66-11,794

WHITFILL, Donald Lee, 1939-

THE ELECTROLYTIC REDUCTION OF BUFFERED MOLYBDATE SOLUTIONS.

The University of Oklahoma, Ph.D., 1966
Chemistry, inorganic

University Microfilms, Inc., Ann Arbor, Michigan

THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

THE ELECTROLYTIC REDUCTION OF BUFFERED MOLYBDATE SOLUTIONS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

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Norman, Oklahoma

1966

THE ELECTROLYTIC REDUCTION OF BUFFERED MOLYBDATE SOLUTIONS

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ACKNOWLEDGMENT

The author wishes to thank Dr. Bernard O. Heston for suggesting and directing this work.

He also wishes to thank the faculty, staff, and fellow students of the Chemistry Department for their friendliness and helpfulness.

He is especially grateful to his wife, Bernice, for her understanding and help while in graduate school.

IN

MEMORY

OF

Mother and Wayne

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THE ELECTROLYTIC REDUCTION OF BUFFERED MOLYBDATE SOLUTIONS

CHAPTER I

INTRODUCTION

It has been known for many years (1) that on electrolysis of solutions of molybdic acid, MoO_3, a blue color appears near the cathode, upon which there eventually forms a dark blue-black deposit. This substance was identified as $Mo_3O_8 \cdot 5H_2O$ by Manchetti (2), but this identification was not verified by other workers (3). Although there was no certainty as to the exact composition of the product there was no doubt that the molybdenum was present in a lower oxidation state than it was originally. It is thus possible to bring about the reduction of Mo(VI) electrolytically and the first definite application of this process to the preparation of lower oxidation state molybdenum compounds seems to have been made by Chilesotti (4). This author electrolyzed solutions of molybdic acid in hydrochloric acid with a mercury cathode and found that the molybdenum could be reduced to the (III) state. By the addition of the chlorides of alkali metals or of ammonium, after reduction, it was possible to isolate from the solution double salts of the type M_3MoCl_6, where M is potassium, and $M_2MoCl_5 \cdot H_2O$, where M is rubidium, cesium, or ammonium. In view of the ease with which trivalent molybdenum compounds are oxidized it was essential to separate anode and cathode compartments. A further investigation by Foerster and Fricke (5) showed that the nature of the salt isolated depended on the acid concentration; in the presence of relatively dilute

hydrochloric acid the $M_2MoCl_5 \cdot H_2O$ type was obtained on boiling after reduction and addition of the alkali chloride but if the solution was warmed to 80° C and kept saturated with hydrogen chloride gas while cooling, salts of the type M_3MoCl_6 crystallized out. The experimental details of Chilesotti were modified to a slight extent by Rosenheim and Braun (6) who electrolyzed a solution of 20 g $MoO_3 \cdot 2H_2O$ dissolved in 150 cc of hydrochloric acid (s.g. = 1.142) and 200 cc of water, with a mercury cathode. After reduction was complete various fluorides were added and the following double salts were isoltaed: $MMoF_4 \cdot H_2O$, where M is potassium or ammonium, and $(NH_4)_3Mo_2F_9 \cdot 2H_2O$. By working in hydrobromic acid solution, and adding ammonium bromide after electrolysis $(NH_4)_2MoBr_5 \cdot H_2O$ was obtained.

A number of observations of general interest were made by Chilesotti (7) in the course of an investigation of the reduction of molybdic acid solutions of various concentrations in hydrochloric acid. He found that during the process the cathode potential always rose slowly at first, then changed suddenly to a more negative value and remained in this vicinity for a period of time, followed by a further rise in potential. He concluded that the reduction occurs in the stages

$$Mo(VI) \longrightarrow Mo(V) \Longrightarrow Mo(III),$$

there being no evidence of a Mo(IV) stage. It was noted that if the hydrochloric acid concentration was about 7 to 9 N, then after complete reduction to the trivalent stage the solution was orange-red, but if the acid was more dilute (2.7 - 4 N), the final solution was deep olive-green. The difference in color was attributed to the presence of some divalent molybdenum in the green solution. Foerster and Fricke (5) concluded, however, that this is highly improbable and that the color variation is

due to the presence of different complex ions in equilibrium with simple Mo(III) ions. Wardlaw and his coworkers (8) have been able to isolate two isomeric molybdenyl monochlorides of the formula $MoOCl \cdot 4H_2O$, a brown substance separating from the red solution and a green substance from the green solution.

Moeller (9) states that the lower oxidation states of molybdenum are quite generally reducing in character and undergo fairly ready conversion to the (VI) state. The uncomplexed tripositive ion of molybdenum appears to be capable of existence in aqueous solution. However, all the lower oxidation states are best characterized in various complex ions and compounds. Information on these materials is at best incomplete and requires considerable systemitization. A variety of reducing agents (including Mo(III)) convert molybdates into colloidal molybdenum blues, the compositions of which approach $Mo_8O_{23} \cdot XH_2O$ (11). In studying the electrolytic reduction of molybdate solutions some idea of the complexity of the polymolybdic acids that are being reduced is gained by the following series of ions, reported by Jander, Jahr, and Heukeshoven (11), as formed by the addition of hydrogen ion to an alkaline molybdate solution:

$$MoO_4^{=} \longrightarrow Mo_3O_{11}^{-4} \longrightarrow HMo_3O_{11}^{-3} \longrightarrow HMo_6O_{21}^{-5} \longrightarrow$$

$$H_2Mo_6O_{21}^{-4} \longrightarrow H_3Mo_6O_{21}^{-3} \longrightarrow H_7Mo_{12}O_{41}^{-3} \longrightarrow$$

$$H_7Mo_{24}O_{78}^{-5} \longrightarrow H_9Mo_{24}O_{78}^{-3} \longrightarrow H_{12}Mo_{24}O_{78}.$$

Glasstone and Hickling (12) indicate that at a smooth platinum cathode the first stage of reduction is accompanied by very marked polarization (0.4 to 0.6 volt) in 8 N hydrochloric acid. This was

attributed to the formation on the cathode of an oxide containing both hexa- and pentavalent molybdenum. By coating the electrode, and thus diminishing its area, these oxide coatings not only increase the effective current density, but also prevent access of the ions to be reduced. These factors all tend to bring about an increase in the measured cathode potential.

Cotton (13) states that the following oxides of molybdenum are definitely established: MoO_3; Mo_2O_5; MoO_2. However, there are unquestionably various other stoichiometric oxides, and in the MoO_2-MoO_3 system seven intermediates such as Mo_8O_{23}, Mo_4O_{11} and $Mo_{17}O_{47}$ are known. The last of these has been shown to have MoO_6 octahedral and MoO_7 pentagonal bipyramidal units in the structure. The most important of the oxides is MoO_3. It is the ultimate product of heating the metal or other compounds, such as the sulfides, in oxygen. MoO_3 is a white solid at room temperature but becomes yellow when hot and melts to a deep yellow liquid at 795° C. It boils at 1155° C. It is the anhydride of molybdic acid, but it does not form hydrates directly. The hydrates $MoO_3 \cdot 2H_2O$ and $MoO_3 \cdot H_2O$ can, however, be precipitated from approximately neutral solutions of molybdates. The crystal structure of MoO_3 is a very rare type of layer structure in which each molybdenum atom is surrounded by a distorted octahedron of oxygen atoms. Mo_2O_5 is a violet solid soluble in warm acids and is also a good conductor of electricity, better than MoO_2. It can be prepared by heating the required quantity of finely divided molybdenum with MoO_3 at 750° C. When ammonia is added to solutions containing Mo(V), $MoO(OH)_3$ is precipitated, and this can be dried by heating to give Mo_2O_5. Molybdenum (IV) oxide, MoO_2, is

obtained by reducing MoO_3 with hydrogen below 470° C (above this temperature reduction proceeds to the metal) and by reaction of molybdenum with steam at 800° C. It is a brown-violet solid with a coppery luster, and it has fair electrical conductivity. It is insoluble in nonoxidizing mineral acids but dissolves in concentrated nitric acid with oxidation of the molybdenum to Mo(VI). The blue oxides of molybdenum are obtained by mild reduction of acidified solutions of molybdates or of suspensions of MoO_3 in water. The exact nature of these blue substances is not certain (10), but the following facts seem definite. The solid substances are not of uniform composition; they vary in formula within the limits $MoO_{2.5}$ and MoO_3. Thus the mean oxidation state of the metal atoms is between (V) and (VI). This could be due to the presence of metal atoms in both of these oxidation states occupying metal sites in oxygen - defective MoO_3 lattices. The intense colors are then not surprising, since phases or compounds containing an element in two different oxidation states characteristically have intense colors due to electron transfer absorption bands. It seems very probable, though it is not conclusively proved, that the aqueous solutions of the blue oxides are colloidal.

Senderoff and Brenner (14) electrolyzed aqueous solutions of Na_2MoO_4 under pressure at temperatures up to 300° C. No attempt was made to characterize the product exactly, but they concluded a hydrated oxide was formed. Kayeko and Yntema (15) reported that metallic Mo can be electrodeposited from aqueous solutions of MoO_3 containing high concentrations of salts. Formates, acetates, propionates, fluorides, and phosphates of Na, K, and NH_4 were used. The optimum pH range as

measured with a glass electrode was 5.5 to 6.8. The current density was varied from 0.06 to 3.3 amp/cm^2. The temperature was controlled between 30° and 55° C. Deposits were obtained on Cu, Ni, and Fe electrodes. They reported oxide formation when bath conditions differed from those listed above. Senderoff (16) reported that he could not duplicate these results. He reported only oxide formation. Goncharenko (17, 18) investigated the cathode deposit obtained during the electrolysis of aqueous solutions of molybdates. He reported a mean valency of 4.91 for the black oxide obtained on a platinum cathode. This oxide had been dried to a constant weight at 200° C. His results indicated the composition of the cathode deposit could be expressed approximately by the formula $Mo_2O_5 \cdot 2H_2O$. He also proposed that some of the molybdenum atoms could be trivalent, and some hexavalent, in the ratio Mo(III): Mo(VI) = 1:2. Evidence for this is found in investigation of the disproportionation of Mo(V) in alkaline solution (19).

A number of investigators have employed the polarographic technique in studying the reduction of molybdates. Von Stackelberg (20) found that molybdate does not produce a wave from neutral or alkaline solutions, but a well-defined wave is obtained in sulfuric acid solutions. The polarographic reduction of Mo(VI) in sulfuric, hydrochloric, perchloric, and phosphoric acid media was studied by Höltje and Geyer (21). In all they observed two to four waves, depending on the acidity, which they ascribed to reduction to Mo(V), to the red Mo(III), to the green Mo(III), and to $Mo(OH)_3$. Carritt (22) investigated the polarography of Mo(VI) and Mo(III) in various concentrations of sulfuric and hydrochloric acids, and employed the coulo-

metric analysis technique at controlled potential to determine reduction states. He found that in 0.3 M hydrochloric acid the polarogram of Mo(VI) comprises two waves, which result from reduction to Mo(V) and Mo(III), with half-wave potentials of -0.26 v. and -0.63 v. vs. S.C.E. The first diffusion current plateau was incompletely developed but the total diffusion current was well defined. In the same medium Mo(V) yielded a single wave ($E_{\frac{1}{2}}$ = -.60 v. vs. S.C.E.) corresponding to a two electron reduction to Mo(III). When controlled potential reduction was done on hydrochloric acid solutions of Mo(VI) and Mo(V) at a mercury cathode the green form of Mo(III) was produced with virtually 100% current efficiency. Solutions of Mo(III) in 0.3 M hydrochloric acid showed no cathodic wave, but an incompletely developed anodic wave appeared at -0.22 v. vs. S.C.E. In 0.8 M hydrochloric acid Carritt observed three waves on the polarogram of Mo(VI). The half wave potentials were -0.12 v., -0.25 v., and -0.55 v. vs. S.C.E. The first two waves were not completely resolved. He found that controlled potential reduction of the Mo(VI) solution at a mercury cathode at a potential (-0.15 v.) between the first and second waves produced a solution of +5 molybdenum which showed only the wave at -0.55 v. This led Carritt to conclude that the first two waves in the original Mo(VI) polarogram corresponded to the reduction to Mo(V) of two different molybdenum species in sluggish equilibrium. He did controlled potential reduction of Mo(V) solutions at -0.75 v. which produced a solution of green Mo(IV) with nearly 100% current efficiency. The calculated current consumption for a one electron reduction was 401 coulombs and the value observed after the current decreased virtually to zero was 403 coulombs. He found no cathodic wave

for the Mo(IV) solution, but an incompletely developed anodic wave was observed at the same potential (-0.15 v.) as the anodic wave of Mo(III). Carritt concluded that Mo(IV) is produced only by the reduction of Mo(V), and that controlled potential reductions of solutions of Mo(VI) at the same potential proceeds directly all the way to the Mo(III) state. This latter condition would be the one that prevails in reduction of Mo(VI) solutions at the dropping electrode at potentials corresponding to the total diffusion current. More recently polarograms of Mo(VI) have been determined in solutions of varying molybdenum and sulfuric acid concentrations. Kolthoff and Hodara (23) found that, under suitable conditions, two clearly defined waves A and B are observed. They attribute wave A to the reduction of Mo(VI) to (V) and wave B to the reduction of Mo(V) to (III). In 5 M sulfuric acid they found that wave A was split into two waves, A_1 and A_2, the heights of which were diffusion controlled. These waves were attributed to the presence of different species of Mo(VI). In dilute sulfuric acid they found that wave B is split into two waves, B_1 and B_2, which were diffusion controlled. These were attributed to the reduction of different species of Mo(V). Under the varying conditions the half wave potential of A_1 varied from +0.02 to +0.13, A_2 from -0.11 to +0.04, B_1 from -0.26 to -0.43, and B_2 from -0.55 to -0.74.

The purpose of this investigation was to study the oxide products obtained upon reduction of molybdate solutions containing acetate, formate, and oxalate as buffers. This problem was of interest due to the fact that International Business Machines uses a process whereby oxide films are plated from a formate buffered molybdate solution.

These oxide films are converted to the sulfide and used as lubricating surfaces on the iron parts. Since little is known of the electrolysis process, or the nature of the oxide film, this investigation was initiated. In general there are three goals of this study:

(1) determining the nature of the oxide film,

(2) determining how conditions of electrolysis (pH, potential, and buffer) affect this film,

(3) and obtaining a general idea as to the nature of the electrode reactions.

The methods used in this investigation were a combination of polarography followed by controlled potential electrolysis.

CHAPTER II

EXPERIMENTAL

Polarography

Preparation of Ammonium Molybdate Solutions

All solutions used in the polarographic investigation were 10^{-4} M in $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. They were prepared by dissolving 12.3595 g of "Baker's Analyzed" $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in distilled water and diluting to the mark in a one liter volumetric flask. This 0.01 M stock solution was used to make further dilutions to the required concentration. For the 10^{-4} M molybdate solutions a 10 ml aliquot was transferred by pipet into a one liter volumetric flask and diluted to the mark.

Buffered Solutions. All buffered solutions were prepared by dissolving the ammonium salt of the desired buffer in the 10^{-4} M ammonium molybdate solution and then adding the acid of the buffering anion to reach the desired pH. All solutions were made 0.1 M in the desired buffer. The pH was measured with a Beckman Zeromatic pH meter using a Beckman glass electrode and a saturated calomel reference electrode. The pH meter was standardized each time at a pH of 5.0 against pHydrion buffers distributed by the Micro Essential Laboratorys. The three buffering solutions used in the investigation were acetate, formate, and oxalate. The respective buffers were prepared from: Baker and Adamson reagent grade ammonium acetate and glacial acetic acid,

Fisher reagent grade ammonium formate and Eastman 98% formic acid, Mallinckrodt reagent grade ammonium oxalate and Baker and Adamson reagent grade oxalic acid.

Potassium Chloride Solutions. These solutions were prepared by dissolving 0.1 mole/l of Mallinckrodt reagent grade potassium chloride in the 10^{-4} M ammonium molybdate solution.

Acetate, Formate, and Oxalate Solutions

These solutions were prepared by dissolving 0.1 mole/l of the ammonium salt of each respective anion in distilled water. They were prepared in 100 ml volumetric flasks.

Saturated Potassium Chloride Solution

A saturated solution of potassium chloride was kept prepared for use in the saturated calomel reference electrode. This solution was prepared by placing excess Mallinckrodt reagent grade potassium chloride in distilled water.

Apparatus Used

Polarograph. All polarograms were run on a Sargent Model XXI visible recording polarograph.

Constant Temperature Bath. All polarograms were run at 25±0.01° C thermostated by a Sargent model SW thermonitor.

Polarographic Cell. A standard Sargent H cell was used as the polarographic cell. A saturated calomel reference electrode was prepared in one side of the cell. A sintered glass disk, augmented by an agar plug containing potassium chloride, minimized intermixing of the test solution and the solution in the reference cell.

Dropping Mercury Electrode. A standard type dropping mercury electrode with a mercury reservoir adjustable for height, to regulate drop time, was used.

Polarograms of the Supporting Electrolytes

In order to determine the potential range that each supporting electrolyte was capable of withstanding without reduction, each one was checked by running a polarogram over the range 0 to -2.0 v. vs S.C.E. In these polarograms, as well as all others, certain standard procedures were used. All potentials are versus the saturated calomel (S.C.E.) reference electrode. The drop time for the dropping mercury electrode (d.m.e.) was 4.0 sec. per drop. Each test solution was flushed for thirty minutes with nitrogen before the polarogram was run.

Ammonium Formate. A wave began developing at -1.54 v. The recorder went off scale at -1.97 v.

Ammonium Acetate. A good residual current curve was obtained past -1.4 v. A large maximum occured between -1.4 and -2.0 v.

Ammonium Oxalate. A wave began to develop at -1.45 v. The recorder went off scale at -1.98 v.

Potassium Chloride. A wave appears at -1.90 v.

Polarograms of Ammonium Molybdate Solutions

Since the supporting electrolytes are good only out to -1.4 v. these polarograms were run over a one volt range from 0 to -1.0 v. It was not found necessary to use any type of maximum suppressor in these polarograms. The polarograms in each supporting electrolyte at the various pH values all had similar characteristics in that they were not

good "analytical" polarograms. The waves that appeared did not rise sharply but were sloping. In practically all cases a sharp diffusion plateau was not reached. The half-wave potentials were determined by drawing the best lines possible parallel and through the center of the residual current and the diffusion plateau. A line was then drawn half way between these two, intersecting the wave. This point of intersection was taken as the half wave potential. These values are listed in Table 1.

TABLE 1

POLAROGRAPHIC DATA[a]

	Half Wave Potentials			
pH	KCl	Acetate	Formate	Oxalate
6.1				0.7[e]
5.6		0.9		
5.2			0.44 0.65	
4.1	0.62			
4.0		0.63 1.0	0.59[c]	0.38 0.65 0.8
3.0		0.58 0.9[d]	0.54[b]	0.25 0.5 0.9

[a]Reduction potentials versus saturated calomel electrode.

[b]Contains two reduction steps.

[c]Two reduction steps not apparent here.

[d]Very small and ill defined wave.

[e]Very small wave, no diffusion plateau.

Plots of E vs log i/i_d-i. Since the polarograms were all of the same general nature a representative group will be used to illustrate the n values (electron change) calculated by this method. By checking the simplified equation for the polarographic wave

$$E_{d.m.e.} = E_{\frac{1}{2}} - \frac{RT}{nF} \ln \frac{i}{i_d - i},$$

one sees that a plot of $E_{d.m.e.}$ vs log i/i_d-i should have a slope of $.059/n$ at 25° C, where n is the electron change, i is the current, and i_d is the total diffussion current. Table 2 lists the n values obtained from three polarograms obtained with the formate buffer.

TABLE 2

PLOTS OF E vs log i/i_d-i FOR AMMONIUM MOLYBDATE IN AMMONIUM FORMATE BUFFER

pH	Electron Change (n)
5.2	0.238
4.0	0.362
3.0	0.420

The values indicate our inability to get electron change values by this method due to the irreversibility of the reduction process.

Controlled Potential Electrolysis

Preparation of Ammonium Molybdate Solutions

All solutions used in the controlled potential electrolysis investigation were prepared by dissolving 14.40 g of Mallinckrodt analytical reagent molybdic acid in distilled water and diluting to the mark in a one liter volumetric flask. These solutions are 0.1 M in Mo(VI) as shown by reducing the Mo(VI) to Mo(III) in a zinc reductor

and then titrating with standard potassium permanganate. Buffered solutions were prepared in the same manner as those used in the polarographic investigation.

Standardization of Potassium Permanganate

Potassium permanganate was standardized against sodium oxalate by the Fowler-Bright method and stored in a brown glass-stoppered bottle.

Standardization of Ceric Sulfate

A standard solution of ceric sulfate was prepared according to the directions of Williard and Young (24). This solution was standardized against iron wire using ferroin as an indicator.

Sodium Oxalate Solutions

Standard sodium oxalate solutions were prepared by dissolving 3.3503 g of Mallinckrodt analytical reagent sodium oxalate in distilled water and diluting to the mark in a 500 ml volumetric flask. The sodium oxalate had previously been dried for two hours at 110° C and then stored in a desiccator over magnesium perchlorate. These were remade each month.

Sulfuric Acid

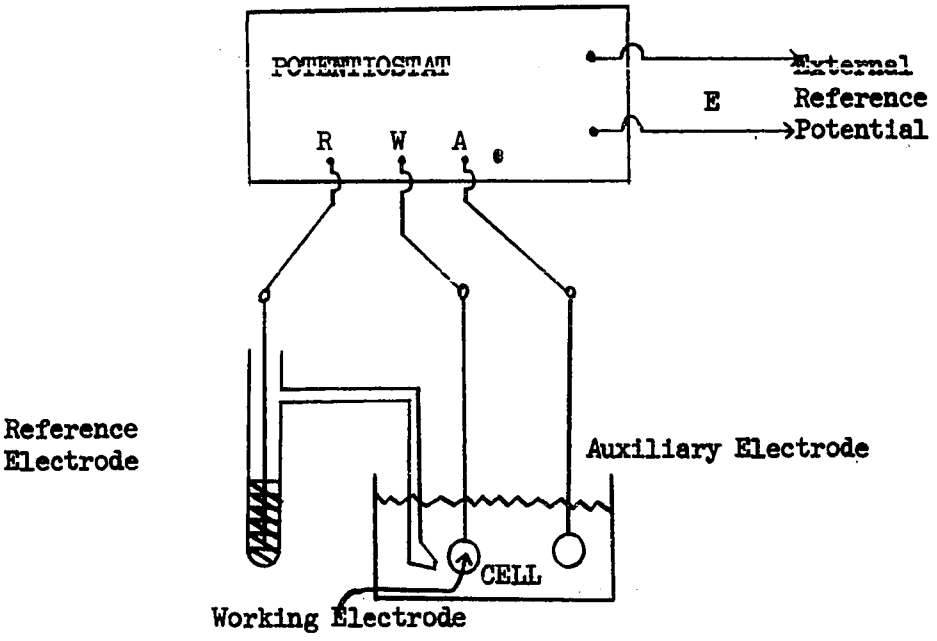
A 1.8 N sulfuric acid solution was used as solvent and eluant in the Jones reductor. It was prepared by diluting Mallinckrodt analytical reagent sulfuric acid with distilled water.

Apparatus

Potentiostat. This instrument is used to maintain constant potential at the working electrode in an electrolysis cell. The working electrode may function either anodically or cathodically.

In a typical electrolysis experiment utilizing the potentiostat there are three electrodes; working electrode, auxiliary electrode, and reference electrode. (See Figure 1.)

Fig 1 -- Potentiostat Circuit



The working electrode is to be maintained at some constant potential with respect to the reference electrode, say -0.5 volt versus the saturated calomel electrode. Into the potentiostat is fed a potential of -0.5 v. at terminal E; the instrument will then maintain a potential of -0.5 v. between R and W (the reference electrode and the working electrode) with W being negative with respect to R. Current flows between W and A (the working electrode and the auxiliary electrode) in direction and magnitude sufficient to maintain W at the desired potential relative to R.

The instrument used in this investigation was built at the Field Laboratory of Socony Mobil Oil Co. in Dallas, Texas. It has a rise time

of 12 micro sec. It can deliver about 40 volts and can flow up to 1 amp depending upon the load into which it works. The potentiostat has a very low output impedence; of the order of 0.1 ohm. A Fisher type S potentiometer was used to supply the external reference potential.

Automatic Titrator. All potentiometric titrations were done on a Metrohm E 336 Potentiograph. It is a variable speed visible recording titrator capable of plotting potential-volume curves or derivative curves ($\Delta E/\Delta V$ vs. Vol.).

Jones Reductor. A Jones (zinc) reductor was made according to the instructions of Kolthoff and Sandell (25).

Electrolysis Cell. A 100 ml tall form beaker was used as the electrolysis cell vessel. A cylindrical platinum electrode was used as the working electrode with a smaller gauze platinum electrode placed in the center as an auxiliary electrode. The working electrode had a circumference of 3.9 cm and a height of 5.4 cm. A saturated calomel electrode similar to the one described by Lingane (26) was used as the reference electrode. The solution to be electrolyzed was stirred by a magnetic stirrer.

Analysis of Lower Oxidation State Molybdenum Oxides

The analysis of lower oxidation state molybdenum oxides by normal analytical methods is very difficult due to the insolubility of these oxides in water and non-oxidizing acids. The percentage molybdenum can be obtained simply enough by igniting the oxides to MoO_3 at 500° C. Here we have

$$\text{Percentage Mo} = \frac{\text{Mo}/\text{MoO}_3\ (\text{wt. } \text{MoO}_3) \times 100}{\text{sample wt.}} = \frac{(0.6666)(\text{g. of } \text{MoO}_3) \times 100}{\text{sample wt.}}.$$

This method will yield the percentage molybdenum in the sample, but gives no indication of the oxidation state, which is of interest in unknown mixed oxides of molybdenum.

In order to determine the oxidation states of such oxides an attempt was made to titrate them in hot 6 M H_2SO_4 with $KMnO_4$. A small excess of permanganate was added to the solution, coloring it a faint pink. This speeded up the dissolution of the oxide. When the solution became colorless, another small amount of permanganate was added. In this manner the sample could be placed in solution and the number of equivalents of oxide determined. The obvious disadvantages of this method are the slowness of analysis and the difficulty in reaching a precise endpoint.

If an attempt is made to add excess $KMnO_4$ and then back titrate with a standard oxidant, such as sodium oxalate, the reaction proceeds stepwise in the acid solution. This is due to the action of the manganous ion on the reduction of permanganate ion to manganese dioxide. (27, 28)

$$2\,MnO_4^- + 3\,Mn^{++} + 2H_2O = 5\,MnO_2 + 4H^+$$

For this reason a quantitative determination of the excess permanganate ion is not possible in the acid solution.

It was felt that ceric sulfate would possibly be more suitable for the determination, since no intermediate oxidation states could hinder the reduction of Ce(IV) to Ce(III). A check in a reference text of analytical chemistry (29) revealed two references where such a method had been used to determine Cr(III) and V(IV). (30,31) In this method, excess ceric sulfate was added, and the excess titrated with

sodium oxalate. This end point cannot be determined by using the disappearance of color of the Ce(IV) ion, since this precedes the actual end point. For this reason, a suitable indicator must be used (such as ferroin), or the end point determined potentiometrically. Since a Metrohm E336 Potentiograph was available, the latter method was chosen in the analysis of the molybdenum oxides. The sodium oxalate solution was prepared by placing 3.3689 g of reagent grade sodium oxalate (previously dried for two hours at 110° C) in solution and diluting to 500.00 ml. This gives a calculated normalty of 0.1006.

A standard solution of ceric sulfate was prepared according to the directions of Williard and Young. (24) This solution was standardized against iron wire and found to be 0.0416± 0.0001 N.

Three samples were prepared by placing 10 ml of the ceric sulfate solution in 100 ml of 1.8 N sulfuric acid. These were titrated potentiometrically at an elevated temperature (70-80° C). The normality of the ceric sulfate determined by this method was 0.0423±0.0003 N. Since the reaction of the oxalate with Ce(IV) is relatively slow, (30, 31) the deviation from the previously determined normality is in the expected direction.

The method was checked for the analysis of molybdenum oxides by determining the percentage molybdenum in three samples of MoO_2. (32) The MoO_2 was dried for 1.5 hours at 100° C and three samples weighed out. These samples were placed in excess ceric sulfate and 1.8 N sulfuric acid. They will dissolve only slowly (2-3 hours) in this solution on heating and stirring by a magnetic stirrer-heater combination. The excess ceric sulfate was titrated with sodium oxalate at an

elevated temperature using a potentiometric endpoint. The results are given in Table 3, followed by a sample calculation.

TABLE 3

ANALYSIS OF MoO_2

Sample No.	Sample Wt.(g)	Vol. of $Ce(SO_4)_2$ Added (ml)	Vol. of Oxalate to Titrate Excess (ml)	Vol. of $Ce(SO_4)_2$ Reacting With Oxide (ml)	Percentage Mo_b
I_a	0.1011	45.18	2.95	38.16	75.44
II	0.1096	45.20	1.81	40.89	74.41
III	0.1021	45.12	2.90	38.22	74.70

[a]Used for sample calculation.
[b]Pure MoO_2 has percentage Mo = 74.99 versus 74.85% experimentally determined above as the average.

Since the slow reaction at the endpoint of the oxalate -Ce(IV) titration causes the normality to be in error, a titer was determined each time in determining the excess ceric sulfate. Determining ml of ceric sulfate/ml of oxalate aided in reducing any error due to the slowness of the endpoint, or due to decomposition of the oxalate solution. The normality of the ceric sulfate solution was taken as that determined versus the iron wire.

(I) Titer of $Ce(SO_4)_2$ solution = 2.38 ml of $Ce(SO_4)_2$/ml of oxalate

(a) (2.95 ml of oxalate) (2.38 ml of $Ce(SO_4)_2$/ml of oxalate) = 7.02 ml of $Ce(SO_4)_2$ in excess

(b) 45.18 ml - 7.02 ml = 38.16 ml reacting with the oxide

(c) 38.16 ml (0.0416 N) = 1.587 meq. = 1.59 meq.

(d) [(1.59 meq.) (1.97 mg of Mo/meq.)/101.1 mg] x 100 = Percentage Mo

(e) Percentage Mo = 75.44%

As an additional check on the method a sample of Na_2MoO_4 was dried to a constant weight at 110° C and analyzed for percentage molybdenum. Two samples were weighed out, placed in solution in 1.8 N H_2SO_4 and passed through a zinc reductor into excess ceric sulfate solution. The zinc reductor reduces Mo(VI) to Mo(III). The Mo(III) is oxidized back to Mo(VI) by the Ce(IV) and the excess Ce(IV) is determined as before by potentimetric titration with sodium oxalate at an elevated temperature. The results are given in Table 4, followed by a sample calculation.

TABLE 4

ANALYSIS OF Na_2MoO_4

Sample No.	Sample Wt.(g)	Vol. Of Ceric Sulfate Added (ml)	Vol. Of Sodium Oxalate To Titrate Excess (ml)	Vol. Ceric Sulfate Reacting With Mo(III) (ml)	Percentage Mo[b]
I[a]	0.1581	28.75	2.55	25.92	47.13
II	0.1687	30.43	2.70	27.43	46.82

[a]Used for sample calculation.

[b]Na_2MoO_4 has % Mo = 46.59 versus average of 46.97 experimentally determined above.

I. Titer = 1.11 ml. of ceric sulfate/ml. of sodium oxalate.

Normality of ceric sulfate = 0.090l.

(a) (2.55 ml. of oxalate)(1.11 ml of ceric sulfate/ml of oxalate) = 2.83 ml.

(b) 28.75 ml. - 2.83 ml. = 25.92 ml. of ceric sulfate.

(c) 25.92 ml. (0.090l N) = 2.33 meq.

(d) [(2.33 meq.)(31.98 mg/meq.)/158.1 mg] x 100 = % Mo

Percentage Mo = 47.13

By combining the two previous analytical methods, the oxidation state of the molybdenum oxide can be determined by taking the ratios of the amount of ceric sulfate required to titrate a sample before and after it is run through the zinc reductor. If x is designated as the valence change resulting from the oxidation of Mo(VI - x) to Mo(VI) by V_1 ml of ceric sulfate and V_2 ml of ceric sulfate are required to oxidize the Mo(III) to Mo(VI) after passing the solution through the zinc reductor, then:

$$V_1/x = V_2/3.$$

When this was done for the MoO_2 (32) the results are listed in Table 5.

Characteristics of Electrolysis

The observations made during the electrolysis of the ammonium molybdate solutions containing no buffering agent and those containing the acetate, formate, and oxalate buffers were very similar. On beginning the electrolysis the current would be high and slowly drop off to near zero as the electrolysis proceeded. A typical set of current-time data are given in Table 6.

TABLE 5

DETERMINATION OF OXIDATION STATE OF MoO_2

Sample No.	Sample Wt. (g)	Vol. Of $Ce(SO_4)_2$ For Mo(IV) To Mo(VI)	Vol. Of $Ce(SO_4)_2$ For Mo(III) To Mo(VI)	Oxidation Number Change[a]
1	0.1535	24.97	42.69	1.75
2	0.1631	26.64	46.20	1.73
3	0.1498	24.21	40.95	1.77

[a]Average of 1.75 vs 2.00 for pure MoO_2.

TABLE 6

CURRENT TIME DATA FOR FORMATE BUFFERED SOLUTION

pH	Time (min)	Current (milliamps)	Potential
4.0	0	600	-0.65 v.
	5	300	
	7	200	
	12	100	
	50	40	
	60	35	
	245	20	

As the electrolysis proceeds the electrode becomes covered with a brownish black oxide film. As this film covers the electrode, the current falls off, until eventually the reduction of the molybdate species is practically zero. During the electrolysis a small amount of hydrogen gas is produced at the cathode, with either O_2 or CO_2 being evolved at the anode. The production of hydrogen also falls off as the oxide film covers the cathode surface. More hydrogen is produced as the pH is lowered. During electrolysis the solutions all change color. Ammonium molybdate solutions change to a very light blue. The acetate and formate buffered solutions turn blue. The formate solutions turn a darker blue than the other two solutions. As the pH is lowered the solutions turn a darker blue. At a pH of 3.0 a clean platinum surface catalyzes the reduction in formate such that a reaction occurs between the molybdate ion and formate ion at the electrode surface when it is placed in the solution, with the subsequent production of the characteristic molybdenum "blues" (10). Investigation revealed that palladium and gold would produce this reaction also, but to a much smaller extent. Gold will produce only a very small amount of blue color over a period of hours. The catalytic effect of the clean platinum surface was not strong enough to produce this reaction in the acetate and oxalate solutions. The oxalate buffered solutions turn light brown upon electrolysis instead of blue. This is probably a colloid also, since tungsten and molybdenum have similar reactions in this respect. The tungsten "bronzes" are as characteristic as the molybdenum "blues." The small amount of oxide produced during an electrolysis (50 to 100 mg) requires that a series

of electrolyses be run to produce enough sample for analysis.

Ignition of Oxide Samples

A series of electrolyses were run to obtain samples for ignition to MoO_3. These samples were air dried at room temperature and then scraped off the platinum electrode and stored in a desiccator over magnesium perchlorate. When sufficient oxide was obtained it was dried to a constant weight at 110° C. The dried oxide was then placed in crucibles and ignited in an electric muffle furnace at 500° C. The lower oxidation state oxides are converted to MoO_3. The data obtained are listed in Table 7.

TABLE 7

COMPOSITION OF OXIDES OBTAINED AT CONTROLLED POTENTIAL

Buffering Agent	Potential vs. S.C.E.	pH	Dried Oxide Weight (g)	MoO_3 Weight (g)	% Mo	Average
None*	0.60	5.40	0.1572	0.1550	65.72	65.72
Acetate	0.65	5.30	0.1217	0.1184	64.83	
			0.1293	0.1255	64.65	64.74±.13
	0.60	4.00	0.1024	0.0950	61.84	
			0.1144	0.1062	61.88	61.86±.03
Formate	0.65	5.20	0.1580	0.1527	64.42	
			0.1557	0.1504	64.39	64.41±.02
	0.65	4.00	0.1035	0.0989	63.70	
			0.1043	0.0994	63.53	63.62±.12
Oxalate	0.75	6.30	0.1448	0.1323	60.91	
			0.1727	0.1573	60.72	60.82±.13
	0.75	4.00	0.1017	0.0920	60.30	
			0.1321	0.1187	59.90	60.10±.03

*Used for sample calculation.

Sample Calculation.

(1) Percentage Molybdenum = $\frac{Mo/MoO_3\ (MoO_3\ Weight)}{(Dried\ Oxide\ Weight)} \times 100$

(2) Percentage Mo = $\frac{(0.6666)(0.1550\ g)}{(0.1572\ g)} \times 100$

(3) Percentage Mo = 65.72

Titration of Oxide Samples

Samples were obtained as before and placed in excess ceric sulfate. The excess ceric sulfate was back titrated with sodium oxalate. The data obtained are given in Table 8.

TABLE 8

OXIDATION NUMBERS OF DRIED OXIDES OBTAINED AT CONTROLLED POTENTIAL

Buffer	Pot.	pH	Oxide Weight	Vol. of Ceric Sulfate (ml)	N of Ceric Sulfate	Ox. No. of Mo	Average
None*	0.60	5.40	0.1126	18.26	0.0576	4.64	
			0.1144	18.93		4.61	
			0.1236	19.95		4.64	4.63
Acetate	0.65	5.30	0.1110	15.74	0.0576	4.78	
			0.1431	20.42		4.78	4.78
	0.60	4.00	0.1148	8.60	0.0544	5.37	
			0.1156	8.41		5.38	
			0.1006	7.25		5.40	5.38
Formate	0.65	5.20	0.1034	15.89	0.0576	4.67	
			0.1125	17.66		4.65	
			0.1066	16.70		4.66	4.65
	0.65	4.00	0.1004	12.17	0.0544	5.01	
			0.1116	13.49		5.01	
			0.1032	12.47		5.01	5.01
Oxalate	0.75	6.30	0.0597	8.65	0.0576	4.68	4.68
	0.75	4.00	0.1014	14.00	0.0544	4.80	
			0.1030	14.28		4.79	4.80

*Used for sample calculation.

Sample Calculation.

(1) Percentage Molybdenum = 65.72 (from Table 7.)

(2) (0.6572) (0.1126 g) = 0.0740 g of Mo

(3) (18.26 ml) (0.0576 N) = 1.0518 meq.

(4) $\frac{74.0 \text{ mg of Mo}}{1.0518 \text{ meq.}} = 70.36$ g/eq.

(5) Change in ox. no. = $\frac{\text{at. wt.}}{\text{eq. wt.}} = \frac{95.94}{70.36} = 1.36$

(6) Oxidation number = 6.00 - 1.36 = 4.64

In order to minimize the possibility of air oxidation a series of electrolyses were run where the samples were not air dried before analysis. The oxide covered cathode was rinsed carefully with distilled water and placed in excess ceric sulfate solution. The excess was back titrated with sodium oxalate (V_1). The sample was then run through the zinc reductor into excess ceric sulfate and the excess again back titrated with sodium oxalate (V_2). The data obtained are given in Table 9.

Sample Calculation.

(1) $\frac{7.78 \text{ ml.}}{x} = \frac{14.85 \text{ ml.}}{3.00}$

(2) $x = \frac{(3.00)(7.78)}{14.85} = 1.57$

(3) oxidation number = 6.00 - 1.57 = 4.43

Uncontrolled Potential Electrolysis

All solutions, equipment, and procedures were the same as used in the controlled potential electrolysis. The potentiostat was used as a d.c. power source by connecting only the working and auxiliary electrode leads. The reference electrode was left out of the circuit.

In this case the potential controlling factor was the evolution of hydrogen gas at the working electrode. During these electrolyses a large amount of hydrogen gas was evolved and the current remained constant at 700 ma.

TABLE 9

OXIDATION NUMBERS OF UNDRIED OXIDES OBTAINED AT CONTROLLED POTENTIAL

Buffer	Potential	pH	Elect. Time (min.)	V_1 (ml)	V_2 (ml)	Ox. No. of Mo	Average
None*	0.70	5.40	30	7.78	14.85	4.43	
			30	8.74	15.83	4.34	4.38
Acetate	0.60	5.0	60	6.02	11.73	4.46	
			30	3.96	7.92	4.50	
			30	4.78	10.45	4.63	4.53
	0.60	4.0	30	2.35	5.50	4.72	
			30	3.64	7.54	4.55	
			90	6.47	12.69	4.47	4.58
Formate	0.65	5.0	120	15.04	28.25	4.40	
			36	5.68	11.64	4.54	
			30	6.26	12.95	4.55	4.50
	0.65	4.0	30	7.25	14.03	4.45	
			30	7.31	14.10	4.44	
			30	7.40	14.44	4.46	4.45
Oxalate	0.70	6.3	30	3.64	6.69	4.37	4.37
	0.75	5.0	30	1.90	3.70	4.46	
			30	2.16	4.37	4.52	4.49
	0.75	4.0	120	5.50	10.42	4.42	
			60	2.74	5.52	4.51	
			60	3.67	6.87	4.40	4.44

*Used for sample calculation.

Sample Calculation.

(1) $\frac{7.78 \text{ ml.}}{x} = \frac{14.85 \text{ ml.}}{3.00}$

(2) $x = \frac{(3.00)(7.78)}{14.85} = 1.57$

(3) oxidation number = 6.00 - 1.57 = 4.43

Ignition of Oxide Samples

A series of electrolyses were run to obtain samples for ignition to MoO_3. These samples were air dried at room temperature and then scraped off the platinum cathode and stored in a desiccator over magnesium perchlorate. When sufficient oxide was obtained it was dried to a constant weight at 110° C. The dried oxide was then placed in crucibles and ignited in an electric muffle furnace at 500° C. The lower oxidation state oxides are converted to MoO_3. The date obtained are listed in Table 10.

TABLE 10

COMPOSITION OF OXIDES OBTAINED WITH UNCONTROLLED POTENTIAL

Buffer	pH	Dried Oxide Weight (g)	MoO_3 Weight (g)	Percentage Mo	Average
None	5.40	0.1529	0.1482	64.61	
		0.4126	0.4004	64.69	64.65±.06
Acetate	5.30	0.1591	0.1528	64.02	
		0.1538	0.1472	63.80	63.91±.15
	4.00	0.1060	0.0974	61.25	
		0.1023	0.0940	61.25	61.25±.00
Formate	5.20	0.1105	0.1066	64.31	
		0.2477	0.2385	64.18	64.24±.09
	4.00	0.1021	0.0981	64.05	
		0.1049	0.1010	64.18	64.12±.09
Oxalate	6.30	0.1139	0.1092	63.91	
		0.1188	0.1135	63.69	63.80±.15
	4.00	0.1033	0.0981	63.30	
		0.1211	0.1153	63.47	63.38±.12

Titration of Oxide Samples

Samples were obtained as before and placed in excess ceric sulfate. The excess ceric sulfate was back titrated with sodium oxalate. The data obtained are given in Table 11.

TABLE 11

OXIDATION NUMBERS OF DRIED OXIDES OBTAINED WITH UNCONTROLLED POTENTIAL

Buffer	pH	Oxide Weight	Vol. of Ceric Sulfate (ml)	N of Ceric Sulfate	Ox. No. of Mo	Average
None	5.40	0.1034	16.26	0.0576	4.65	
		0.1033	16.37		4.65	
		0.1060	16.39		4.68	4.66
Acetate	5.30	0.1221	19.05	0.0576	4.6[illegible]	
		0.1218	19.09		4.64	
		0.1237	19.36		4.64	4.64
	4.00	0.1049	12.94	0.0544	4.95	
		0.1058	12.99		4.95	
		0.1127	13.43		4.88	4.96
Formate	5.20	0.1225	18.62	0.0576	4.70	
		0.1244	19.13		4.68	
		0.1296	19.78		4.69	4.68
	4.00	0.1015	12.83	0.0544	4.97	
		0.1499	19.93		4.92	
		0.1222	15.29		4.98	4.96
Oxalate	6.30	0.1285	18.30	0.0576	4.77	
		0.1164	16.79		4.75	
		0.1808	25.86		4.75	4.75
	4.00	0.1033	10.93	0.0544	5.14	
		0.1021	10.88		5.13	
		0.1105	11.68		5.12	5.13

A series of samples were prepared as before, but were dried for 24 hours at 110° C under a nitrogen atmosphere. The data obtained are listed in Table 12 for ignitions and titrations done on three sets of oxides.

TABLE 12

ANALYSIS OF OXIDES OBTAINED WITH CONTROLLED POTENTIAL AND DRIED UNDER NITROGEN

Buffer	pH	Oxide Wt. (g)	Vol. of $Ce(SO_4)_2$*	% Mo	Ox. No. of Mo	Average
None	5.4	0.1038	22.32	67.92	4.35	
		0.1040	22.19		4.36	
		0.1009	21.32		4.38	4.36
Formate	5.2	0.1018	22.13	66.65	4.30	
		0.1039	22.44		4.31	
		0.1055	22.85		4.35	4.32
Oxalate	6.3	0.1033	20.61	61.43	4.26	
		0.1042	20.87		4.31	
		0.1019	20.62		4.28	4.28

*Normality of ceric sulfate = 0.0544.

Since ignitions were not done on all of the oxides the remainder of the data are given in Table 13. The equivalent weights of the oxides dried under nitrogen are listed along with the equivalent weights of those dried in air.

A series of electrolyses were run where the samples were not air dried before analysis. All procedures were the same as those outlined for the data presented in Table 9, except the potential was not controlled. The data obtained are given in Table 14.

TABLE 13

EQUIVALENT WEIGHTS OF OXIDES OBTAINED WITH UNCONTROLLED POTENTIAL

Buffer	pH	Oxide Wt. (g)[a]	Vol. of $Ce(SO_4)_2$[b]	Eq. Wt. Under N_2	Average	Eq. Wt. in Air	Average
None	5.4	0.1038	22.32	85.78		110.00	
		0.1040	22.19	85.95		109.89	
		0.1009	21.32	86.98	86.27	112.77	110.89
Acetate	5.3	0.1017	21.39	87.67		111.00	
		0.1067	21.96	89.66		110.73	
		0.1024	20.85	90.62	89.32	110.45	110.73
	4.0	0.1014	15.28	122.17		149.85	
		0.1028	15.87	119.53		149.01	
		0.1280	19.13	123.08	121.59[c]	154.38	151.08
Formate	5.2	0.1018	22.13	84.83		114.48	
		0.1039	22.44	85.16		113.09	
		0.1055	22.85	85.08	85.02	113.68	113.75
	4.0	0.0777	9.47[d]	91.41		145.00	
		0.0779	9.30	92.74		138.80	
		0.0836	9.95	92.89	92.35	147.23	143.68
Oxalate	6.3	0.1003	20.61	89.55		122.38	
		0.1042	20.89	92.21		120.00	
		0.1019	20.62	90.98	90.91	121.34	121.24
	4.0	0.0792	8.55[d]	102.86		175.08	
		0.0849	8.63	108.85	105.86	172.66	173.87

[a]Oxide weights of those samples dried under nitrogen. See Table 11 for sample weights dried in air.

[b]Normality of ceric sulfate = 0.0544 except where indicated.

[c]Nitrogen flow stopped for unknown period of time.

[d]Ceric sulfate normality = 0.0900.

TABLE 14

OXIDATION NUMBERS OF UNDRIED OXIDES OBTAINED WITH UNCONTROLLED POTENTIAL

Buffer	pH	Elect. Time (min.)	V_1 (ml)	V_2 (ml)	Ox. No. of Mo	Average
None	5.4	30	9.75	18.01	4.38	
		60	15.15	27.91	4.37	4.38
Acetate	5.3	30	5.34	10.49	4.47	
		30	5.01	9.92	4.48	
		30	4.62	9.28	4.51	4.49
	4.0	30	2.13	5.17	4.76	
		30	2.75	6.23	4.68	
		30	2.87	6.60	4.70	4.71
Formate	5.2	30	7.87	14.67	4.39	
		30	8.46	15.03	4.31	
		30	6.66	12.66	4.42	4.37
	4.0	30	5.61	10.92	4.46	
		30	5.32	10.75	4.52	
		30	4.96	10.15	4.53	4.50
Oxalate	6.3	30	7.56	12.54	4.19	
		30	6.59	11.29	4.25	
		30	5.43	8.90	4.17	4.20
	5.0	30	2.39	4.71	4.48	
		60	4.32	8.01	4.39	
		90	7.59	14.23	4.40	
		30	2.57	4.93	4.44	
		30	3.42	6.94	4.52	4.45
	4.0	30	1.68	3.25	4.45	
		30	3.45	5.46	4.10	
		60	6.01	10.45	4.27	
		45	5.08	7.95	4.08	4.23

Spectral Investigation

An ammonium molybdate solution was electrolyzed for two hours using a platinum cathode. The cathode was covered with a black oxide film. The oxide covered cathode was placed in a solution of 3 M sulfuric acid. This solution was kept in a nitrogen atmosphere by

bubbling nitrogen gas through it while being heated and stirred by a magnetic heater-stirrer. During an eleven hour period aliquots were removed and their spectrum run on a Beckman DK-1 over the range 1700-350 millimicrons. No absorption peaks were recorded, indicating the insolubility of the oxide in dilute mineral acids. The oxide would dissolve slowly in concentrated sulfuric acid on heating. The reflectance spectrum of the black oxide powder was obtained using the reflectance attachment on the Beckman DK-1. No peaks were recorded. A gradual increase in absorption, as noted for metals, was recorded over the range 1700-350 millimicrons.

Magnetic Susceptibility Study

The magnetic susceptibility of the black oxide obtained by electrolysis of an ammonium molybdate solution was done at room temperature. It was measured with a Curie-Chevenaux type balance where the sample was suspended in a glass bucket by a quartz spring on a quartz fiber in a magnetic field. The oxide was found to be diamagnetic.

Powder Pattern X-Ray Study

A x-ray powder pattern was run on oxide samples and the MoO_3 obtained on ignition of the samples, obtained by electrolysis of acetate, formate, and oxalate buffered solutions. A Norelco x-ray generator mounted with a variable speed diffractometer and a scintillation

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The author wishes to express his appreciation to Dr. Wyman K. Grindstaff for his help in obtaining the spectral data and for doing the magnetic susceptibility work.

counter was used to obtain the data. Copper K-alpha radiation was used in all cases. The black oxide is amorphous and does not give a diffraction pattern. The diffraction pattern of the MoO_3 was found to match exactly the "d" group spacings given for MoO_3 in the Index to the Powder Diffraction File (1964). This indicates that complete oxidation is occuring on ignition.

Current-Time Study

A current-time plot was obtained on a controlled potential electrolysis of an ammonium molybdate solution. A Varian G-14 variable speed recording potentiometer was used to obtain the plot. The data obtained was compared with a mathematical evaluation of competing first or pseudo-first-order reactions done by Gelb and Meites (33). This comparison is done by plotting ln i/i_0 (where i is the current at time "t" and i_0 is the current when t = 0) against time. The data obtained are given in Table 15 and the plots shown in Figure 2. The experimental data are placed as points on the graph.

This data corresponds most closely to the system where

$$A + n_1e \xrightarrow{k_1} B$$

$$B \xrightarrow{k_2} C$$

$$C + n_2e \xrightarrow{k_3} D.$$

The three calculated plots are for (a) $k_1:k_2:k_3$ = 1:3:2; (b) 1:1.1:0.8; (c) 1:0.1:0.5.

The author wishes to express his appreciation to Dr. Raymond L. Kerns for doing the x-ray powder pattern work, and to the Geology Department of the University of Oklahoma for the use of their equipment.

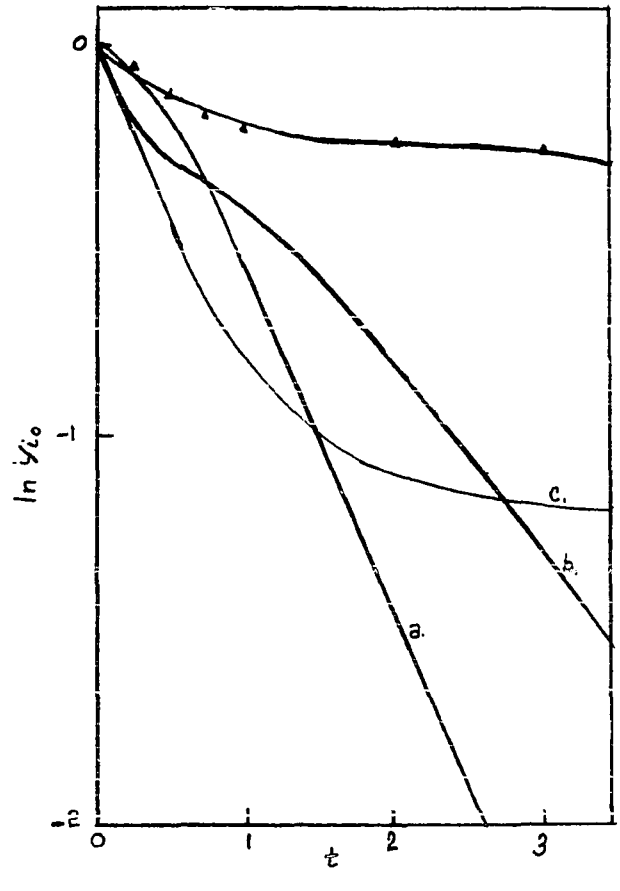
TABLE 15

CURRENT-TIME DATA*

Time (min)	i(ma)	i/i_o	ln i/i_o
0.00	270	1.000	0.0000
0.25	255	0.945	-0.0566
0.50	240	0.889	-0.1177
0.75	225	0.834	-0.1815
1.00	215	0.797	-0.2269
2.00	210	0.778	-0.2510
3.00	205	0.759	-0.2758
4.00	190	0.703	-0.3524
4.25	180	0.667	-0.4050
4.50	180	0.667	-0.4050

*Potential controlled at -0.65 v. vs. S.C.E.

Fig 2 -- Plot of ln i/i_o vs time.



Solubility Study

As indicated previously the oxide was found to be insoluble in dilute mineral acids, but soluble in concentrated sulfuric and nitric acid. It was insoluble in concentrated ammonium hydroxide and potassium hydroxide.

Summation of Data

All of the data listed in previous tables are summarized in Table 16. In this table the dependence of the composition and oxidation numbers of the oxides on pH and potential is indicated. A zero (0) indicates no change occurs, a plus sign (+) indicates the value increased and a minus sign (-) indicates the value decreased. The changes due to a change in pH are for those occuring in going from a pH of 5.0 to a pH of 4.0. The changes due to a change in potential are for those occuring in going from controlled to uncontrolled potential.

Example. In the acetate buffer the percentage molybdenum decreases (-) on going from a pH of 5.0 to 4.0 for both controlled and uncontrolled electrolyses. The composition does not change (0) with a change in potential at either a pH of 5.0 or a pH of 4.0. The oxidation number increases (+) in the dried oxide on going from a pH of 5.0 to 4.0 at both controlled and uncontrolled potential.

TABLE 16

SUMMATION OF DATA

Buffer	Composition Dependence of Dried Oxide on pH	Composition Dependence of Dried Oxide on Potential	Oxidation Number Dependence of Dried Oxide on pH	Oxidation Number Dependence of Dried Oxide on Potential	Oxidation Number Dependence of Undried Oxide on pH	Oxidation Number Dependence of Undried Oxide on Potential
	Cont.-Unc.	5 - 4	Cont.-Unc.	5 - 4	Cont.-Unc.	5 - 4
None	.....	0 0	.....	0 0	.....	0 0
Acetate	- -	0 0	+ +	- -	0 +	0 +
Formate	0 0	0 0	+ +	- -	0 -	0 +
Oxalate	0 0	+ +	+ +	+ +	0 0	- -

CHAPTER III

DISCUSSION

The polarographic data obtained in this investigation is in agreement with that previously obtained in other systems. Upon inspection of the "half-wave" values given in Table 1, one sees that in general the number of waves increases as the pH is lowered. The only exception to this is in the formate buffered solutions, where a very small wave is noted at -0.44 v. followed by a larger wave at -0.65 v., when the pH is 5.2. On lowering the pH in this buffer a single wave results at pH values of 4.0 and 3.0 This is opposite to what happens in the acetate and oxalate buffers, where more waves appear at the lower pH values. No quantitative explanation will be attempted for these dissimilarities, since coulometric analysis techniques would need to be employed using a mercury cathode to obtain more information about the reduction steps. In this investigation the author was interested in the product obtained on a solid platinum electrode, therefore an investigation such as indicated above was not done. In general, if one considers the possible change of species in solution (11) as the pH is lowered, along with the complexing ability of the buffers, it appears quite likely that multiple reduction steps would be noted. Since formate has demonstrated its ability to act as a reducing agent in solutions of low pH, the possibility exists that an intermediate

reduction step does not appear, but instead reduction to the (III) state occurs in one step. Acetate and oxalate are not as strong reducing agents and might not possess this ability. The lack of a sharply rising wave coupled with an indefinite diffusion current plateau indicate the irreversibility of the reduction process. The electron change values listed in Table 2 verify this when plots of E vs log i/i_d-i are made. For these reasons the polarographic data will be used only to indicate the potentials at which controlled potential electrolyses should be performed. Since mercury and platinum will possess very different properties as working electrodes, no assurance is given that the electrolysis potentials on the platinum working electrode will be the same as those for the dropping mercury electrode. A scan of potentials around these values, using the potentiostat, indicates that they are correct potentials to use, since no appreciable electrolysis occurs until these potentials are reached.

The electrolysis process involves the reduction of an anion species, therefore it is diffusion controlled. The negative ion must approach the cathode by diffusion and convection against an adverse potential gradient. In the reduction of acid solutions of molybdate, the species present are very complex. In this discussion no attempt will be made to discuss the reduction process for a specific species and the word "molybdate" will be used to refer to a negatively charged oxy-molybdenum(VI) ion. As indicated by the data in the previous tables, the electrolysis process falls off for the reduction of molybdate as the working electrode becomes coated with the black oxide film. This is in agreement with data obtained by Heston (34) when reduction

of formate buffered molybdate solutions was done on steel. This can be attributed to the fact that the oxide film is non-conducting, and the reduction process ceases when the electrode surface is covered. It also can be explained by a model whereby an adverse potential gradient builds up as the oxide film thickens on the electrode surface, until a point is reached where the molybdate ion cannot diffuse through the film to be reduced. A model such as this has been proposed by Wagner (35). In either case, the result is the same. Only a small amount (50 to 100 mg) of oxide product is obtained on the electrode surface. As a result of this, nothing is to be gained by doing electrolyses for an extended length of time. Most electrolyses in this investigation were run from 30 to 90 minutes.

When electrolyses are done on the different buffered solutions, the results are quite similar. In all cases a brownish-black oxide film is formed on the cathode surface. This film forms with varying speeds and in varying amounts depending on the buffer. The order of appearance in both speed and amount decreases in the order: formate > acetate > oxalate. The oxide films formed from the formate buffer have a more smooth and lustrous appearance than those from the acetate or oxalate buffers. The films formed in the oxalate buffer are more adherent and more difficult to scrape from the electrode surface. It appears to be the tightest film, since it is much thinner. The best films are obtained from formate and oxalate buffers. Those formed from acetate buffers have poor adherent properties.

A weight loss is noted when the films are air dried at 110° C. A further weight loss is noted when the dried oxides are ignited at

500° C. This is contrary to what would be expected, since the MoO_3 formed on ignition has the highest oxygen to molybdenum weight ratio. It would be expected that the oxide would gain weight on ignition to the highest oxidation state. This indicates that a hydrated oxide is formed in the reduction process, and all of the water and/or hydroxides are not removed on drying to a constant weight at 110° C. Thus a weight loss is noted on ignition at the higher temperature. The percentage molybdenum in the dried oxides is found to range from 60-65%. This range could be expected due to different amounts of hydration occuring in the solutions of different buffer and pH. The percentage molybdenum will be highly dependent on the amount of drying.

When the oxidation numbers for the oxides are determined they are found to lie in the range 4.63 to 5.38 for the dried oxides and 4.20 to 4.71 for the undried oxides. These values indicate that a mixed oxide is formed on reduction, which is then partially reoxidized in the drying process. Therefore, the oxide obtained on the cathode will not have the same oxidation number as one that is dried before analysis. This was shown to be true by doing a sequence of determinations:

(1) oxides were air dried at 110° C before analysis, (Table 8, 11)

(2) oxides were dried under nitrogen at 110° C before analysis, (Table 12, 13)

(3) oxides were analyzed before drying. (Table 9, 14)

In all cases the air dryed oxides have a higher oxidation number than those dryed under nitrogen, or those analyzed before drying.

Comparable values were obtained for the oxidation numbers of the oxides dried under nitrogen and the undried oxides. This indicates the values obtained for the undried oxides by using the zinc reductor are correct, and the inability to obtain the exact oxidation number of MoO_2 (Table 5) by this method must be due to higher oxidation state species present in the commercially prepared MoO_2.

The oxides obtained at controlled potential electrolysis have an oxidation number of $4.50 \pm .05$, independent of changes in buffer or pH. No other overall correlation is found between oxidation number changes and changes in the electrolysis conditions. No consistent change in oxidation numbers is noted when going from controlled to uncontrolled potential, or on lowering the pH, in the different buffers. This, coupled with the fact that the oxidation number does not change in the unbuffered solutions, indicates the buffer plays a part in the electrolysis mechanism. Again, this could be attributed to the difference in reducing abilities of the buffers. Each buffer will be discussed separately. From the data given in the tables on the dried oxides it is apparent that an oxide of higher oxidation number is obtained on drying, due to oxidation. In this discussion the products formed on the electrode will be considered, by using the data for the undried oxides, in an attempt to correlate the product formation with a possible electrolysis mechanism.

In the acetate buffer the oxidation number is not changed by a change in pH at controlled potential, or in going from controlled to uncontrolled potential at a pH of 5.0. The oxidation number is increased from 4.49 to 4.71 as the pH is lowered in an uncontrolled

potential electrolysis. The oxidation number is increased from 4.58 to 4.71 in going from controlled to uncontrolled potential at a pH of 4.0. Both of these would indicate a dependence on hydrogen ion concentration for the electrolysis process in acetate buffer.

In the formate buffer the oxidation number obtained is independent of pH at a controlled potential, and independent of potential at a pH of 4.0. The oxidation number increases from 4.37 to 4.50 when the pH is lowered in an uncontrolled potential electrolysis, and decreases from 4.50 to 4.37 at a pH of 5.0 when going from controlled to uncontrolled potential. Again this could indicate a dependence on the hydrogen ion concentration for the electrolysis mechanism.

In the oxalate buffer the oxidation number is independent of pH at controlled potential in the same pH regions as studied above for the acetate and formate buffers, but is lower at a pH of 6.3. This anomaly might be attributed to a difference in complexed species at the higher pH, since the oxalate is the best complexing agent of the buffers studies. In the same pH region as studied for acetate and formate the oxidation number decreased from 4.45 to 4.23 on lowering the pH with uncontrolled potential and decreases from 4.44 to 4.23 on going from controlled to uncontrolled electrolysis at a pH of 4.0. This would indicate more dependence on potential and less on pH in this buffer.

The changes noted for the three buffers can be represented in a sequence as listed:

	Acetate		Formate		Oxalate	
	Cont.	Uncont.	Cont.	Uncont.	Cont.	Uncont.
pH = 5.0		4.49	4.50 →	4.37		4.45
		↓		↓		↓
pH = 4.0	4.58 →	4.71		4.50	4.44 →	4.23

For the acetate, lowering the pH produces the same result as increasing the potential. In the formate, lowering the pH reversed the change brought about by increasing the potential. This indicates the possibility that the amount of evolved hydrogen is important in the electrolysis mechanism, whereby the hydrogen acts as the reducing agent. The resulting reduction is not taken to as low an oxidation state as when the cathode itself is doing the reduction. This would not be true in the case of the oxalate, since this effect is not noted in this buffer. Another piece of evidence pointing to this possibility is the fact that the controlled potential electrolyses, where less hydrogen is evolved, are independent of buffer and pH.

The x-ray analysis data gave no help on the oxide itself, since the oxide is amorphous. It did indicate the validity of the compositions obtained on igniting the oxides since the MoO_3 produced was shown to be free of impurities.

The combination of solubility and magnetic susceptibility data indicates the fact that no (III) or (V) states are present in the oxide. The solubility data matches that of MoO_2 most closely, since Mo_2O_5 and $Mo(OH)_3$ are soluble in mineral acids. The fact that the oxide is diamagnetic indicates no unpaired electrons present, as would be the case for the (III) and (V) states. If these facts are considered, along with the fractional oxidation states, the oxidation states of the mixed oxide must be (IV) and (VI). A possible reaction scheme,

that is somewhat like the scheme of Gelb and Meites (33) that fit our data most closely, is as follows:

(1) Mo(VI) is reduced to Mo(V),

(2) Mo(V) can then be reduced further to Mo(IV) or,

(3) Mo(V) can disproportionate to Mo(VI) and Mo(IV).

Since the disproportionation could occur to varying degrees in the different solutions, the fractional oxidation states that were determined are quite plausible. A reaction scheme is given below for the controlled potential case where the oxidation number was $4.50 \pm .05$.

$$4e^- + 4\ Mo(VI) \longrightarrow 2\ Mo(V)$$

$$(1) \qquad 2\ Mo(V) \longrightarrow Mo(IV) + Mo(VI)$$

$$(2) \quad 2e^- + 2\ Mo(V) \longrightarrow 2\ Mo(IV)$$

$$6e^- + 4\ Mo(VI) \longrightarrow 3\ Mo(IV) + Mo(VI).$$

The part played by the hydrogen, as advocated before, would be consistent with this mechanism since the Mo(V)→Mo(IV) reduction might be done by the hydrogen to a smaller extent than that done on the electrode itself. This would allow more disproportionation to occur, increasing the oxidation number of the oxide.

CHAPTER IV

SUMMARY

A polarographic and controlled potential electrolysis investigation has been done on ammonium molybdate solutions buffered by acetate, formate, and oxalate in the pH range 4.0 to 6.3. The investigation indicated that:

(1) the black oxide obtained as product in the electrolyses is a hydrated, mixed oxide of Mo(IV) and Mo(VI),

(2) the oxidation number of the oxide is dependent on the potential, pH, and buffer, to varying degrees,

(3) the oxide is subject to air oxidation at elevated temperatures, and the dried product has a higher oxidation number than that obtained on the electrode.

An electrolysis mechanism was proposed where Mo(V) is formed, followed by simultaneous disproportionation to Mo(VI) and Mo(IV), and reduction to Mo(IV). The possibility of evolved hydrogen acting as the reducing agent in some cases is indicated.

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