# CXI.—The Oxidising Properties of Sulphur Dioxide. Part IV. Molybdenum Sulphates.

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CHILESOTTI, in a paper on the electrolytic reduction of solutions of molybdic anhydride in hydrochloric acid (Z. Elektrochem., 1906, 12, 173), concluded from potential measurements that the molybdenum was first completely reduced to the quinquevalent condition and that further reduction produced tervalent molybdenum without the intermediate formation of quadrivalent compounds. Depending on the concentration of the hydrochloric acid, the colour of the solution containing tervalent molybdenum could be either orange-red or green. The green colour was only obtained when the concentration of acid was less than 7N. In acid of higher concentration, the green stage was not reached and the colour of the tervalent molybdenum solutions was orange-red. Moreover, the production of the green colour was accompanied by a considerable fall of potential, although the alteration in permanganate titre was very small. This is in accord with the powerful reducing properties of the green solutions. They are extremely sensitive to air oxidation and immediately on exposure to air recover the orange-red colour. Chilesotti, with a certain amount of reserve, suggested that the appearance of the green colour might be due to the formation of small masses of molybdenum dichloride which had not been detected chemically, and that in the orangered solutions bivalent molybdenum was not produced. The existence of two differently coloured solutions of chromic chloride is well known. Peligot (Compt. rend., 1844, 19, 783; Ann. Chim. Phys., 1844, 12, 537) first succeeded in obtaining green crystals of chromium trichloride, [Cr(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub>]Cl<sub>2</sub>H<sub>2</sub>O, by treating the insoluble violet anhydrous chloride with water in the presence of a small quantity of chromium dichloride.

"It is therefore possible," states Chilesotti, "that traces of molybdenum dichloride formed at the end of the reduction would favour the transformation of the molybdenum trichloride to the green form, which, on disappearance of the dichloride, would revert to the orange-red isomer."

It was thought, therefore, that it might be of interest to investigate the reactions of sulphur dioxide with the lower molybdenum compounds in view of the possible stages of oxidation and also to determine whether there was any distinctive difference in the reactivity of the green and orange-red solutions with this gas. In connexion with Chilesotti's hypothesis, it is worthy of note that whilst cuprous chloride, stannous chloride, or other reducing agents (Rohland, Z. anorg. Chem., 1899, 21, 37; Drucker, Z. physikal. Chem., 1901, 36, 173) have the power of causing solution of the insoluble chromium chloride, they are ineffective in the case of the anhydrous molybdenum trichloride.

Reference to the literature showed that the stage to which solutions of molybdic anhydride are reduced has been the subject of considerable investigation. Wernke (Z. anal. Chem., 1875, 14, 1) carried the reduction with zinc and sulphuric acid approximately to the condition  $Mo_{12}O_{19}$ . Dudley (J. Amer. Chem. Soc., 1893, 15, 519), using Jones's reductor, obtained slightly different results. Doolittle and Eveson (ibid., 1894, 16, 234), and Jones (Amer. Inst. Min. Eng., 1889, 90, 18, 705) obtained results similar to those of Wernke. Blair and Whitfield (J. Amer. Chem. Soc., 1895, 17, 747) and Millar and Frank (ibid., 1903, 25, 919) reduced the anhydride approximately to the stage Mo24O37. Noves and Frohman (J. Amer. Chem. Soc., 1894, 16, 553), by replacing air with carbon dioxide, effected a reduction corresponding to  $Mo_2O_3$ . Randall (Amer. J. Sci., 1907, [iv], 24, 313), using ferric alum in the reducing flask and decolorising with phosphoric acid according to Reinhardt (Chem. Ztg., 1889, 13, 323), obtained reduction to Mo<sub>2</sub>O<sub>3</sub>. Scott (J. Ind. Eng. Chem., 1920, 12, 575), using a rotating zinc reductor, showed that the reduction reached the Mo<sub>2</sub>O<sub>3</sub> stage. There seems little doubt, therefore, that under favourable conditions molybdic anhydride is reduced by zinc and sulphuric acid to the tervalent condition. The only reference to any lower stage being reached is an early investigation by von der Pfordten (Annalen, 1884, 222, 155) in which possible reduction to Mo<sub>5</sub>O<sub>7</sub> is mentioned.

Although Chilesotti carried out his detailed potential measurements in the presence of hydrochloric acid in the case of the green and orange-red solutions, he mentions that sulphuric acid solutions give analogous results. We have therefore carried out our experiments in the presence of this acid, as at fairly high temperatures the concentration of sulphuric acid solutions is more easily controlled than the concentration of hydrogen chloride solutions,

#### EXPERIMENTAL.

For the investigation of the reaction between sulphur dioxide and reduced solutions of molybdic anhydride in sulphuric acid, the apparatus shown in Fig. 1 was finally adopted.

The reduction of the solution was accomplished electrolytically in the cell A. This consisted of an outer glass vessel, which was used as the cathode chamber and was closed with a large rubber

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bung. Through a hole in the centre of this passed a porous pot which served as the anode chamber. The electrodes were of smooth platinum, and the voltage was varied according to the concentration of the sulphuric acid, but was usually adjusted to give a current of 7—8 amperes. The cathode and the anode chambers were filled with the solution of ammonium molybdate and sulphuric acid. To prevent its temperature rising, the cell was immersed in a bath through which cold water continuously circulated. During the reduction, a stream of nitrogen was passed through the solution by means of the tube, a, in the cathode chamber. By suitably adjusting the taps, all air could be cleared from the apparatus. When the solution was completely reduced,



portions were forced into the burette, D, for analysis, whilst the remainder was transferred to the flask, B. The latter was provided with a double-surface condenser to minimise evaporation during the experiment. With taps 5 and 7 closed and 6 open, a stream of sulphur dioxide was passed through the reduced solution for half an hour at room temperature and then for twelve to fifteen hours with the temperature of the water-bath surrounding the flask kept constant at 90°.

### Description of the Phenomena.

The colour of the completely reduced solution depended on the concentration of the acid present. In highly concentrated acid, the solution was salmon-pink, whereas with less concentrated acid it was either olive-green or bright green. On passage of sulphur

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dioxide into the salmon-pink solution, the colour changed immediately to reddish-brown and then to carmine-red. If the solution was initially bright green, it became successively olive-green, brown, and carmine-red, whilst the olive-green solution became brown and finally carmine-red. The colour changes were accompanied by an opalescence, but on raising the solution to 90° the finely divided precipitate was coagulated. The colour of the solid thus produced varied from dark brown to light brown, according as the acid was concentrated or dilute. A deposit of sulphur gradually accumulated in the mouth of the flask and in the condenser. After the sulphur dioxide had passed for the required time, it was replaced by a current of nitrogen. The passage of this gas was continued until sulphur dioxide could no longer be detected at the exit tube. The solution, after cooling in the nitrogen stream, was forced through the glass-wool filter into the conical flask, C, by closing taps 8 and 10 and opening taps 9, 7, 11, and 15. By suitable rearrangement of taps, the red liquid was forced into the burette, E.

# Quantitative Aspect of the Reaction.

The quantitative study of the reaction depends on a consideration of the nature of the initial and final solutions. In attempting to determine the stage of oxidation or reduction of a sulphuric acid molybdenum solution, it is necessary in the first place to know the total molybdenum content. Then since potassium permanganate solution will oxidise any reduced molybdenum solution to the sexavalent stage, one can readily deduce the exact constitution from a consideration of these two factors. After a detailed investigation of various methods for titrating reduced molybdenum solutions with standard potassium permanganate, we drew the conclusion that the best results were obtained when the fully reduced molybdenum solution was run directly into a stoppered flask containing ferric alum acidified with sulphuric acid and through which a current of nitrogen was passing. To determine the total molybdenum two methods were used. In the case of the initial solutions, these were boiled with hydrogen peroxide to effect oxidation to the sexavalent stage, and the molybdenum was precipitated as the trisulphide and weighed as the oxide in the usual way. This was done to determine whether the initial solution was reduced to the tervalent condition. Our experiments indicated that only when the solution was reduced to the stage developing the bright green colour, was reduction to the tervalent state complete.

The total molybdenum in the final red solution was estimated

by means of the apparatus shown in Fig. 2, which is a modification of the Jones's reductor. Wedged in the bottom of the tube above the tap is a perforated disk which supports a glass-wool filter,  $l_{2}^{1}$  inches deep. The tube is then filled with small pieces of pure sheet zinc, bent into V-shape to prevent clogging as far as possible. Twenty c.c. of the red solution from burette E were used in each determination. In carrying out a determination, the reductor was first algorid with 21 per cent subhuric acid

first cleaned with  $2\frac{1}{2}$  per cent. sulphuric acid. The acid concentration of the red solution was adjusted to approximately 3N. It has been found advantageous to adjust the acid concentration to this normality, for if sufficient acid is not present, hydrolysis of the reduced molybdenum solution will occur, whilst if the acid is too concentrated, hydrogen sulphide will be formed, which will affect the permanganate Ten c.c. of hot  $2\frac{1}{2}$  per cent. sulphuric titre. acid were introduced into the reductor and followed by the molybdenum solution, heated almost to boiling. The red solution was allowed to remain in the reductor until it was completely reduced to the green stage and then run directly into the flask containing ferric alum solution, through which nitrogen continuously passed. Any molybdenum remaining in the reductor was removed by successive washings with hot  $2\frac{1}{2}$  per cent. sulphuric acid. The contents of the flask were then titrated with standard permanganate. Blank experiments were always carried out and the necessary adjustments made.  $N_2^{-1}$ The accuracy of the method, which has been established by other investigators, is confirmed by the following typical results : Found : weight of  $MoO_3$  in a given sample (a) by the gravimetric method = 0.1318 gram, (b) by the reduction method = 0.1320 gram. The result



in the case of the reductor method is calculated on the assumption that the reduced solution is tervalent, and this assumption appears to be justified. The stage of oxidation of the final red solution is given by the expression  $6 - 3t_1/t_2$ , where  $t_1$  is the permanganate titre and  $t_2$  the titration value of the same volume of the red solution after passing through the reductor.

Degree of Oxidation.—Approximately 500 c.c. of the solution after reduction in the cell were allowed to react with sulphur dioxide for twelve to fifteen hours, the reaction flask being immersed in a bath kept constantly at  $90^{\circ}$ .

## TABLE I.

Concentration of molybdenum solu- per	tion = 100 c.c	0∙25 g c.	ram of	molyb	dic ar	nhydride
Normality of acid	2 3·78	$2.75 \\ 3.89$	4 4∙04	$7 \\ 4 \cdot 26$	$\begin{array}{c} 10 \\ 4\cdot 33 \end{array}$	15N $4\cdot 20$
Concentration of molybdenum solu	tion = 100 c.	2·5 gr e.	ams of	molyb	dic ar	hydride
Normality of acid Oxidation stage $Mo_{\circ}O_x$ , where $x =$	$\frac{2}{3\cdot 76}$	5 4	·15	$7 \\ 4.20$		10N 4·20

The table clearly shows that the extent to which oxidation by sulphur dioxide occurs depends on the acid concentration. In acid of low concentration the stage where x = 4 is not reached, whilst in the more concentrated acid this stage is surpassed. However, in no case does the oxidation proceed to the quinquevalent condition. There is no evidence that the concentration of the molybdenum materially affects the degree of oxidation.

Composition of the Precipitate.—The solid which separated out in the reaction between sulphur dioxide and the tervalent molybdenum solution mentioned above consisted of an intimate mixture of sulphur and a molybdenum sulphide. The colour of the deposit varied from dark brown to light brown, according to the amount of sulphur present. Chloroform extracted a large proportion of sulphur and left a dark brown powder which was practically insoluble in concentrated hydrochloric acid, only slightly soluble in warm, yellow ammonium sulphide, and contained molybdenum and sulphur. After prolonged extraction of the powder with chloroform, analysis of the residue failed to give concordant results, probably owing to the difficulty of completely extracting occluded sulphur. The residue was undoubtedly a sulphide of molybdenum, but not the trisulphide.

Degree of Oxidation in Dilute Acids.—Experiments were carried out with the tervalent molybdenum solutions in normal acid, and although the reaction with sulphur dioxide was apparently identical with that in acid of higher concentration, the results indicated the operation of some disturbing factor. The equilibrium values obtained under similar conditions varied considerably in different experiments, and were not of the order one would have expected from a consideration of the results given in Table I. When the acid concentration was reduced to semi-normal, a quite different phenomenon was exhibited on passage of the sulphur dioxide. A large part of the molybdenum was precipitated during the

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experiment as a black mud, which behaved chemically as a molybdenum hydroxide, and is probably a mixture of  $MoO_2, H_2O$  and  $Mo(OH)_3$ . The final solution had a pale yellow colour, and although containing practically no molybdenum, it had an appreciable permanganate titre, the end-point being very indefinite. Only after long and vigorous boiling was the solution decomposed with deposition of sulphur. On boiling with dilute sulphuric acid, relatively large quantities of hydrogen sulphide were evolved. By addition of alkali, a small, greenish-brown precipitate was obtained, readily soluble in hydrochloric acid to a pinkish-brown solution, which on reduction with zinc acquired an olive-green colour. Apparently the solution contained thionic acids with a small quantity of molybdenum.

# Reaction of Hydrogen Sulphide with Tervalent Molybdenum Solutions.

The reaction of hydrogen sulphide with tervalent molybdenum solutions receives mention in Miller's "Inorganic Chemistry," 1878, p. 714, which states "hydrogen sulphide slowly produces a brown precipitate of hydrated sulphide, soluble in ammonic hydric sulphide." Beyond this, no further information seems available. Our own experiments show that hydrogen sulphide may be passed through a green tervalent molybdenum solution for two or three hours without producing any effect, but if this saturated solution be sealed in a flask, a black precipitate will separate in the course of a few days. Qualitative tests on the precipitated sulphide indicate that it is identical in its chemical reactions with the brown sulphide obtained in our oxidation experiments. Quantitative analyses indicate that it is a sesquisulphide of molybdenum with varying water content.

# Reaction of Sulphur with Tervalent Molybdenum Solutions.

The green tervalent molybdenum solution was allowed to react with finely powdered, recrystallised sulphur in a flask through which a current of carbon dioxide was passing. Hydrogen sulphide was slowly evolved at the ordinary temperature and the green solution gradually turned brown. On immersing the flask in a bath of boiling water, hydrogen sulphide was evolved in considerable quantity, the solution eventually turning red. This reaction is of interest as showing the powerful reducing properties of the green solution. No sulphide was precipitated in these experiments. Quadrivalent molybdenum solutions were not reactive with sulphur.

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# Reactions of Acidified Tervalent Molybdenum Solutions with Sodium Tetrathionate and Sodium Trithionate.

Reference to recent literature on the stability of the polythionic acids gives many conflicting opinions. Riesenfeld and Feld (Z. anorg. Chem., 1921, 119, 225) state that in the presence of acid, of the three polythionic acids, tetrathionic acid is the least stable and decomposes relatively quickly into tri- and penta-thionic acids. Trithionic acid decomposes more slowly with formation of sulphur dioxide, whilst pentathionic acid decomposes only in the course of months, with separation of sulphur. Foerster and Hornig (Z. anorg. Chem., 1922, 125, 86) state that, of the polythionic acids and their salts, the tetrathionates are the most stable, the trithionates the most unstable, whilst the pentathionates occupy a mean position. Moreover, they state that a high concentration of hydrogen-ion retards the decomposition of tetraand penta-thionic acids, but not of trithionic acid. These facts are of especial interest, for it has already been stated that when sulphur dioxide reacts in dilute acid molybdenum solutions, there seems good reason to suppose that a formation of thionic acids occurs and that the solution is comparatively stable. We considered, therefore, that the interaction of sodium tetrathionate and the reduced molybdenum solution might indicate whether our hypothesis was justified.

Sodium tetrathionate was placed in the reaction flask and a tervalent molybdenum solution in 3N-sulphuric acid run in, when hydrogen sulphide was immediately evolved in the cold. The reaction was allowed to proceed for twenty-one hours in a current of nitrogen, which expelled the hydrogen sulphide as it was formed. A brown precipitate formed, insoluble in hydrochloric acid and only slowly dissolved by yellow ammonium sulphide. The precipitate was not the outcome of reaction between the hydrogen sulphide and the green solution, for it has already been shown that a precipitate is only formed by saturating the solution with hydrogen sulphide and keeping it for a considerable time. Sodium tetrathionate treated with 3N-sulphuric acid is not reactive in Hydrogen sulphide is only evolved on vigorous boiling. the cold. The precipitated sulphide, therefore, appears to be a decomposition product of the initially formed molybdenum tetrathionate. The hydrogen sulphide evolved may have been due to the decomposition of this unstable tetrathionate or to the reduction of free tetrathionic acid by the tervalent molybdenum solution. It will also have been formed by the action of liberated sulphur on the green solution. It seems quite conceivable, therefore, that when sulphur dioxide is passed into the reduced molybdenum solution

an initial reduction to tetrathionic acid occurs. Such a hypothesis can account for the abnormal results obtained in dilute acid and for the production of a mixture of molybdenum sulphide and sulphur in the more concentrated acids.

Sodium trithionate reacts similarly with the tervalent molybdenum solution. However, experiments with trithionic and tetrathionic acids have led us to the conclusion that tetrathionic acid is the more stable and we incline, therefore, to the view that the initial reduction product of the sulphur dioxide is tetrathionic acid.

# The Reducing Action of Sulphur Dioxide.

One of the characteristic tests for molybdenum is the production of a blue colour when sulphur dioxide or hydrogen sulphide is passed into an acid solution containing sexavalent molybdenum. This coloration is due to the formation of molybdenum-blue, an oxide of the form  $Mo_2O_5, xMoO_3$ . If, however, sufficient acid is present, no such reduction will be effected. Edgar (Amer. J. Sci., 1908, [iv], 25, 332) proposed to estimate vanadium in the presence of molybdenum by boiling the solution with sulphur dioxide in the presence of definite concentrations of sulphuric acid, whereby the vanadium would be reduced but the sexavalent molybdenum would be unaffected. In our experiments, a solution containing 2.5 grams of molybdic anhydride per litre of 2.5Nsulphuric acid gave a faint blue colour on treatment with sulphur dioxide for eight hours at 90°, but with higher concentration of acid no reduction was noted. Evidently reduction of sexavalent molybdenum solutions can be inhibited by the presence of sufficient sulphuric acid, the normality of which will depend on the concentration of molybdic anhydride present.

We then investigated the reaction of sulphur dioxide with solutions of molybdenum corresponding to stages of oxidation slightly higher and slightly lower than the quinquevalent condition. The following table presents a few typical results obtained with solutions containing 3 grams of molybdic anhydride per litre of sulphuric acid of definite acidity, which were reduced electrolytically to definite stages and treated at 90° with a slow stream of sulphur dioxide. Ten c.c. of solution were used for each titration.

TABLE	II.
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	C.c. of KMnO <sub>4</sub>	C.c. of	KMnO₄.		
Normality of	required	Initial	Final	Time in	
sulphuric acid.	for Mo <sup>v</sup> .	value.	value.	hours.	Remarks.
- 1	$2 \cdot 1$	1.9	1.9	12)	Molybdenum-
1	$2 \cdot 1$	1.9	1.9	24 Ì	blue formed
1	2.1	$2 \cdot 15$	2.15	24	No change
3	3.8	4.30	4.30	40	"

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The above table clearly shows that solutions containing molybdenum in the quinquevalent condition were unaffected by the passage of sulphur dioxide, whereas those with molybdenum corresponding to a slightly higher stage of oxidation gave rise to molybdenum-blue. As the titrations did not vary before and after the reaction with sulphur dioxide, and as no sulphur was produced, it did not appear that oxidation had taken place. Solutions of the same concentration and titre as the first two solutions mentioned above were heated for a long period in a current of nitrogen, and it was found that they also gave rise to molybdenum-blue, proving that the sulphur dioxide had no specific effect on the reaction. Undoubtedly the formation of molybdenum-blue in all cases was the outcome of the equilibrium which has been established for hydrochloric and sulphuric acid solutions containing molybdenum in the quinque- and sexa-valent conditions :

In solutions corresponding to a stage just above the quinquevalent, sexavalent and quinquevalent molybdenum are present, and in accord with the above equilibrium they will form molybdenum-blue in greater or smaller amount, depending on the acid concentration. Molybdenum-blue is insoluble in 34 per cent. sulphuric acid, but in 56 per cent. acid it dissolves, giving rise to a yellow solution, whilst with 85 per cent. acid a green solution is obtained. In acid of high concentration we have found that yellow and green solutions are produced when sulphur dioxide reacts at 90° with molybdenum solutions at a slightly higher stage of oxidation than the quinquevalent. These effects are produced not by a specific action of the sulphur dioxide, but by the establishment of the above equilibrium relationship (see Abegg, "Anorganische Chemie," IV, p. 627).

In solutions representing a stage of oxidation below the quinquevalent stage, but greater than the maximum oxidation stage reached by reaction of the sulphur dioxide with tervalent molybdenum, namely,  $Mo_2O_{4\cdot 2}$ , no reaction with the sulphur dioxide was observed.

## Discussion of Results.

A consideration of the titrations and the reactivity of the green and red solutions has led us to the conclusion that only when the vivid green colour is obtained in the reduction of acid molybdenum solutions is the tervalent stage attained. Moreover, on oxidation, this vivid green colour reverts to an olive-green, brown, and then red, as shown by the reactions with sulphur dioxide and air. It seems, therefore, that the red solution mentioned by Chilesotti is not in the tervalent condition.

From the results of the investigation, two facts stand out prominently. First, the degree of oxidation by sulphur dioxide of a tervalent molybdenum solution is dependent on the acid concentration. Secondly, under the most favourable conditions of acidity, the oxidation only proceeds to a stage represented approximately as Mo<sub>2</sub>O<sub>4.2</sub>. Chilesotti (loc. cit.) has shown in connexion with the molybdenum chlorides that in the reduction from the sexavalent stage the only distinct stages shown are those of the quinquevalent and tervalent compounds. It seems justifiable to assume that the sulphates will in all probability follow a similar course and on this conception the stage  $Mo_2O_{4,2}$  is the result of the presence in the solution of certain proportions of tervalent and quinquevalent molybdenum. Moreover, the limited oxidation of tervalent molybdenum seems to point to the possibility of an equilibrium being established between the sulphates corresponding to these two stages. Although in the oxidation process precipitation of molybdenum sulphide occurs in addition to sulphur, the equilibrium reaction would be best expressed by the equation :  $Mo_2(SO_4)_3 + SO_2 + 2H_2SO_4 \Longrightarrow Mo_2(SO_4)_5 + S + 2H_2O$ . . (2) Such an equation indicates the favourable influence of acid concentration on the degree of oxidation. On the other hand, neither sulphur nor sulphur dioxide has been shown to reduce molybdenum sulphate solutions corresponding to a degree of oxidation greater than  $Mo_2O_{4\cdot 2}$  and less than the quinquevalent stage. This phenomenon is entirely analogous to that exhibited by the iron phosphates in their reactions with sulphur dioxide (T., 1920, 117, 1241), and an explanation similar to that given there seems applicable to the present case. Undoubtedly the non-reducibility of molybdenum sulphates, whether in the sexavalent condition in the presence of sufficiently concentrated acid or between the stages of oxidation represented by  $Mo_2O_{4\cdot 2}$  and  $Mo_2O_5$ , is due to the presence of stable complexes which on ionisation give rise to complex anions containing the molybdenum. Nevertheless, it is quite conceivable that at the moment of its formation by oxidation of the tervalent molybdenum with sulphur dioxide, the quinquevalent molybdenum sulphate, before being taken up in the form of a complex, may be reactive with the finely divided sulphur or the sulphur dioxide, the equilibrium relationship being thereby established.

In dealing with molybdenum sulphate solutions containing molybdenum corresponding to stages between  $Mo_2O_5$  and  $MoO_3$ , the action of the sulphur dioxide is not specific, as such solutions form molybdenum-blue in accord with equation (1).

#### Summary.

1. Sulphur dioxide oxidises solutions of tervalent molybdenum in sulphuric acid to stages intermediate between the ter- and quinque-valent conditions, sulphur and a molybdenum sulphide being precipitated.

2. The degree of oxidation increases with increasing acid concentration, the maximum oxidation stage being approximately  $Mo_2O_{4\cdot 2}$ .

3. Sulphur dioxide does not reduce sulphuric acid solutions of molybdenum corresponding to stages between  $Mo_2O_{4.2}$  and  $Mo_2O_5$ .

4. Sulphuric acid solutions of molybdenum corresponding to stages slightly greater than  $Mo_2O_5$ , when treated with sulphur dioxide, give rise to molybdenum-blue. This result is not a specific effect of the sulphur dioxide, but the realisation of the equilibrium shown in equation (1).

5. The reduction of molybdenum in the sexavalent condition by sulphur dioxide is inhibited by the presence of sufficiently concentrated sulphuric acid.

6. Tervalent molybdenum solutions in semi-normal sulphuric acid react differently with sulphur dioxide, tetrathionic acid probably being produced.

7. A simplified reductor method for the estimation of molybdenum is described.

In conclusion, we wish to express our thanks to the Department of Scientific and Industrial Research for a grant to one of us (N. D. S.) which has enabled this investigation to be carried out, and to the Chemical Society for a grant towards the purchase of some of the materials.

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