ACTION OF MOLYBDENUM DIOXIDE UPON SILVER SALTS.

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IT has been shown (*Ztschr. anorg. Chem.*, **1**, 360) that metallic molybdenum precipitates metallic silver from ammoniacal argentic solutions, but no record seems to have been made of the fact that molybdenum dioxide behaves similarly. This, however, was observed to be the case on introducing dioxide, prepared by the reduction of trioxide in a current of hydrogen, into an aqueous argentic nitrate solution for the purpose of learning whether any metal was present in the dioxide. All of the material dissolved on the application of a gentle heat. The solution was especially rapid in the presence of a slight quantity of ammonia. The silver separated in crystalline leaflets. Attempts were made to discover whether the reaction was really quantitative. The results are as follows:

1. 0.1057 gram brown dioxide, prepared by the reduction of ordinary molybdic acid in an atmosphere of hydrogen, precipitated from a slightly ammoniacal argentic nitrate solution 0.1755 gram metallic silver.

2. 0.1772 gram of dioxide precipitated 0.2915 gram of metallic silver. The latter was washed with dilute ammonia and with water.

Thinking that possibly the dioxide as prepared for the preceding precipitations did not really represent that oxide, but a mixture of oxides, recourse was had to a method first suggested by Manro and Pauebianco (*Gazz. chim. ital.*, **11**, 501). Muthmann (*Annalen der Chem.*, **238**, 116) employed this method with success. It is, briefly, the fusion of eight grams of dehydrated ammonium molybdate, seven grams of molybdic acid, fourteen grams of ignited potassium carbonate and seven grams of boric acid in a capacious and well-covered platinum crucible. The mixture should be held for several hours in a liquid condition. On cooling, a brittle mass results; it contains crystals of the dioxide. It can be readily detached from the crucible. The brown oxide was purified by washing with ammonia water and then with pure water. The two reductions made with this oxide resulted as follows:

3. 0.3698 gram of oxide precipitated 0.6250 gram of silver.
4. 0.5287 gram of oxide threw out 0.8799 gram of silver.

In both cases ammonia, sufficient to precipitate silver oxide and again dissolve it, was added to the argentic solutions. The precipitated silver was also washed with ammonia water and finally with pure water.

If the ratio between the dioxide and the silver be deduced from the figures given in the preceding experiments it will be found to approach

$$1MoO_2 : 2Ag,$$

and then the calculated or theoretical quantity of silver required for the dioxide used in the various experiments would be

	Calculated Ag.	Found Ag.
1	0.1783 gram.	0.1752 gram.
2	0.2990 "	0.2915 "
3	0.6240 "	0.6250 "
4	0.8765 "	0.8799 "

The results in 3 and 4 agree more nearly with the theoretical requirements than those in 1 and 2, doubtless because the oxide used in those experiments was a true molybdenum dioxide. Their variation from the theory may be ascribed in 3 to slight solubility of the precipitated metal in ammonia, and in 4 to minute traces of molybdic acid in the silver.

Additional trials were made to arrive at more concordant results, but success was not achieved, although in every instance the resulting silver approximated the ratio previously established. This reaction, while apparently useless for quantitative purposes, is yet of interest as it shows that the precipitation of metallic silver is not confined to metallic molybdenum, but that it even extends to the dioxide and perhaps to other mixed oxides of which the dioxide may be a part.

It is of interest to note in connection with the conduct of molybdenum dioxide as outlined in the preceding paragraphs, the further analogy established between it and the dioxides of other metals of Group VI. Thus, tungsten dioxide reduces not only copper and mercuric salts, but also precipitates metallic silver from ammoniacal silver solutions, and uranium dioxide, prepared by reduction of the oxalate in a current of hydrogen, dissolves in silver nitrate with the separation of metallic sliver. Molybdenum dioxide showed no reducing action upon copper and mercuric salt solutions.

Among the non-metals of Group VI we observe in the deportment of sulphites towards silver nitrate, in the breaking down of silver sulphite into metallic silver on the application of a gentle heat, a behavior analogous to that exhibited by molybdenum dioxide, and which we may consider as an additional contribution to the many already well-established analogies, existing among the derivatives of the elements constituting Group VI of the Periodic System.

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