[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Studies of the Reducing Action of Mercury. II. Stability of Quinquivalent Molybdenum Solutions. A Method for the Determination of Molybdenum by Reduction with Mercury and Titration with Ceric Sulfate

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Introduction

The volumetric determination of molybdenum has been studied frequently and many methods have been developed involving the reduction of molybdenum and subsequent titration with standard oxidizing agent. In practically all of these studies the reduced molybdenum solution has been protected from the air either by an atmosphere of some inert gas or by running the reduced solution into an excess of oxidizing agent. A few workers have reduced molybdenum to the quinquivalent stage and titrated this lower state without any precaution against air oxidation, but there seems to have been no systematic study of the stability of quinquivalent molybdenum solutions.

This investigation is concerned with the stability of quinquivalent molybdenum solutions and a new method for the determination of molybdenum based on reduction in acid solution with mercury, followed by titration with ceric sulfate solution using as indicator the ferrous complex of *o*-phenanthroline.

Chilesotti[1] observed that mercury would reduce a molybdic acid solution to the trivalent state if the hydrochloric acid concentration were about 9 *N*. This fact was carried no further than the preliminary observation. McCay and Anderson[2] observed qualitatively that molybdenum solutions were reduced by mercury.

Someya[3] reduced molybdenum to the quinquivalent state with bismuth amalgam. The extent of the reduction depended on the presence or absence of air and on the concentration of hydrochloric acid.

Stehlik[4] reduced molybdenum to the quinquivalent state with stannous chloride and titrated the reduced solution potentiometrically with standard ceric sulfate. Lang and Gottlieb[5] have proposed a new volumetric method for the determination of molybdenum. Their primary reducing agent is stannous chloride, and a thorough study of the effect of acidity on this reaction has been made.

Walden, Hammett and Edmonds[6] studied the reduction of molybdenum solutions in the silver reductor and also the titration of quinquivalent molybdenum with ceric sulfate using the *o*-phenanthroline ferrous complex indicator. The titration apparently was satisfactory, but the silver reduction technique did not give reproducible results.

Apparatus and Materials

All potentiometric titrations were performed in the classical manner using a saturated calomel reference electrode and bright platinum wire indicator electrode. Calibrated glassware was used.

The solutions used in the stability studies were prepared from purified molybdic oxide. The standard ammonium molybdate solutions were standardized by the silver molybdate method of McCay.[7] Typical data for the standardization of one such solution were: 0.1038, 0.1038, 0.1039. The standard ceric sulfate solutions which contain traces of iron were standardized against Bureau of Standards sodium oxalate according to the method of Willard and Young.[8]

In the experiments involving the shaking of molybdenum solutions and mercury, all the agitation was done by machine. This machine was run by an electric motor so that the rate of shaking was fairly constant. The motion was a short vertical stroke which kept the mercury splashing through the solution. The containers used were 250-ml. glass-stoppered soft glass bottles or, in case the solution was to be heated, glass-stoppered Pyrex Erlenmeyer flasks.

o-Phenanthroline Ferrous Complex as Indicator for the Titration of Quinquivalent Molybdenum with Ceric Sulfate

Several titrations of samples of quinquivalent molybdenum solutions with standard ceric sulfate were followed both potentiometrically and colorimetrically. It was soon found that the potentiometric end-point was vague, extending over a range of several drops of reagent. Graphs of the data showed a small secondary break within the larger one. Such behavior was encountered by Furman and Schoonover,[9] and they found the small secondary break was caused by iron in the ceric sulfate reagents. Iron was found to be present in the reagents used in our work, and the irregularity of the potentiometric curves is attributed to this cause. However, the end-point as indicated by the *o*-phenanthroline in the colorimetric titra-

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(1) Chilesotti, *Z. Elektrochem.*, **12**, 146 (1906).

(2) McCay and Anderson, THIS JOURNAL, **43**, 2372 (1921).

(3) Someya, *Z. anorg. allgem. Chem.*, **152**, 368 (1926).

(4) Stehlik, *Collection Czechoslov. Chem. Communications*, **4**, 418 (1932).

(5) Lang and Gottlieb, *Z. anal. Chem.*, **104**, 1 (1936).

(6) Walden, Hammett and Edmonds, THIS JOURNAL, **56**, 350 (1934).

(7) McCay, *ibid.*, **56**, 2548 (1934).

(8) Willard and Young, *ibid.*, **50**, 1322 (1928).

(9) Furman and Schoonover, *ibid.*, **53**, 2561 (1931).

tions was very sharp and satisfactory. The ferrous iron formed during the addition of the reagent to the reduced molybdenum solution must be oxidized by more ceric sulfate before the *o*-phenanthroline end-point occurs, so that the error caused by the iron in the potentiometric titrations is eliminated in the colorimetric method.

For the colorimetric titration, the acid concentration must be at least 2 *N* and the molybdenum concentration at the end-point must not exceed 0.25 g. per 300 ml. of solution. Otherwise, a red precipitate which is not destroyed by an excess of ceric sulfate tends to form and obscures the end-point. The formation of this precipitate is dependent on the simultaneous presence of cerous, molybdate, and *o*-phenanthroline ferrous ions in acid solution.

The procedure adopted in this work was to add 5–10 ml. of concentrated sulfuric acid to the quinquivalent molybdenum solutions which were already 2 *N* in hydrochloric acid. If necessary, the mixture was diluted with 2 *N* hydrochloric acid in order to keep the molybdenum concentration below the limit mentioned. Then two drops of 0.025 *M* *o*-phenanthroline ferrous complex indicator solution was added and the titration with ceric sulfate carried out at room temperature. Such a procedure was entirely satisfactory, the reaction being very rapid at room temperature and the color change at the end-point exceedingly sharp.

Stability of Quinquivalent Molybdenum Solutions

A concentrated solution of quinquivalent molybdenum was prepared by electrolytic reduction according to the method of Foerster and Fricke.[10] Portions of this reduced solution were diluted with water and hydrochloric acid to give (1) a solution 0.1 *M* in molybdenum and 2 *N* in hydrochloric acid and (2) a solution 0.1 *M* in molybdenum and 4 *N* in hydrochloric acid.

During the course of this work, samples of these two stock solutions of quinquivalent molybdenum were titrated at intervals in order to determine their respective normalities and follow the slow air oxidation of the reduced molybdenum. The relative instability of the solutions is evident from the following data.

QUINQUIVALENT MOLYBDENUM IN 2 *N* HCl

Days	0	2	8	14	44	202
Normality	0.08092	0.07978	0.07854	0.07565	0.06981	0.00505

QUINQUIVALENT MOLYBDENUM IN 4 *N* HCl

Days	0	1	3	4	5	6
Normality	0.1356	0.1353	0.1344	0.1325	0.1315	0.1298

The foregoing data show that quinquivalent molybdenum solutions are relatively unstable over extended periods of time, but the solutions are not appreciably oxidized in six or eight hours. It is thus possible to work with quinquivalent molybdenum solutions without precaution to exclude air if the solutions are to be oxidized within a short time. The acid concentration of such solutions must be above 1 *N*, however, for quinquivalent molybdenum is very unstable in neutral solution and tends to deposit molybdenum blue.

Reduction of Molybdic Acid by Mercury

Procedure.—The method of reduction is very similar to that described by McCay and Anderson.[2] The bottles or flasks used as reductors contained about 25 ml. of pure mercury. The sample of molybdate solution was pipetted directly into the reductor and the calculated volume of concentrated hydrochloric acid added to bring the acid concentration up to 3 *N*. The reductors were then agitated by machine, but vigorous shaking by hand is quite satisfactory. The sample is completely reduced with only five minutes of shaking. After the reduction, the solution is decanted from the mercury onto a filter, the filtrate being received in a 600-ml. beaker. The mercury and calomel in the bottle are washed five times with 20-ml. portions of dilute (1–5) hydrochloric acid, the mercury mass being well shaken with the wash solution each time, the solution then decanted through the filter. (No detectable amount of hydrogen peroxide is formed during the few seconds the dilute hydrochloric acid wash liquid is shaken with the mercury.)[11] In this manner, all of the mercury and some of the calomel is kept in the bottle. Such bottles are ready for use as mercury reductors again, for it is not necessary to start with fresh mercury each time. Four reductors were used in this way for at least seventy-five times each with no more care than that described above.

The reduced solution from the mercury reductor was titrated colorimetrically with ceric sulfate as described in the preceding section.

The reduction by mercury of molybdic acid solutions containing hydrochloric acid is very rapid, the solution changing almost immediately to light reddish-brown in color, which is typical of quinquivalent molybdenum in dilute acid. Five minutes of vigorous shaking is sufficient to cause quantitative reduction, further shaking having no effect.

TABLE I

DETERMINATION OF MOLYBDENUM BY REDUCTION WITH MERCURY AND TITRATION WITH STANDARD CERIC SULFATE SOLUTION

Molybdenum taken, g.	Error in molybdenum found, g.
0.2494	−0.0002
.2494	− .0001
.2494	.0000
.1968	− .0004
.1968	− .0005
.0806	− .0001
.0806	− .0001
.0806	− .0002

Effect of Acid Concentration.—The hydrochloric acid content of the molybdate solutions at the time of reduction has a marked effect on the state to which it is reduced. When the acid concentration is below 1 *N*, molybdenum blue frequently precipitates and interferes with complete reduction. When the hydrochloric acid concentration is between 1.5 and 3.5 *N* the reduction proceeds quantitatively to the quinquivalent state. However, if the acid concentration is above 4 *N*, reduction to the trivalent state becomes evident and in 9 *N* hydrochloric acid it is easily possible to reduce molybdenum completely to the trivalent state by shaking with mercury. (In strong acid, the solution of molybdenum in the trivalent state is sal-

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(10) Foerster and Fricke, *Z. angew. Chem.*, **36**, 458 (1923).

(11) Furman and Murray, THIS JOURNAL, **58**, 429 (1936).

mon pink in color.) The trivalent molybdenum solution is not stable in air, however, and if filtered and titrated with ceric sulfate the results may be low by 1% or more, due to air oxidation. Data illustrating this effect of acid concentration were obtained by reducing equal samples of molybdate at various acidities. The samples contained 0.1593 g. of molybdenum. When the hydrochloric acid concentration was 2, 3 and 3.5 *N*, the molybdenum found was 0.1592, 0.1591 and 0.1593 g. When the acid concentration was 4 *N*, the value for molybdenum found was 2% high, and when the acidity was stepped up to 9 *N*, the molybdenum found was 1.5% low on the basis of reduction to the trivalent state.

The dependence on acid concentration of the oxidation-reduction potentials of the systems Mo^6/Mo^5, Mo^5/Mo^3, and $Hg/Hg_2Cl_2/HCl$ has been studied. Curves showing these relations are plotted in Fig. 1. The data for the molybdenum systems were taken from the work of Foerster, Fricke and Hausswald[12] and the mercury system data were taken from the work of Ellis,[13] Linhart,[14] and Randall and Young.[15] Reduction to the trivalent state should begin when the Mo^5/Mo^3 system is less than 0.17 volt below the mercury system, and reduction to the trivalent state should be complete to 1 part per 1000 when the mercury system is more than 0.17 volt below the Mo^5/Mo^3 system. From the curves as plotted, reduction to the trivalent state should begin at about 1.5 *N* hydrochloric acid and be complete at about 6.5 *N* acid. Our experience was that reduction to the trivalent state did not interfere until the acid concentration became more than 3.5 *N*. Reduction to the trivalent state at lower acidities is probable, but any trivalent molybdenum formed is very likely oxidized by air during the filtration process.

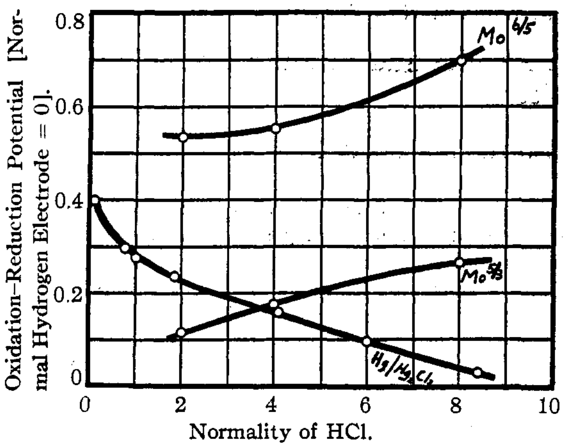

Fig. 1.—Graphs of oxidation–reduction potentials, E_0' referred to the *N* hydrogen electrode as zero, against normality of hydrochloric acid. Equimolecular mixtures of Mo^{vi} and Mo^{v} or of Mo^{v} and Mo^{iii}, respectively, were present in the solutions.

Effect of the Wash Liquid.—It was evident at the start of this work that water is not a satisfactory wash liquid. It either does not get the molybdenum away from the mercury-calomel particles or some molybdenum is oxidized when pure water is used as a wash liquid. However, 2 *N* (1–5) hydrochloric acid was found to serve the purpose quite satisfactorily.

Determination of Molybdenum in the Presence of Certain Impurities.—Phosphate and arsenate frequently are associated with molybdenum and their effect on this procedure is of interest. It was found that the addition of either phosphate or arsenate ions in amounts up to 0.25 g. did not interfere with the determination of molybdenum samples of equal weight. There was a slight slowing of the rate of reduction with the occasional appearance of molybdenum blue in the early part of the reduction, but reduction to the quinquivalent state was complete in five minutes in every case.

In any analysis where the preliminary separation of other elements must be carried out before the molybdenum can be determined by this method, the solution will contain large amounts of ammonium salts. It was found that as much as five grams of ammonium salts as chlorides and sulfates did not interfere with the determination of 0.1 g. samples of molybdenum by this method.

Effect of Copper Salts.—Copper ions will cause a determination of molybdenum by this method to be seriously in error, even if the amount of copper present is only a fraction of a milligram. This subject of the interference of copper in the determination of molybdenum by the mercury reduction method will be considered more fully in a later paper. Suffice it to say at this time that the very slow air oxidation of quinquivalent molybdenum is apparently an autoxidation reaction and, like many reactions of this class, it is strongly catalyzed by minute amounts of copper.

Analysis of Unknowns by this Method.—Professor E. R. Caley prepared a solution of ammonium molybdate from pure molybdic oxide. The weight of molybdic oxide actually taken by Professor Caley was 6.0177 g. per 500 ml. of solution. Aliquot portions (25 ml.) of this solution were analyzed by one of us (M.) and the results calculated back to the original basis of 500 ml. of solution. The results found by the mercury reduction method were 6.0219, 6.0100, 6.0219, 6.0030 and 6.0129 g. of MoO_3 per 500 ml. of solution. The average of these values is 6.0139 g.

One of us (F.) prepared a mixture of iron and molybdenum by grinding known amounts of pure molybdic oxide, ferric oxide and potassium chloride in an agate mortar. The other (M.) then determined the percentage of molybdenum in the resulting powder by the mercury reduction method. Samples were dissolved in dilute hydrochloric acid, the iron removed by double ammonia precipitation according to the procedure of Hillebrand and Lundell,[16] and the molybdenum determined in the filtrate. The percentage of molybdenum found by the mercury reduction method was 33.20, 33.10, 33.09, 33.10—average 33.12. The percentage of molybdenum actually taken by weight in the preparation of the sample was 33.02.

Acknowledgments.—Gratitude is here expressed to Professors Leroy W. McCay and E. R.

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[12] Foerster, Fricke and Hausswald, *Z. physik. Chem.*, **146**, 81 (1929).

[13] Ellis, THIS JOURNAL, **38**, 737 (1916).

[14] Linhart, *ibid.*, **39**, 2601 (1917).

[15] Randall and Young, *ibid.*, **50**, 989 (1928).

[16] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., N. Y., 1932, p. 251.

Caley for their interest and suggestions in this work.

Conclusions

1. Solutions of quinquivalent molybdenum are sufficiently stable in air at room temperature to be employed in any analytical procedure which is complete in a few hours time.

2. Molybdic acid solutions may be quantitatively reduced to the quinquivalent state by shaking with metallic mercury for five minutes if the hydrochloric acid concentration of the solution is between 2 and 3.5 *N*.

3. Quinquivalent molybdenum may be titrated with ceric sulfate at room temperature using the *o*-phenanthroline ferrous complex indicator if certain critical conditions are observed.

4. The mercury reduction method for determining molybdenum is rapid and accurate. The presence of considerable quantities of phosphate, arsenate or of ammonium salts is without effect upon the accuracy of the molybdenum determination.

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The Systems Lithium Chloride–Water–Ethyl Alcohol and Lithium Bromide–Water–Ethyl Alcohol[1,2]

BY JOHN P. SIMMONS, HENRY FREIMUTH AND HARRY RUSSELL

The lithium halides show a marked tendency to dissolve in organic liquids, particularly the alcohols,[3] and to form addition products with them. The systems lithium chloride–water and lithium bromide–water have been carefully explored and the existence of four hydrates of each halide has been shown.[4] A study based on the phase rule of the ternary systems, lithium chloride–water–ethyl alcohol and lithium bromide–water–ethyl alcohol has not been attempted, the only related work being that of Santiago Pina de Rubies[5] which consisted of solubility measurements of lithium chloride in mixtures of water and ethyl alcohol and analyses of the solid phases.

The following data are the experimental results of a phase rule study of the two systems lithium chloride–water–ethyl alcohol and lithium bromide–water–ethyl alcohol.

Preparation of Materials

Anhydrous Lithium Chloride and Lithium Bromide.—Hydrated lithium chloride or bromide dried by heating under ordinary conditions suffers some hydrolysis, giving products which contain about 98.50% lithium salt and 1.50% lithium hydroxide. Drying these salts in an atmosphere of hydrogen chloride or hydrogen bromide was avoided because of the special apparatus required and because but small amounts of the salt could be made at a time. Drying by heating a mixture of lithium salt and corresponding ammonium salt did not give a product sufficiently free of lithium hydroxide. The method finally adopted consisted in drying triply recrystallized hydrated lithium chloride and bromide in an electric oven at 110°. The residue was treated with absolute alcohol whereupon the lithium salt dissolved, giving a turbid solution due to the presence of lithium hydroxide in suspension. This solution was filtered until clear and the filtrate evaporated to dryness. Analyses of the residue gave for lithium chloride 99.90% purity and for lithium bromide a purity of 99.88%. These products were considered of sufficient purity for the purpose desired and were stored in an oven at 110° until needed.

Ethyl Alcohol.—Absolute ethyl alcohol was prepared by refluxing laboratory absolute alcohol with freshly ignited lime for twelve hours. The alcohol was then distilled off, again refluxed with lime and again distilled. The product obtained gave a boiling point of 78.2°. The alcohol was stored in a bottle from which it could be siphoned and which was equipped with a phosphorus pentoxide guard tube.

Experimental Part

Ten solutions of alcohol and water were prepared, varying in composition from 7.53 to 94.43% alcohol by weight. These with pure water and absolute alcohol were used with anhydrous lithium chloride and bromide in this investigation. Complexes of known content of lithium chloride, water and alcohol and of lithium bromide, water and alcohol were placed in solubility tubes and allowed to come to equilibrium at 25.00 ± 0.02°.

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(1) The investigation of the system lithium bromide–water and ethyl alcohol was offered as partial fulfilment of the requirements for the degree of Master of Science by Mr. Henry Freimuth.

(2) The investigation of the system lithium chloride–water and ethyl alcohol was offered as partial fulfilment of the requirements for the degree of Master of Science by Mr. Harry Russell.

(3) Turner and Bissett, *J. Chem. Soc.*, **105**, 1783 (1914); J. Simon, *J. prakt. Chem.*, **20**, 371 (1879).

(4) Hüttig and Steudemann, *Z. physik. Chem.*, **126**, 105 (1927).

(5) S. Pina de Rubies, *Anal. soc. españ fís. quím.*, **11**, 422 (1912); **12**, 242 (1914).