, fitted tight. The suction was turned on, and 100 cc. of hot, acidulated water (5 cc. of sulphuric acid in 100 cc.) passed through the reductor, followed immediately by the molybdate solution, and this in turn by 100 to 150 cc. of wash-water containing 3 cc. of sulphuric acid, taking care that the solution never went below the level of the zinc. When sufficient wash-water had passed through, the stop-cock of the reductor was turned off and the titration made at once. A blank was run and the iron in the zinc allowed for. The important conditions were: Time of passage, 7-10 minutes; temperature, 70°-75° C.; volume of molybdate solution, 200 cc.; acidity, 10 cc. concentrated sulphuric acid; length of column of zinc, 15 inches (not amalgamated). Results were:

Ammonium molybdate solution. cc.	$KMnO_4$. cc.	MoO_3. Gram.	Value of $KMnO_4$ in grams of MoO_3.
25	51.00	0.2007	0.003935
26	53.15	0.2088	0.003928
20	40.70	0.1606	0.003946
20	40.60	0.1606	0.003955
21	42.80	0.1687	0.003941
25	50.90	0.2007	0.003943
19	38.80	0.1526	0.003933
20	40.70	0.1606	0.003946
20	40.65	0.1606	0.003951
25	50.90	0.2007	0.003943
		Average,	0.003942

As the theoretical strength of the permanganate would be 0.003903 if the reduction were to Mo_2O_3, it is evident that this has not been attained, but that the reduction is to a point a little below midway between $Mo_{24}O_{37}$ and Mo_2O_3.

Experiment IV. Another Attempt to Reach Mo_2O_3.—The solution was first passed through a short reductor (Experiment I) and then was treated as in Experiment III, using an atmosphere of carbon dioxide, etc. Results were:

Ammonium molybdate. cc.	$KMnO_4$. cc.	MoO_3. Gram.	Value of 1 cc. $KMnO_4$ in grams MoO_3.
25	51.10	0.2007	0.003927
26	53.18	0.2088	0.003926
20	40.93	0.1606	0.003921
21	42.95	0.1687	0.003951
19	38.85	0.1526	0.003951
18	36.76	0.1446	0.003933
23	46.97	0.1847	0.003932
		Average,	0.003933

The volume at the first reduction was 100 cc., containing 5 cc.

concentrated sulphuric acid after passing the first reductor; it was made up to 200 cc. after 5 cc. more of sulphuric acid had been added. The time of passage was eight to ten minutes. The results do not differ sufficiently from those of Experiment III to deserve comment.

In order to test the rapidity of reoxidation by air, two more portions, each containing 0.1606 gram of molybdenum trioxide, were reduced, as just described, in an atmosphere of carbon dioxide, then before titration a blast of air was forced through, in one case for three, in the other for four minutes.

A. Blast for 3 minutes required 39.08 cc. $KMnO_4$ or 1 cc. = 0.004109.
B. " " 4 " " 38.50 " " " 1 " = 0.004171.

Had there been no reoxidation, 40.83 cc. of $KMnO_4$ would have been required. The reoxidation to $Mo_{12}O_{19}$, equivalent to 0.004133, would have been accomplished in three and one-half minutes under those conditions.

Experiment V.—Identical with II except that amalgamated zinc was used. Results were:

Ammonium molybdate solution. cc.	$KMnO_4$. cc.	MoO_3. Gram.	Value of $KMnO_4$ in grams MoO_3.
20	39.9	0.1606	0.004027
25	49.9	0.2007	0.004022
21	42.0	0.1687	0.004016
20	40.0	0.1606	0.004015
26	51.9	0.2088	0.004023
23	46.0	0.1847	0.004015
		Average,	0.0040196

The reduction does not proceed quite as far as with the unamalgamated zinc, although the difference is hardly more than the experimental error. The average result is very close to reduction to $Mo_{24}O_{37}$, while the three lowest and most concordant results agree exactly with the calculated value for that oxide—0.004015.

Experiment VI.—This is a repetition of IV, except that amalgamated zinc was used. The results were:

Ammonium molybdate. cc.	$KMnO_4$. cc.	MoO_3. Gram.	Value of $KMnO_4$ in grams of MoO_3.
25	51.0	0.2007	0.003935
25	50.8	0.2007	0.003951
29	59.1	0.2329	0.003941
26	53.0	0.2088	0.003940
24	48.8	0.1927	0.003949
21	42.7	0.1687	0.003951
20	40.6	0.1606	0.003955
20	40.7	0.1606	0.003946
21	42.6	0.1687	0.003960
		Average,	0.0039475

This is practically the same result as with the unamalgamated zinc, though here, as in the preceding experiment, there is a tendency for the amalgamated zinc to give a slightly less complete reduction.

Experiment VII.—Reduction with Zinc Foil in a Flask.—Twenty cc. of the standard ammonium molybdate solution were diluted to 100 cc. and placed in a flask with four pieces of thin sheet zinc, 1 inch square, and 15 cc. of sulphuric acid, and boiled for twenty minutes. The solution became deep green in color, but on dilution to 300 cc. with *cold* water it changed to port-wine color. The results were 39.1 cc. and 38.9 cc. of the permanganate solution, so that the reduction was very nearly equivalent to $Mo_{12}O_{19}$.

Average result, 1 cc. $KMnO_4$ = 0.004118.
Theory for $Mo_{12}O_{19}$, 1 cc. $KMnO_4$ = 0.004133.

The same experiments were repeated, except that the solution was boiled for half an hour and then diluted to 300 cc. with *hot*, air-free water. The solutions retained their deep green color and required 40 cc. and 40.15 cc. of permanganate for their reoxidation. These results are equivalent to 0.004015 gram MoO_3 and 0.004000 gram MoO_3 per cubic centimeter of permanganate, agreeing with reduction to $Mo_{24}O_{37}$, as obtained in Experiment II.

Magnesium and aluminum were also tried, but without satisfactory results.

Experiment VIII.—Blair's[1] conditions for the reduction of molybdenum were followed exactly. Twenty cc. of the ammonium molybdate solution was diluted to 150 cc., 20 cc. of sulphuric acid added and finally 5 grams of pulverized zinc. The solution was heated in order to start the reaction and then the stopper, containing a tube bent twice at right angles, was inserted. The other end of the tube dipped into a saturated solution of sodium bicarbonate. After complete solution of the zinc, which usually required about an hour, the green solution was immediately titrated with permanganate. Results were as follows:

$KMnO_4$. cc.	MoO_3. Gram.	Value of $KMnO_4$ in grams of MoO_3.
41.5	0.1606	0.003870
41.3	0.1606	0.003888
41.6	0.1606	0.003861
41.4	0.1606	0.003879
	Average,	0.0038745

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[1] "Chemical Analysis of Iron," 3rd edition.

The calculated value for reduction to Mo_2O_3 is 0.003903. The results show that this reduction is fully obtained, but the method is not as satisfactory as the reductor.

CONCLUSIONS.

In general, we have confirmed Blair's statements in all respects and have not succeeded in obtaining reduction to Mo_2O_3 in a reductor. Our work has emphasized the importance of absolute uniformity in the conditions for both reduction and titration with with those used when the factor was obtained, as stated by W. A. Noyes. There is no definite stopping point at $Mo_{24}O_{37}$, though the reduction under the usual conditions proceeds very close to this point.

When the reduction is accomplished under the following conditions: Length of column of 20-30 mesh zinc, 15 inches; time of passage, about 6 minutes; temperature, 70°-75° C.; volume, 200 cc.; acidity, 10 cc. of concentrated sulphuric acid; and the titration is made in the reductor flask without dilution or delay, but using no atmosphere of carbon dioxide, the factors are: For unamalgamated zinc, iron standard of permanganate times 0.88 gives MoO_3 standard; times 0.01579 gives phosphorus standard; when the "yellow precipitate" is titrated. For amalgamated zinc these factors are 0.8842 and 0.01586. The factors based on reduction to $Mo_{24}O_{37}$ are 0.8832 and 0.01584, using the atomic weights of 1903.

PART II.

Bismuth ammonium molybdate was prepared as follows: Ten cc. of the standard bismuth nitrate solution (described in the preceding article) were run into a beaker and 100 cc. of the ordinary acid ammonium molybdate reagent were added, the solution diluted to about 200 cc. and heated on an asbestos disk by a Bunsen burner. While the heating was in progress, ammonia (sp. gr. 0.96) was run in from a burette and the solution stirred vigorously. The addition of ammonia caused the formation of a precipitate and gave a yellow color to the solution which, as the neutral point was approached, disappeared, and a bluish tint was noticeable. This was used as an indication that sufficient ammonia had been added. The solution must be very hot, but not boiling, and the precipitate pure white. It was washed free from molybdenum by a 3 per cent. solution of ammonium sulphate, then into a clean beaker with hot water. Ten cc. of sulphuric acid were added, and the solution was reduced and titrated under conditions of Experiment II. Assuming that there are present in the precipitate 2 molecules of MoO_3 for each atom of bismuth, the strength of the permanganate solution is 0.002896 gram bismuth per cubic centimeter. The results of three determinations were:

$KMnO_4$. cc.	Bi taken.	Bi found.	Calculated BiMo ratio.
39.60	0.1155	0.1147	1 : 1.986
39.75	0.1155	0.1151	1 : 1.993
39.70	0.1155	0.1150	1 : 1.991

The reduction and titration were then made according to the conditions of Experiment III; the bismuth value of the permanganate becomes 1 cc. = 0.002854. The results were:

$KMnO_4$. cc.	Bi taken.	Bi found.	Calculated BiMo ratio.
40.40	0.1155	0.1153	1 : 1.997
40.35	0.1155	0.11515	1 : 1.994

As methyl orange was not found a satisfactory indicator in the precipitation of bismuth by this method, others were tried and congo red was adopted as the most convenient. We next carried out the precipitationas follows: To the solution containing bismuth nitrate and 5 per cent. of free nitric acid, a decided excess of the ordinary molybdate reagent was added; there should be no precipitate produced at this point. A few drops of congo red were added and then very dilute ammonia slowly from a burette, with stirring; in a short time a white precipitate began to appear. We continued to add ammonia (in the cold) till the indicator became pink; next a few drops of dilute nitric acid were added so that the color was lilac (just neutral). The solution was warmed on a thick asbestos pad, but not to boiling. The precipitate collected and filtered well. It looked like silver chloride and was extremely easy to wash. The indicator was decomposed on heating and separated out as a pink lake, which adhered to the filter-paper.

Under the conditions given, the precipitation is absolutely complete, but if too much nitric acid is added, so that the indicator is turned back to a decided blue color, the precipitate does not collect or filter as well and the filtrate may contain traces of bismuth.

Two precipitates made in this way were analyzed as follows: After decomposition by ammonium sulphide, the bismuth sulphide was dissolved in nitric acid and weighed as oxide. The molybdenum was precipitated from the ammonium sulphide filtrate by making slightly acid with hydrochloric acid and allowing to stand for several hours. The sulphide was dissolved in aqua regia, evaporated to small volume, neutralized with ammonia and then precipitated as lead molybdate. The results were:

No. 1. Weight $PbMoO_4$ 0.7558 gram = Mo 0.1977 gram.
" Bi_2O_3 0.2456 gram = Bi 0.2202 gram.
Atomic ratio Bi : Mo : : 1 : 1.95.
No. 2. Weight $PbMoO_4$ 0.6172 gram Mo = 0.1615 gram.
" Bi_2O_3 0.1951 gram Bi = 0.1747 gram.
Atomic ratio Bi : Mo : : 1 : 2.007.

Two portions of 10 cc. each of the standard bismuth solution were precipitated and the precipitates analyzed for ammonia. After deducting the relatively large amount present as ammonium sulphate, 0.0588 gram,[1] from the total ammonia, 0.06722 gram, the ammonia (NH_3) in combination with 0.1155 gram of bismuth was 0.0084 gram in one case, and 0.0598—0.05182 or 0.00806 gram in the other. These values give Bi : NH_3 ratios of 1 : 0.9- and 1 : 0.85 respectively or 4.24 and 4.06 per cent. $(NH_4)_2O$ compared with the theory for $BiNH_4(MoO_4)_2$, 4.76 per cent. Although these precipitates were sucked dry on a Büchner funnel to remove as much as possible of the excess of ammonium sulphate,[2] the relatively large quantity of ammonium as sulphate renders the accurate determination of that existing in combination with the bismuth a matter of difficulty.

The following experiments were made to see whether there was any variation in the composition of the precipitate when formed according to the three methods given. The results are in grams of bismuth, obtained by the titration method already fully described.

A. Riederer's conditions; methyl orange indicator; solution just acid with nitric acid; bismuth taken, 0.1280; found, 0.1278.

B. Congo red as indicator; solution neutral; bismuth taken, 0.1280; found, 0.1285 and 0.1288. (These slightly high results may be due to the carrying down of molybdenum by the indicator to form a lake.)

C. No indicator; solution made slightly alkaline; bismuth taken, 0.1280; found, 0.1274 and 0.1277.

CONCLUSION.

The peculiar properties of this precipitate,—that it cannot be

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[1] Calculated from the SO_4 determined as $BaSO_4$.

[2] As suggested by Professor W. A. Noyes.

washed with water or dried without decomposition, make the determination of its composition a matter of extraordinary difficulty, as everything must be found by ratios, and the ammonia determination is complicated by the ammonium sulphate present. But from the preceding determinations and others by other workers, there seems to be no doubt that the ratio of bismuth to molybdenum is as one is to two and that if the formula is not $BiNH_4(MoO_4)_2$, the variation is extremely slight and not such as to prevent the use of this precipitate for the volumetric determination of bismuth.

QUANTITATIVE LABORATORY,
June 20, 1903.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE CONSTITUTION OF POTASSIUM RUTHENIUM NITROSOCHLORIDE IN AQUEOUS SOLUTION.

BY S. C. LIND.

Received June 15, 1903.

THIS salt is the one which led Claus in 1845 to identify ruthenium as a new metallic element. He supposed it, however, to have the formula K_2RuCl_6, and, therefore, to belong to the well-known class of salts represented by K_2PtCl_6. In 1888, A. Joly[1] showed that this is not the case, but that the compound is a mononitroso salt of the formula K_2RuCl_5NO. The properties of this salt and analyses of it by several authors are presented in Freeny's "Encyclopedie Chimique."[2] J. L. Howe[3] has confirmed this interesting discovery and has described the salt very fully, and given new analytical data in regard to it.

The properties presented by this salt, its rather unique formula, and also its relation to several other analogous ruthenium salts, have made a study of its constitution in aqueous solution of interest. Such an investigation was undertaken at the suggestion of Dr. Jas. L. Howe, to whom the author is indebted for the salt used in the following measurements. His analyses were made on this same sample; they will be found in his article referred to above. The author also desires to acknowledge his indebtedness

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[1] *Compt. Rend.*, **107**, 994 (1888).

[2] "Encyclopedie Chimique," III, **17**, 1, 179-181.

[3] This Journal, **16**, 388 (1894).