[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY No. 60.]

THE ELECTROLYTIC DETERMINATION OF MOLYBDENUM.

BY LILY GAVIT KOLLOCK AND EDGAR F. SMITH.

Received July 5, 1901.

MORE than twenty years ago Smith,[1] in describing his experience in the electrolysis of solutions of ammonium molybdate, wrote: "The deposition, although complete, was so very slow that this method of determination was practically of little value." During the last few months attention has again been given in this laboratory to the subject. Sodium molybdate ($Na_2MoO_4.2H_2O$) was dissolved so that 0.1302 gram of molybdenum trioxide was present in 125 cc. of solution, which was exposed for several hours to the action of a current of 0.1 ampere and 4 volts. The temperature of the electrolyte was 75° C. No precipitation occurred upon either electrode. Upon adding two drops of concentrated sulphuric acid to the liquid, it at once assumed a dark blue color. As the current continued to act, this color disappeared and the cathode was coated with a black deposit—the hydrated sesquioxide.[2] On removing the colorless liquid and testing it with ammonium thiocyanide, zinc, and hydrochloric acid, evidences of the presence of molybdenum failed to appear. In the following experiments the molybdenum deposit was a brilliant black in color and so adherent that it could be washed without detaching any particles. Usually the colorless liquid was removed with a siphon, cold water being introduced without interrupting the current. The deposit was not dried, but while yet moist it was dissolved from off the dish in dilute nitric acid and the solution carefully evaporated to dryness, the residue being heated upon an iron plate to expel the final traces of acid. White molybdic acid remained. It was noticed several times that blue spots existed here and there in the mass, but these were removed by moistening the residue with nitric acid and evaporating a second time to dryness. This procedure was adopted in all the trials given below. Concordant results could not be obtained by merely drying the hydrate at a definite temperature. The same was true also on attempting to ignite the hydrate to trioxide. Loss then occurred from sublimation and volatilization.

[1] *Am. Chem. J.*, 1, 337.

[2] *Ibid.*, 1, 338.

RESULTS.

	Molybdenum trioxide present in grams.	Sulphuric acid added. cc.	Dilution. cc.	Temperature. °C.	Current.	Voltage.	Time. Hours.	Molybdenum trioxide found in grams.	Error in grams.
1	0.1302	0.1	125	70	$N.D._{.10^7} = 0.022$ A	2.0	$4\frac{5}{6}$	0.1299	— 0.0003
2	0.1302	0.1	125	80	$N.D._{.10^7} = 0.045$ A	2.25	$2\frac{1}{4}$	0.1302	....
3	0.1302	0.1	125	70	$N.D._{.10^7} = 0.04$ A	2.2	$4\frac{1}{2}$	0.1302	....
4	0.2604	0.2	125	75	$N.D._{.10^7} = 0.04$ A	2.0	7	0.2603	— 0.0001
5	0.1541	0.2	125	85	$N.D._{.10^7} = 0.04$ A	1.9	$2\frac{2}{3}$	0.1541	....
6	0.1541	0.2	125	80	$N.D._{.10^7} = 0.035$ A	2.1	4	0.1540	— 0.0001

The method is accurate, is easy of execution, and, as will be observed, requires comparatively little time. There seems to be no apparent reason why it should not replace some of the older and less reliable methods pursued in the determination of this element.

One of the first directions in which it seemed that the method could be made useful, was in the determination of the molybdenum content of the mineral molybdenite. By fusing the latter with a mixture of pure alkaline carbonate and nitrate, sodium molybdate and sulphate would be formed. If the sulphur was not to be determined, after dissolving out the fusion with water, and filtering out the insoluble oxides, it would only be necessary to acidulate the alkaline liquid with dilute sulphuric acid and proceed with the electrolysis; but in cases where an estimation of the sulphur was desired, it was thought that acetic acid would answer for the purpose of acidulation. To ascertain the latter fact the experiments given below were instituted. The solution, acidified with this acid, did not acquire a blue color on passing the current through it. The deposit of hydrated oxide was very adherent and was readily washed. It will, however, be noticed that a longer time is necessary for the complete precipitation. It is also advisable not to add the entire volume of acetic acid at first, but to introduce it gradually from time to time, from a burette.

RESULTS.

	Molybdenum trioxide present in grams.	29 per cent. acetic acid added. cc.	Dilution. cc.	Temperature. °C.	Current.	Voltage.	Time. Hours.	Molybdenum trioxide found in grams.	Error in grams.
1	0.1541	1	125	85	$N.D._{.10^7} = 0.075$ A	4.4	$7\frac{1}{2}$	0.1541	....
2	0.1541	1	125	85	$N.D._{.10^7} = 0.075$ A	4.4	3	0.1540	— 0.0001
3	0.1541	1	125	80	$N.D._{.10^7} = 0.05$ A	2.5	6	0.1543	+ 0.0002

In the last experiment, 5 grams of sodium acetate were added in order to increase the conductivity of the solution and also to ascertain what effect an excess of this salt would have, because, if the acetic acid were used to acidify the alkaline solution obtained by the decomposition of molybdenite, a great deal of this salt would be present. The concordant results justified the next step, which was to decompose weighed amounts of pulverized molybdenite with sodium carbonate and nitrate, then take up the fusion with water, filter out the insoluble oxides, acidify with acetic acid, boil off the carbon dioxide, and electrolyze. The liquid poured off from the deposit of the sesquihydroxide was heated to boiling and precipitated with a hot solution of barium chloride.

RESULTS OBTAINED FROM MOLYBDENITE.

	Molybdenite in grams.	Molybdenum found in per cent.	Sulphur found in per cent.
1	0.2869	57.37	38.28
2	0.1005	57.15	38.33
3	0.1388	56.83	37.87

MOLYBDENUM-SULPHUR RATIO.

(1)	1 : 2.004
(2)	1 : 2.012
(3)	1 : 1.998

From several experiments, which will not be recorded here, there is a possibility of separating molybdenum electrolytically from tungsten, the latter, of course, being present as an alkaline tungstate. Further work, however, will be necessary to fully establish this hope.

The experience detailed above proves conclusively that molybdenum must also be included in the list of metals which can be determined with the aid of the current and the analysis of molybdenite, as outlined, is vastly better than the usual procedures.

UNIVERSITY OF PENNSYLVANIA.

A COMPARISON OF THE SOLUBILITY OF ACETYLENE AND ETHYLENE.

BY SAMUEL AUCHMUTY TUCKER AND HERBERT R. MOODY.

Received June 12, 1901.

NO satisfactory or convenient method for the separation of acetylene and ethylene has yet been devised. The two gases exhibit such a similarity in their solubility that very few