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The Electrolytic Preparation of Molybdenum From Fused Salts
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Major: Physical Chemistry, Department of Chemistry
Minors: Organic Chemistry, Inorganic Chemistry
Pages in thesis, 94, Words in abstract, 500

ABSTRACT

Compounds representative of each of the valence states of molybdenum were investigated with regard to their suitability for use in the electrolytic preparation of molybdenum from fused salts. Satisfactory results were obtained with solutions of potassium hexachloromolybdate (III) in molten mixtures of alkali halides. The electrolysis of a solution of K_3MoCl_6 in a 1:1 mixture (by weight) of KCl and NaCl at current densities of 3 to 100 amp/dm² and a temperature of 900°C resulted in the deposition of coarse powders of pure molybdenum at the cathode. The optimum concentration of the molybdenum salt was 3 to 5 mole %.

The electrolysis of a solution of K_3MoCl_6 in the eutectic mixture of KCl and LiCl at current densities of 3 to 100 amp/dm² and temperatures between 600° and 900°C resulted in the deposition of pure molybdenum in various forms at the cathode. At 3 amp/dm² and 600°C coherent thick electrodeposits were produced. At higher current density and temperature fine powders of molybdenum were produced. The optimum concentration of the molybdenum salt was about 4 mole %.

The deposits from both solutions were found to be 99.9+ % molybdenum and the oxygen content was as low as 0.026%. The density of the coherent deposits was 9.6, or 94% of the theoretical density of molybdenum. The deposits adhered well to the cathode and were easily separated from the adhering electrolyte by leaching with dilute hydrochloric acid. The current

efficiency for metal deposition was 'close to 100% in both solutions.

All electrolyses were performed in an argon atmosphere, and all materials were carefully dehydrated, because it was found that contamination by oxy-compounds resulted in low current efficiency and impure deposits.

The polarization and equilibrium potentials were determined in the following solutions: 1) pure solutions of K_3MoCl_6 in the $KCl-LiCl$ mixture, 2) a sample of the same solution after exposure to air, 3) a solution of K_2MoO_4 in the same alkali halide mixture. It was found that the potential of a molybdenum electrode in the last two solutions was 0.3 to 0.4 volts more noble than in the first solution. It was also shown that the electrode process which is associated with the more noble potential is the deposition of molybdenum oxides. It was concluded, therefore, that pure molybdenum could not be deposited from solutions containing oxy-compounds, since the deposition of oxides would occur preferentially. This was confirmed by X-Ray diffraction and chemical analyses.

The deposition of molybdenum from the pure solutions of K_3MoCl_6 in the alkali halide mixture occurs with very low polarization in the temperature range of 700° to $900^{\circ}C$ but with somewhat higher polarization at $600^{\circ}C$. There is some evidence that the reaction mechanism at $600^{\circ}C$ differs from that at higher temperatures.

Equilibrium potentials of zinc, iron, copper, and silver in solutions of their salts in the same alkali halide mixture were measured. The position of these elements in the E.M.F. series in the molten alkali halide solvent is in the order listed. The position of molybdenum

in this series is between copper and silver. The potential measurements provided evidence for the existence of complex halo-metal anions in the alkali halide solvent at 600°C. A new reference electrode for the measurement of potentials in molten salts, i.e., the Ag / AgCl (1) electrode, was used for these measurements.

A new method of preparation of MoCl_2 and an improved method of preparation of K_3MoCl_6 are described.

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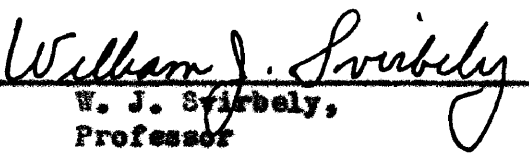
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THE ELECTROLYTIC PREPARATION OF MOLYBDENUM FROM FUSED SALTS

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Thesis submitted to the Faculty of the Graduate School
of the University of Maryland in partial
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1952

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THE ELECTROLYTIC PREPARATION OF MOLYBDENUM FROM FUSED SALTS

INTRODUCTION

In recent years there has been a notable increase in interest in refractory metals which has been largely instigated by requirements for materials which are stable and inert, both physically and chemically, at exceptionally high temperatures. The high temperature alloys in use today (titanium, for example) can be used up to a temperature of about 1000°C, beyond which they are of little value. Above this range molybdenum and tungsten seem to have the best possibilities, with most of the interest centered on molybdenum because of its availability in this country. The United States produces over 85% of the world's total production of molybdenum ores and concentrates and has large proven reserves of ores¹.

The properties of molybdenum which make it of special interest are its high melting point, high Young's modulus, high hot hardness, and good strength at high temperatures. These properties are well beyond the range of the heat resistant alloys used today. An exhaustive discussion of the properties of molybdenum has been published by R. M. Parke².

In view of the great interest in this metal, a research program was initiated to develop, if possible, electrolytic methods for the production of pure molybdenum powders, and also of coherent molybdenum electrodeposits. The latter is of particular interest since it would provide a means of bypassing the rather complicated powder-metallurgy techniques now used for producing molybdenum objects. When only surface properties are important,

a coating of molybdenum may be applied to an object, thus conserving much of this critical metal and further enabling one to take advantage of the structural properties of the metal comprising the bulk of the piece. In addition, electroforming of parts with molybdenum would result not only in the elimination of powder metallurgy operations but also of many difficult fabrication steps.

The prices (in 1951) of various forms of molybdenum metal and of some molybdenum compounds are listed in Table I.

TABLE I. Prices of Molybdenum Metal and Some Molybdenum Compounds

<u>Material</u>	<u>Price</u> (per pound of molybdenum contained)
Molybdenite ore concentrate	\$ 1.00
Molybdic oxide (Technical)	1.14
Molybdenum metal powder	3.25
Molybdenum wire	9.00
Molybdenum sheet (rolled)	13.50 - 25.00

On examining the costs of molybdenum in its progress from ore to fabricated metal, we find that its price almost triples during the purification and reduction of the oxide to make metal powder, triples again in going from powder to wire, and multiplies by from four to ten times in being pressed and rolled into sheet. The advantages of an alternative means of producing the powders are evident and the desirability of producing electroformed shapes from molybdenum salts need not be further belabored.

CHAPTER I

HISTORICAL

The commercial method of producing the metal consists of reducing pure molybdic oxide or ammonium molybdate with hydrogen to form a fine powder which is then worked by powder metallurgy methods. Recently, a method of producing ingots by vacuum arc-melting has been brought to a stage of pilot plant operation³. In this process, the molybdenum powder is sintered to make an electrode which is then melted in vacuum in a water-cooled copper mold by an electric arc. A method for producing molybdenum deposits on objects has recently been described⁴ which involves the reduction of molybdenum pentachloride vapor by hydrogen in a sealed vessel at about 20 mm pressure and a temperature of 800° to 1100°C. The deposited molybdenum metal is said to adhere well to various metals under suitable conditions. Another method for producing molybdenum deposits⁵ employs the thermal decomposition of molybdenum carbonyl at pressures below 0.1 mm and at temperatures of about 600°C.

Since the present study involves the electrolysis of fused salts for the production of molybdenum, there are three major fields of investigation which will be reviewed in this section. They are: 1) the electrolysis of fused electrolytes; 2) the electrolysis of solutions of molybdenum compounds; 3) the electrolysis of molybdenum compounds in fused electrolytes.

The first published study on the electrolysis of fused electrolytes was that of Sir Humphry Davy with fused potassium hydroxide⁶. It is of interest to note that Davy, in this first instance of obtaining a

metal, potassium, from a fused electrolyte, found it necessary to protect it from the atmosphere. Other work in this field has been published by Davy, Faraday, and others. A thorough and systematic examination of the electrochemical and chemical properties of fused electrolytes was carried out by Lorenz ⁷ and his students over a period of many years, the results of which were collected and published in 1906. This work contains practically all that was known about fused electrolytes up to that time. A symposium on the electrolysis of molten salts was published by the Electrochemical Society ⁸ in 1925 and a symposium summarizing the considerable volume of recent work by Russian workers was published ⁹ in 1935. Recent individual workers in the field are Kroll ¹⁰, Drossbach ¹¹, and Driggs and Lilliendahl ¹².

The second field indicated, that of electrolysis of solutions of molybdenum compounds, is one which contains a large amount of conflicting information and an unusually large quota of unreliable reports. After a thorough analysis of the literature and many attempts to duplicate published claims, one can state with certainty that no electrodeposit whose major constituent is molybdenum metal has been obtained by the electrolysis of aqueous or organic electrolytes, with the possible exception of deposits which grow to only a few microns in thickness and then cease forming. It is extremely difficult to determine the properties or composition of deposits as thin as these. This opinion is in concurrence with that of Childs ⁴ et al, and Lander and Germer ⁵. Chilcotti ¹³ attempted to deposit molybdenum from a number of aqueous solutions but obtained negative results. A patent ¹⁴ on the electrodeposition of molybdenum from a saturated solution of molybdic acid was issued in 1927. In a communication in 1932 ¹⁵, the electrodeposition of molybdenum from aqueous citrate solutions was announced and further data promised but so far none has been forthcoming. A patent

on the electrodeposition of molybdenum from alkaline molybdate solutions¹⁶, an article on the use of molybdic acid in sulfuric acid¹⁷ for this purpose, two Russian patents¹⁸ on the deposition of molybdenum, one from an alkaline and the other from an acid solution, and an article on deposits from a number of different baths¹⁹ are further examples of claims which have not been corroborated. There are others to be found in the bibliographies of some of the papers cited.

Since the work of Kaycki and Yntema¹⁹ is the most recent paper on electrodeposition of molybdenum from aqueous solutions, it was decided to perform an exhaustive check of their work in this laboratory. The details are given in the appendix. It was concluded that when one considers all the evidence, the process described in their paper produces, at best, a mixture of MoO_2 and molybdenum metal of such low thickness that the disastrous effect on the physical properties of molybdenum of even traces of oxides are completely masked by the properties of the base metal. An indication of the nature of the deposit as it might appear in bulk is given by the fact that attempts to plate significant thicknesses of the material give only smut and loose powders beyond the initial thin layer.

It should be noted that alloys containing as much as 50% Mo with iron, nickel, or cobalt as the second element may be obtained by electrolysis of acidic or slightly alkaline citrate solutions²⁰. Deposits of somewhat lower Mo content alloyed with iron or cobalt can be obtained from concentrated alkali solutions²¹. Examination of the properties of these alloy deposits when built up to a thickness of 0.001" to 0.002" shows that when the molybdenum content exceeds about 25 to 30% the deposits have a high oxide content, are very weak and usually crumble on stripping of the base

metal. Unfortunately, alloys of molybdenum with the iron group metals in which the molybdenum content is less than about 90% cannot be used at high temperatures because of the solubility properties of these alloys. For example, the phase diagram for Ni-Mo shows a eutectic temperature near 1400°C and no solid solution stability below 99% Mo²². The phase diagram for Fe-Mo has a eutectic temperature near 1500°C and no solid solution stability below 89% Mo²³. The phase diagram for Co-Mo has a eutectic temperature near 1400°C and no solid solution stability below 96% Mo²⁴.

There has been much work done in organic and other low-temperature non-aqueous systems, but little has been published because of the lack of positive results. K.Wolf²⁵ electrolyzed molybdenum dichloride in alcohol saturated with HCl gas and obtained at the cathode small amounts of molybdenum together with oxychlorides. A solution of molybdenum hexachloride (no evidence has been found for the existence of this compound) in acetone²⁶ is claimed to give a molybdenum deposit on electrolysis. Molybdenum pentachloride in liquid ammonia²⁷ is said to give molybdenum deposits on electrolysis.

In reviewing the work on the electrolysis of fused salts of molybdenum, an interesting process is described in Omelin²⁸ with reference to two review articles²⁹, one of which is clearly a translation of the other, and neither of which gives the original reference to the process described. In this process molybdenum pentachloride, silica, and sodium chloride are heated and the effluent vapors passed through molten sodium chloride which is electrolyzed. Molybdenum is said to deposit at the cathode which may be either copper or molten lead. A search through the literature indicates that this process may be that originally

described by Gin³⁰. Another process recommends a mixture of calcium molybdate and molybdenum carbide dissolved in bauxite³¹, while still another recommends the electrolysis of molten calcium molybdate³². Kratky and Bruckner³³ electrolyze a melt of barium or calcium chloride and after the electrolysis has begun, a water-free molybdenum salt is added. The calcium or barium metal already present in the bath from the initial electrolysis is said to reduce the molybdenum salt to molybdenum metal. Forland³⁴ recommends a mixture of equimolar proportions of molybdenum pentachloride, sodium chloride, and aluminum chloride which melts below 200°C. It is claimed that the low melting point of the mixture permits electrolysis at 200°C without appreciable volatilization of the molybdenum pentachloride. The procedure, as described by Forland, was repeated. The electrolysis was performed in a U-tube and it was observed that copious evolution of fumes both of the molybdenum pentachloride and the aluminum chloride occurred. The cathode deposit was a very fine spongy black powder which reacted with water with the evolution of gas. Andrieux reports the cathodic deposition of molybdenum from a molten bath consisting of borax, sodium fluoride, zinc oxide, and molybdic acid at about 1000°C.³⁵ It should be noted that in another part of this article Andrieux states that similar solutions and conditions with other metals produce borides rather than the free metal.

As a result of work which will appear later in this study, it seems highly improbable that pure molybdenum metal can be deposited from an oxygen-containing melt and that reports indicating that this has been accomplished should be carefully checked.

To conclude this review, note should be made of the excellent monograph by Peharuy which exhaustively covers the literature on the chemistry of molybdenum and its compounds up to about 1926³⁶.

CHAPTER II

EXPERIMENTAL

Scope

In determining the scope of this study it seemed, from an examination of the literature, and from some experience with the electrolysis of molten titanium compounds, that the most promising solvent would be mixtures of alkali chlorides. Therefore, practically all of the work was done in this medium. The molybdenum compounds chosen for investigation were those of greatest stability in each valence state of molybdenum. Of the hexavalent compounds, the molybdates are undoubtedly extremely stable, so sodium molybdate was the compound chosen. No hexachloride is known to exist and the hexafluoride boils at 350°C. The most stable of the quinquivalent compounds is the pentachloride which boils at 268°C. However, it has an appreciable vapor pressure above 150°C. In addition, it is rapidly hydrolyzed by atmospheric moisture at room temperature. Since a fair amount of work with this compound in molten salts has already been done, no further study of it, other than the check of the Forland patent described above was undertaken. Of the tetravalent molybdenum compounds, the complex octacyanide is probably the most stable. It was prepared by us and its properties checked. The tetrachloride decomposes before melting and is decomposed by air, light, etc. Of the trivalent molybdenum compounds the complex hexachloride is the most stable, and proved to be particularly suited to accomplish the purpose of this study. Most of this report deals with the electrolysis of solutions of this compound. The

divalent chloride is the most stable of the simple molybdenum halides and was chosen as the divalent compound to be studied.

Equipment

Since it was decided to do all electrolyses in an inert atmosphere, it was necessary to design equipment for that purpose. The requirements which were set for the equipment included: 1) upper temperature limit of 1000°C; 2) automatic temperature control; 3) manipulable electrodes in a closed system; 4) visibility of electrodes and electrolyte during operation; 5) cathode agitation; 6) sufficiently leak-proof apparatus to maintain an internal pressure of 1 mm Hg and to maintain an adequate protective atmosphere under a reasonably small flow of argon.

It became apparent that the design of such equipment could be greatly simplified if induction heating were used. A photograph of the equipment is shown in Figure 1, and a schematic detail drawing appears in Figure 2A. A pyrex glass cylinder (A, Figure 2A), 70 mm diameter and 45 cm high, closed at the bottom, was placed in the furnace coil (B). The coil was about 6 inches high. It was wound as tightly as possible from flattened copper tubing, and had mica insulation between the turns. The furnace coil was mounted on a transite platform. A ceramic cylinder (C) made from "Alfrax" body and a small amount of binder was placed inside the Pyrex cylinder for the purpose of thermal insulation. The machined graphite crucible (D) made of AGK* graphite was placed inside the ceramic cylinder. The crucible

* National Carbon Company, Cleveland, Ohio

was 6 inches high, 2 inches O.D. and 1/4 inch wall thickness. A thin sheet of mica was placed between the pyrex envelope and the furnace coil since it was found that the mica reduced the tendency to arc through the glass and crack it. A rubber bung (E) was used to close the top of the pyrex cylinder. One central and five peripheral holes were drilled through the bung. Five-inch lengths of tightly fitting glass tubing were inserted in four of these holes and short lengths of rubber tubing were fitted to the tops of the glass tubes. A 1/4 inch diameter rod was inserted through the center hole. This rod (F), serving as a cathode, was about two feet long and was joined at the top to a variable speed stirring motor (G). The joint was made by holding a short length of 1/4 inch rod in a chuck on the rotor of the stirrer and joining the two rods by a tightly fitting rubber coupling which had been coated on the inside with an alundum abrasive powder. Through the holes around the periphery of the bung were inserted a McDaniel refractory thermocouple protection tube, (glazed) (H), long enough to reach the bottom of the crucible and a 1/4 inch diameter tungsten rod which served as the anode holder (I). A molybdenum connector (J) was placed on the end of the anode holder which was inside the vessel. The connector was fastened to the anode holder by a molybdenum set screw. Sheet or rod anodes were inserted into the lower end of the connector and held by a molybdenum set screw. A third peripheral outlet was used as an escape chimney (K) and was fitted with a screw clamp. The fourth outlet (which had no glass tube) contained a stainless steel tube which extended down to within 2 or 3 inches of the top of the crucible. This was used as a gas inlet or evacuation port (L). The fifth hole was closed with a

rubber stopper and used only in the potential and polarization studies discussed later. The furnace coil was water-cooled. It obtained power from an Ajax-Northrup 3KVA mercury spark-gap converter. A Brown controlling pyrometer was placed in the input circuit of the converter. A chromel-alumel thermocouple ran from the thermocouple well (H) to the pyrometer, and temperature control was thus obtained by closing or opening the input circuit of the converter as required by the temperature variations of the system.

Some difficulty with temperature control was encountered because frequently the thermocouple wires were independently heated by induction from the furnace coil and so the true temperature of the electrolyte was not obtained. However, this was not too serious, because the true temperature was recorded on the pyrometer when the furnace went off. Since the pyrometer had a 15 second response time, the melt was eventually brought to temperature and held there. The heating rate was rapid, the melt reaching a temperature of 900°C in about ten minutes. In actual operation, it was usually desirable to turn off the controlling circuit until the melt was near the required temperature, at which time the controlling circuit was turned on and the temperature stabilized at the desired value. An air-cooling coil was placed around the top of the pyrex cylinder near the rubber bung. The thermal insulation provided by the ceramic crucible, and the external cooling supplied by the water stream in the furnace coil, permitted long periods of operation with the charge at 900°C without any softening of the glass. The air-cooling at the top was sufficiently effective to prevent any visible deterioration of the rubber bung.

plating current was supplied by 12-volt 200 ampere rectifiers, and adjusted by a carbon pile and slide wire potentiometer rheostat equipped with 0 to 500 milliamperes, 0 to 5 amperes, and 0 to 30 ampere ammeters and 0 to 12 volt voltmeter. The electrical circuit is shown in Figure 2B. The leads were attached to the anode rod by a battery clip and to the rotating cathode by a lubricated phosphor bronze spring clamp.

General Procedure

Electrolysis. The usual electrolyte used in this work consisted of a mixture of alkali chlorides and a salt of molybdenum. The alkali chloride mixture will henceforth be called the "halide solvent". A typical electrolysis run was performed in a manner designed to exclude, insofar as was possible, traces of moisture or contamination by air. The procedure began with mixing the "halide solvent" in the desired proportions and fusing it at a temperature a few hundred degrees above its melting point in the crucible in which the electrolysis would be done. This was continued until all bubbling ceased and the melt remained quiet for some time. The crucible was then transferred, while the halide solvent was still molten, to the pyrex envelope and placed inside the ceramic cylinder. An auxiliary bung with only two holes (inlet and outlet) was used to close the envelope. The two 3-way stopcocks on the double T-tube (N, Figure 2A) were properly adjusted and the system evacuated to a pressure of about 1 mm Hg read on the manometer (M). The argon stream was passed through the flowmeter* (O)

* Fischer and Porter Flowmeter, Cat. No. 30-1308H

^{was} and admitted to the system. When atmospheric pressure was reached, the outlet in the bung was adjusted so that a pressure of 2-3 cm Hg above atmospheric pressure (read on manometer, P) was maintained in the system. The halide solvent was thus allowed to freeze in the absence of moisture and air.

The anode, cathode, thermocouple, etc. were set into the bung (E) outside of the system. The pyrex vessel was then opened and the previously dried molybdenum compound was quickly added on top of the solid halide solvent. (The method of drying the molybdenum compound was determined by the properties of the compound itself.) The bung and attached equipment were then set in place with the anode and cathode above the crucible. The system was evacuated, filled with argon, and the argon flow continued as before with the pressure inside the vessel above atmospheric pressure. After the flushing of the system was complete, the heating was started, and as soon as the salts melted, the thermowell was inserted into the melt. At the desired operating temperature, the anode and cathode were inserted into the melt, the cathode connected to the stirring motor, the electrical leads placed, and the electrolysis begun. The flow rate of the argon during the run was set at any value between 200 and 3000 cc/minute. The outlet chimney was always adjusted to maintain a pressure above atmospheric pressure inside the system throughout the run. At the end of a run, the cathode, anode, and thermocouple were withdrawn from the melt and allowed to cool in the inert atmosphere while the electrolyte itself was cooled and frozen. The system was not opened until the temperature inside was below 100°C. After removing the bung with

the anode and cathode, the auxiliary bung was quickly inserted and the system was evacuated and filled with argon. Thus the electrolyte was stored in an inert atmosphere for later runs. The rubber sleeves through which the electrodes and thermocouple well were passed were lubricated with silicone stepcock grease and all stationary joints were sealed with Unichrome* stop-off lacquer No. 323.

* United Chromium, Inc., New York, N. Y.

The cathode deposit was separated by first soaking the cathode in boiling 10% hydrochloric acid, which, contrary to some statements in the literature, does not appreciably attack molybdenum. When the adhering salts from the electrolyte were dissolved, the deposit, if powder, was removed by scraping, hammering, chiseling, or whatever procedure was required by the nature of the deposit. The powder was then lightly ground in a mortar and washed with distilled water. The fines and impurities lighter than molybdenum (if any) were held in suspension while the molybdenum settled out. The liquid was decanted. The washing was repeated until the supernatant liquid was practically clear. The molybdenum was filtered off, washed with acetone, and dried.

Except where otherwise indicated, the cathode was a 1/4 inch diameter tungsten rod immersed to a depth of about 3 inches giving a cathode area of 0.15 dm² (2.3 in²). The anode was a pure commercial molybdenum* sheet, 1/2" x 0.030", and it was immersed to the same depth.

* Fansteel Metallurgical Corp., North Chicago, Ill.

The molybdenum anode was used mainly to simplify the investigation of the cathode reactions. It was found early in the work that molybdenum dissolved with 100% current efficiency in the molten chloride electrolyte. As a result, there were no complications introduced by anodic products, oxidation of the electrolyte, or any other factors usually associated with an insoluble anode. Further, in electrorefining, electroplating, or electroforming, a soluble anode is highly desirable since the composition of the electrolyte may be more easily maintained within the desired limits when replacing the deposited metal by solution of an equivalent amount from the anode. In electrowinning where one does not wish to anodically dissolve the metal which one is trying to produce at the cathode, a divided cell with an insoluble anode and any convenient electrolyte may be used. Since it is well known that the anode and cathode reactions are completely independent except insofar as the products of one may reach the other and affect the reaction occurring there, anything established about the cathode reaction using a soluble molybdenum anode would apply equally well to the cathode reaction in a divided cell. Further information about the anode reaction will appear later in this paper.

Analysis. Many analyses for molybdenum were performed using the volumetric Jones Reductor Method³⁷ and a few were performed using the gravimetric method of precipitation in acid solution with α -benzoin oxime³⁸. The volumetric method was much more rapid and quite as accurate. Molybdenum powders for analyses were dissolved by adding weighed quantities to 1:1 nitric acid and allowing the dissolution to occur without heating. On complete dissolution, gassing

ceased and a brown residue remained. Concentrated sulfuric acid was added and the mixture was heated slowly at first to dissolve the brown residue and then strongly until sulfur trioxide fumes appeared. If the nitric acid solution was heated while the metal was dissolving, severe bumping occurred when the brown residue was treated with sulfuric acid.

The solution was cooled, more concentrated sulfuric acid was added, and the solution was evaporated to fumes again. The complete elimination of the nitrate was made certain by the addition of a few ml of sulfurous acid before the second heating. The solution was cooled, diluted to known volume and proper aliquot portions were analysed as indicated in the references given.

When it was desired to determine both trivalent and total molybdenum in solid samples, the samples were dissolved in 10% hydrochloric acid solution which had been prepared with boiled water saturated with nitrogen. The mixture was placed in a stoppered volumetric flask until solution was complete. An aliquot sample was added to ferric ammonium sulfate solution and titrated directly with 0.05N potassium permanganate for trivalent molybdenum, while another sample was run through the Jones reductor and titrated for the determination of total molybdenum. The permanganate solution was standardized against known samples of commercially pure Fansteel molybdenum sheet prepared in the same way as the unknown samples. Agreement between the usual oxalate standardization and the molybdenum metal standardization was usually better than five parts per thousand. Agreement between volumetric and gravimetric methods was of about the same order.

Metallography. The microstructure of the molybdenum deposits was investigated by mounting specimens in bakelite or lucite and cutting them with a carborundum wheel. They were then polished on progressively finer emery paper from 1 G to 3/0 grades. The polishing was finished on a wet felt wheel charged with fine alumina abrasive. The samples were etched with Murakami's reagent, i.e., 10 g potassium ferricyanide, 6 g sodium hydroxide in 200 ml of water.

Sodium Molybdate

12.6 g sodium molybdate dihydrate were melted and held at bright red heat until all the water was removed. A mixture of 55 g potassium chloride and 55 g sodium chloride, which had been previously fused, was added and the solution was electrolyzed in an inert atmosphere at 900°C, 100 amp/dm² for 30 minutes using a molybdenum anode and tungsten cathode. At the end of the run, a black non-metallic appearing powder was observed on the cathode and a trace (less than 0.0001") of adherent deposit of somewhat metallic appearance was found on the anode. In addition, there was a black water-insoluble powder dispersed throughout the melt. One gram of this powder was collected by leaching the ground-up electrolyte with dilute hydrochloric acid (10%), the powder remaining behind as a residue. It was analyzed gravimetrically and found to contain 76.7% Mo, corresponding very closely to the Mo content of MoO₂, i.e., 75%. The cathode deposit of powder was scraped off and analyzed by X-ray diffraction methods. Figure 3A summarizes the diffraction pattern obtained. The deposit clearly contains molybdenum metal, Mo₂O₃ and Mo₂O. A quantitative estimation is difficult since the cubic structure of the molybdenum would normally give more intense

lines than the other compounds, but a fair approximation of the composition would probably be a molybdenum metal content of no more than 50%. The presence of the carbide is interesting since it could only have come from the crucible which was not in contact with the cathode. The carbide evidently formed at the crucible wall, diffused to the cathode and was deposited there.

A run with pure sodium molybdate without any solvent was attempted. 120 g sodium molybdate dihydrate was melted, the water driven off, and the melt was electrolyzed in an inert atmosphere under the same conditions as described above. The molten salt conducted well and the cathode deposit had the same appearance as in the run containing sodium molybdate in the halide solvent. Electrolysis of the pure salt at 3 amp/dm² produced no deposit at all at the cathode.

It is certain that the electrolysis of the molybdate compound does not produce a deposit of pure molybdenum. The main electrochemical reaction seems to be a reduction of the molybdenum to the tri- or tetravalent state with the deposition of the respective oxides. These oxides appear to be fairly stable at the temperature of operation, insoluble in the melt, and not directly reducible any further. Any molybdenum that is present probably results from a secondary chemical reaction or a concurrent electrochemical reaction at low efficiency. Further insight into the electrochemical behavior of molten molybdate solutions will be obtained from the polarization and potential studies discussed below.

Potassium Octacyano Molybdate (IV)

This compound was chosen for investigation because it can be easily prepared in the anhydrous state. It is quite stable in air and may be dehydrated at 110°C without decomposition. It was intended to electrolyze this compound in a solution of molten cyanides.

Preparation. The compound was prepared according to the directions of Bucknall and Wardlaw³⁹ with some modifications. 40 g K_3MoCl_6 (preparation described below) and 80 g KCN were mixed dry in a 400 cc beaker. 240 cc of water were added very slowly with stirring and with gentle heating on a steam bath. As the mixture became a loose paste there was a tendency for a rather violent exothermic reaction to occur. This reaction was controlled by increasing the rate of water addition. If the violent reaction was allowed to proceed, a carbonized insoluble product was formed. After all the water was added, the solution was evaporated to one-half volume and cooled. A green precipitate formed, was filtered off, and discarded. The filtrate was evaporated to incipient crystallization and cooled. The yellow precipitate was filtered off, washed with alcohol and then with ether. It was dried at 110°C . At this point there were 40 gms of material. Samples for analysis were first dissolved in 2 ml water. 10 cc concentrated sulfuric acid was added, and the solution was boiled until it became colorless. Volumetric analysis for molybdenum showed the product to contain only 11.76% Mo. Another sample was treated as above except that the solution was boiled with 15 ml concentrated H_2SO_4 and 5 ml concentrated HNO_3 . This was done to be certain that the tetravalent molybdenum was oxidized to the hexavalent state.

According to Gmelin's Handbuch, the tetravalent cyanide is not reduced by Devarda's alloy (and so probably not by the amalgamated zinc in the Jones reductor) and further, it is oxidized by permanganate solution only to the pentavalent state⁴⁰. The same source indicates that hot nitric acid will oxidize the tetravalent cyanide complex to molybdic acid. This completely oxidized sample was shown to contain only 12.03% Mo.

The balance of the 40 g of product was then dissolved in water, boiled, and evaporated a little. Methanol was added with rapid stirring while the solution was still warm. A yellow precipitate was formed. The methanol addition was continued until the material precipitating where the methanol first hit the solution flashed white. The yellow precipitate was filtered, washed with methanol, and dried at 110°C 18.5 g of product was collected. It was a lemon yellow in color. Analysis showed it to contain 20.6% Mo. Theoretical Mo content of $K_4Mo(CN)_8$ is 20.65%. The yield of pure material was 43%.

In order to determine the nature of the impurity which was present in the original crude product, more methanol was added to the mother liquor from which the $K_4Mo(CN)_8$ was precipitated. A green product precipitated. It was collected on filter paper, washed with methanol and redissolved in water. Silver nitrate was added and a brownish white precipitate was formed. This latter material was dissolved in ammonium hydroxide. Addition of nitric acid precipitated a white powder.

The yellow product gave a yellow precipitate with silver nitrate which on solution in ammonia and reprecipitation with nitric acid gave a yellow precipitate again. Bucknall and Wardlaw report the

formation of yellow $\text{Ag}_4\text{Mo}(\text{CN})_8$ on addition of silver nitrate to $\text{K}_4\text{Mo}(\text{CN})_8$. The only materials which could have been present in the reaction mixture which would be soluble in water and which would give a white precipitate with silver nitrate are potassium chloride or potassium cyanide. The green impurity was undoubtedly one or both of these which had been contaminated with some color adsorbed from the solution.

The pure octacyanide which had precipitated from the reaction mixture was $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$. On heating at 110°C , the water of crystallization was removed without decomposition, as previously found by Rosenheim⁴¹.

Properties. In order to determine the properties at high temperature of $\text{K}_4\text{Mo}(\text{CN})_8$, and of mixtures of this salt and alkali cyanides, a sample of the pure salt was sealed in an evacuated pyrex tube (I). A mixture of composition (II) shown in Table II was sealed in another evacuated pyrex tube and both tubes were heated to 625°C .

TABLE II. Composition of $\text{K}_4\text{Mo}(\text{CN})_8$ - KCN - NaCN mixture.

	<u>Wt. %</u>	<u>mole %</u>
KCN	31.2	37.8
NaCN	35.2	56.4
$\text{K}_4\text{Mo}(\text{CN})_8$	33.6	5.8

The solvent in composition (II), i.e., a mixture of KCN-NaCN containing 40 mole % KCN melts at 502°C . The melting point of the KCN-NaCN system does not reach 600°C until it contains 90 mole % KCN. The pure salt (I) remained solid, and turned black. The tube was allowed to cool to room temperature. When it was opened it was observed that a high gas pressure had built up in the tube as a result

of the thermal decomposition which had occurred. The mixture (II) did not become fluid. It was mostly black but some areas were yellow and others had a dark pink color. This indicated that some solubility exists but the extent of solution was low and amount of decomposition high.

A sample of the decomposed product of the pure sample (I) was subjected to X-ray diffraction analysis. The pattern obtained is summarized in Figure 4. Approximately equal parts of γ -Mo₂N and KCN are present and represent about 25 to 50% of the total sample. A trace of KCNO or K₂MoO₄ may be present and the rest of the sample may be amorphous carbon and therefore not identifiable by X-ray analysis. Gmelin's Handbuch⁴² states that γ -Mo₂N is stable in the lower part of the temperature range between 600°C to 700°C and the β phase stable somewhat below 600°C. The pressure observed in the tube after it was cooled was probably due to liberated cyanogen or nitrogen. In view of the thermal instability of this salt at temperatures required for use in molten salts, and because of its demonstrated low solubility in the most likely solvent for it, it was concluded that it would be pointless to run any electrolysis tests with this material. The tendency to form stable nitrides might be one of the major causes for failure of previous attempts to plate molybdenum from a molten cyanide system.

Molybdenum Dichloride. Molybdenum dichloride is the most stable of the halides of molybdenum. It is the only one which is inert in moist air at room temperature. It may be heated to 600°C in an inert atmosphere without decomposition, and it is the only one which is slowly attacked by nitric acid or aqua regia. Its great stability is attributed to its existence as the polymer, Mo₃Cl₆ or Mo₆Cl₁₂.

Preparation. The best method of preparation in the literature appeared to be that of K. Lindner, et. al.⁴³, who chlorinated molybdenum powder by allowing it to react with phosgene at 610°C. This reaction was attempted both as directed and with a number of modifications, but it was found that it is not satisfactory for the preparation of appreciable amounts of pure material. After consulting the thermodynamics data on the molybdenum halides collected by Quill⁴⁴, a method was devised which proved quite successful. According to Quill, the reactions:



reaches equilibrium with MoCl_4 at a partial pressure of 0.7 atm. and MoCl_5 at a partial pressure of 0.3 atm. at 340°C. Further, at 330°C the reactions:



goes practically to completion (at atmospheric pressure). Lastly, the reaction:



does not begin until a temperature of 530°C is reached and at 600°C the equilibrium pressure of MoCl_4 is only one atmosphere.

By heating molybdenum powder with an excess of molybdenum pentachloride in a sealed tube at 350°C, reaction (2) may be accomplished while reaction (1) would be suppressed by the excess MoCl_5 gas which is present. When the molybdenum powder is all used up, the excess molybdenum pentachloride may be removed and the molybdenum trichloride heated at some temperature below 600°C to form MoCl_2 without reaction (3) occurring to a large extent.

An attempt to reduce molybdenum pentachloride to molybdenum dichloride by reduction with molybdenum at high temperature in one step did not give a pure product. The two-step procedure, however, was quite successful, although it was necessary to perform the final step at 650°C resulting in slight contamination of the MoCl_2 by molybdenum powder. Below this temperature the disproportionation of the trichloride proceeded somewhat slowly.

The following procedure was used: 7.6 g Mo powder was mixed with 36.6 g MoCl_5 (4.6 g MoCl_5 excess). The mixture was placed in a thick-walled pyrex tube 1.5 cm diameter and 30 cm long. The tube was evacuated, sealed and placed in a steel pipe closed at both ends. The entire assembly was allowed to stand in a furnace at 350°C for 48 hours. The tube was tilted during the heating so that most of the product would be at one end. After cooling, the other end was opened and a "condensing angle" was sealed onto the open end. This "condensing angle" was a 12 inch length of pyrex tubing, bent in the middle to an angle of about 120°. The tube was again evacuated and sealed and set in the furnace with the 6 inch length beyond the bend protruding out of the furnace. The temperature was slowly raised and the excess molybdenum pentachloride collected in the cold end. When most of the pentachloride had distilled over (at about 300°C) the temperature was raised to 650°C and held there for 24 hours to effect the disproportionation and further purification. The clear yellow dichloride, $(\text{MoCl}_2)_x$, remained in the hot part of the tube. 14 g of pure material was obtained, giving a yield of 65% based on the molybdenum powder used. Analysis showed that it contained 58.3% Mo. The theoretical value

for the Mo in MoCl_2 is 57.4%. The slight excess of molybdenum in the product was undoubtedly due to free molybdenum metal formed by decomposition of the MoCl_2 . This excess may have been avoided by heating for a much longer time at about 600°C instead of 650°C , but since a small amount of free molybdenum metal would not be harmful in an electrolysis test, it was not considered necessary to do that.

Properties. The material must be used in the condition in which it is produced. Attempts to leach out the free metal with dilute nitric acid resulted in the formation of a hydrate, $\text{MoCl}_2 \cdot x\text{H}_2\text{O}$, from which the water could not be removed without decomposing the salt. The MoCl_2 was slightly soluble in alcohol, but an alcoholate, $\text{MoCl}_2 \cdot x\text{C}_2\text{H}_5\text{OH}$ was formed. Attempts to drive off the alcohol resulted in decomposition.

A sample of the MoCl_2 was mixed with a portion of a eutectic mixture of lithium chloride and potassium chloride (41 mole % KCl , melting point $\approx 352^\circ\text{C}$) which had been previously fused and ground. The mixture had the composition given in Table III.

TABLE III. Composition of MoCl_2 - LiCl - KCl Mixture

	<u>Wt %</u>	<u>Mole %</u>
MoCl_2	12.3	4.4
LiCl	40.3	57.2
KCl	47.4	38.4

This mixture was heated in an evacuated sealed tube to 600°C at which temperature the charge was fluid. On freezing, the charge was bright/^{red} in color. The change in color and the uniform color of the

product was evidence of satisfactory solubility in the halide solvent at a suitable temperature. An electrolysis run was then performed. A similar experiment was made with the sample of molybdenum dichloride which had been hydrated by leaching in nitric acid. A large amount of black decomposition product formed at 600°C and the mixture on cooling had some black material dispersed in a matrix which was only faintly pink. This proved the undesirability of moisture in these compounds.

Electrolysis. For the electrolysis test, the halide solvent was the lithium chloride-potassium chloride mixture described above. 12.0 g of molybdenum dichloride was added to 100 gms of the halide solvent to make a 3.9 mole % solution of the compound. The mixture was melted under argon as described in the general procedure and electrolyzed at 100 amp/dm² for 30 minutes at 600°C. A ragged "treed" deposit of molybdenum was obtained. The deposit was collected and weighed. The current efficiency was found to be 37% based on $\text{Mo}^{2+} \longrightarrow \text{Mo}$ and 55% based on $\text{Mo}^{3+} \longrightarrow \text{Mo}$. The solution, on freezing, was pink and looked very much like those observed in trivalent molybdenum solutions. A sample of the electrolyte was taken and analyzed. Total molybdenum was found to be 4.71% and the reducing power calculated as trivalent molybdenum was found to be 4.27%. From these results it is clear that no divalent molybdenum was present in the bath after the run, since if any were present the reducing power calculated as trivalent molybdenum should exceed the total molybdenum. Further, since it is shown below that the current efficiency from similar trivalent solutions was above 90%, and the deposit was quite dense, the "treed" deposit at low efficiency may be considered as coming from a

trivalent bath only at low concentration. What apparently happened was that the divalent molybdenum was oxidized to the trivalent state at the anode and trivalent molybdenum entered the solution by dissolution of the anode (the latter is proved below) and the plating occurred from the trivalent state. Since the initial concentration of trivalent molybdenum in the bath must have been low, a deposit characteristic of low concentration solutions appeared at the cathode. One may conclude that the divalent molybdenum is either inert at the cathode unless it is first oxidized to the trivalent state, or that molybdenum deposits less readily from the divalent than from the trivalent state.

Potassium Hexachloro Molybdate (III)

This compound proved to be highly effective as an electrolyte for producing pure molybdenum powders and coherent molybdenum electrodeposits.

Preparation. The compound was originally prepared according to the directions of Bucknall et al⁴⁵. Their procedure was based on an electrolytic reduction of a solution of molybdic acid in strong hydrochloric acid, followed by the addition of potassium chloride. This procedure was first described by Chilesotti⁴⁶. A pure anhydrous product was obtained, but since the method involved evaporations under reduced pressure and also the use of very dilute solutions, it was found to be inconvenient for the preparation of large amounts of the salt. Modifications were introduced which not only simplified the preparation but gave some very interesting insight into the chemistry of the formation of this compound. The following procedure is recommended

for the preparation of potassium hexachloro molybdate (III), K_3MoCl_6 .

477 g potassium molybdate was dissolved in 1044 ml water and this solution was added to 1044 ml 12N hydrochloric acid in a beaker. (Note: If the acid is added to the molybdate solution, molybdic acid precipitates and it is very difficult to redissolve.) The beaker was loosely covered with a plastic disc which had one large central hole, two smaller holes near the outer edge at both ends of a diameter, and a third smaller hole near the outer edge. A porous alundum cylinder, closed on the bottom, was filled with 200 ml 12N hydrochloric acid and inserted through the central hole of the cover. This cylinder served as a diaphragm between the anolyte it contained and the catholyte around it. Two sheets of platinum, used as cathodes, were held by platinum wires through corks placed in the two opposite holes in the cover, and a glass tube connected to a nitrogen tank inserted through a cork in the third outer hole of the cover. A half-inch diameter graphite rod, serving as the anode, was inserted in the anolyte. The level of the anolyte was adjusted to the same height as that of the catholyte.

The solution was electrolyzed with a current of 20 amperes (7.2 amp/dm^2 of the cathode area) for eight hours. The time of electrolysis was determined by periodically taking a sample of the catholyte, adding it to excess ferric alum solution and titrating with potassium permanganate. When the reducing power of the catholyte reached a constant value, the electrolysis was stopped. The catholyte was agitated during the electrolysis by a stream of nitrogen, and the anolyte received periodic additions of concentrated hydrochloric acid to replace that

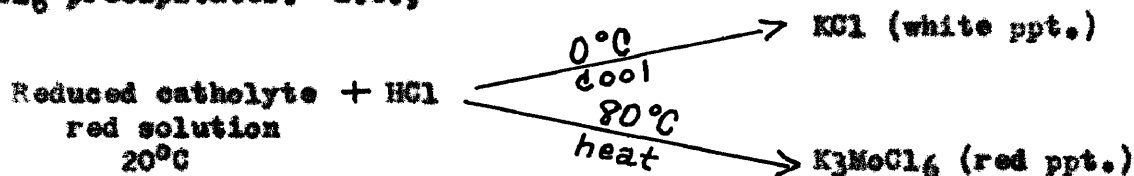
lost both by electrolysis and as spray. The temperature of the catholyte rose to 63°C during the electrolysis and the catholyte became dark red. The catholyte was removed, heated to 93°C , and saturated with hydrogen chloride gas. As the solution cooled, more hydrogen chloride gas was added and crystals of K_3MoCl_6 separated out. These were filtered, washed with 1600 ml of 12N hydrochloric acid, 1600 ml of 1:1 12N HCl - methanol mixture and 1600 ml of methanol. The red crystals were dried by heating under reduced pressure and analyzed. The analysis is given in Table IV.

TABLE IV. Analysis of K_3MoCl_6

	<u>Found</u>	<u>Theoretical</u>
Mo	22.6%	22.5%
Cl	50.2%	49.9%

A yield of 390 g or 69% was obtained.

Properties. While working out the procedure described above, a series of reactions were observed which demonstrate that the $[\text{MoCl}_6]^{-3}$ ion approaches what Biltz calls a penetration complex rather than a normal complex⁴⁷. If the catholyte is reduced and saturated with hydrogen chloride gas without permitting its temperature to rise, and then cooled to near 0°C , potassium chloride precipitates. If, instead of cooling at this point, one heats the solution to above 80°C , K_3MoCl_6 precipitates. i.e.,



This conclusively demonstrates that the reduced catholyte, before heating, contains potassium ions, trivalent molybdenum ions, and chloride ions, and little if any complex ions. On cooling, the potassium chloride crystallizes out because of its insolubility in concentrated hydrochloric acid. On heating, however, the reaction $\text{Mo}^{3+} + 6\text{Cl}^- \longrightarrow [\text{MoCl}_6]^{-3}$ occurs and K_3MoCl_6 precipitates. On cooling the mother liquor from this precipitation more K_3MoCl_6 separates but KCl does not because most of the K^+ has been removed in the precipitation of the complex salt. If $[\text{MoCl}_6]^{-3}$ were in equilibrium with Mo^{3+} and Cl^- the above series of reactions could not possibly occur. Probably the major function of the evaporations used by previous investigators to prepare this salt was the formation of the complex ion by heating, rather than merely concentration of the salts.

K_3MoCl_6 is a brick-red salt. It precipitates without any water of crystallization, but if insufficient hydrogen chloride is added before precipitation, an aquo complex such as $\text{K}_2[\text{MoCl}_5\text{H}_2\text{O}]$ may precipitate. The water cannot be removed from this compound by heating without decomposing the compound. K_3MoCl_6 can be heated in air at 110°C without any decomposition. In the dry state, it is stable to light and practically not hygroscopic. It can be heated in vacuo to at least 600°C without decomposing or melting. This is particularly significant when one remembers that MoCl_3 is unstable above 340°C^{44} , and that at 650°C it is completely decomposed to MoCl_2 and Mo metal. This further demonstrates that the $[\text{MoCl}_6]^{-3}$ ion is a highly stable one with little tendency to disassociate. When very hot its color darkens slightly but it lightens again on cooling. It is rapidly decomposed at 600°C ,

however, if in contact with air or moisture. The standard procedure finally adopted for removing the last traces of adsorbed water from the compound was to heat it in vacuo at 250°C for two to three hours and then to store it in a desiccator.

Electrolysis. The first halide solvent used for electrolyzing K_3MoCl_6 was a 1:1 mixture (by weight) of potassium chloride and sodium chloride. To determine the optimum concentration of molybdenum salts, solutions were prepared in which 13.3 g, 22.2 g, and 33.0 g K_3MoCl_6 were dissolved in 100 g of the halide solvent and electrolyzed at 3, 30, and 100 amp/dm² at 900°C. The most dilute solution gave very fine powders on the cathode which did not appear metallic, although under the microscope, some metallic crystals were observed. Some of this powder was also dispersed in the electrolyte, rather than attached to the cathode. The intermediate concentration produced a deposit of dendritic molybdenum crystals at high current density and a tightly interlaced deposit of molybdenum granules at low current density. The crystals were metallic in appearance and quite pure. The most concentrated solution produced bulky deposits of pure molybdenum powder which were metallic in appearance and which adhered strongly to the cathode. It was apparent from the appearance of the deposits that a high concentration of molybdenum salts was desirable. The 33 g solution was close to the limit of solubility of K_3MoCl_6 in the halide solvent at 900°C. This was therefore chosen as the standard bath for further tests. The temperature was established by this choice of concentration, since at 800°C the melt precipitates a solid phase. In addition, it was found that a more uniform deposit which adhered better to the

cathode could be obtained by using cathode agitation. A cathode rotating at 300 rpm was used. It was also found necessary to pre-electrolyse a freshly prepared solution at low current density (about 5 to 6 amp/dm²) for about 3 ampere-hours in order to obtain the best results. When the best conditions for this solution had been established, cathode current efficiencies were measured at various current densities with the results shown in Table V.

TABLE V. Cathode Current Efficiency of K₂MoCl₆ - KCl - NaCl Solution

<u>Current Density (amp/dm²)</u>	<u>Current Efficiency (Cathode)</u>
3	98%
40	95%
100	96%

The current efficiency was calculated on the basis of the reaction, $\text{Mo}^{3+} + 3e \longrightarrow \text{Mo}$. A typical calculation of current efficiency will be found in the appendix. The cell voltage varied from 45 millivolts at 3 amp/dm² to 1.5 volts at 100 amp/dm².

Until the optimum conditions were established, some difficulties were encountered. For example: 1) In some of the early runs, a black powder was observed to deposit initially on the cathode. On top of this powder a layer of bright molybdenum crystals formed. When this occurred, not only was the adherence of the deposit to the cathode poor, but the current efficiency was reduced to a value anywhere from 50 to 80%. 2) An infusible black material was also observed to float on the electrolyte and slowly disappear during operation. The infusible material in the electrolyte and the black cathode impurity

were collected, washed with dilute hydrochloric acid and water, and dried. They were subjected to X-ray diffraction analysis with the results shown in Figure 3. Figure 3D shows that the infusible material in the electrolyte was mainly Mo_2O_3 with some metallic molybdenum (about 9 parts of the oxide to one of metal). Figure 3C shows that the black powder deposited on the cathode (before the metal plated out as well defined pure crystals), was a mixture of about equal amounts of Mo_2O_3 and molybdenum, very similar in composition to the deposit from the molybdate solution shown in Figure 3A. One cannot be certain that the very finely divided molybdenum co-deposited with the oxide, since the separation of the molybdenum overlayer from the underlying powder was accomplished entirely by physical means. The overlying layer was carefully picked off, the powder was then scraped off the cathode and washed. In any event it is certain that the initial layer of powder was characterized by the presence of oxide. It was these observations that led to the development of the extreme precautions for the exclusion of air and moisture from the salts and from the atmosphere above the plating bath.

Deposits. The deposit from the most dilute baths (i.e. 13.3 g K_2MoCl_6 in 100 g KCl-NaCl) was analyzed and, in spite of its non-metallic appearance was found to contain 96% Mo. An X-ray diffraction pattern for a sample of this deposit (Figure 3B) showed that it contained about 85% Mo metal, with the remainder Mo_2O_3 and Mo_2C . It is possible that with even more rigorous exclusion of air and moisture, even this bath might have given a deposit of pure molybdenum. The molybdenum powder produced, however, is so fine-grained and so

intimately mixed with the oxide that it could not be separated from the oxide and the entire deposit appeared non-metallic.

From the baths of intermediate concentration, the dendrites produced at 100 amp/dm² are shown in Figure 5. The needles are about 0.5 to 1 mm long. Many of the needles consist of a single crystal of molybdenum except for small new crystals which start growing at sharp edges, points, etc. The hardness of these needles as measured with the Eberbach microhardness tester was 295 Vickers.

At 3 amp/dm² a nodular deposit was obtained which superficially seemed coherent. On scraping, most of the nodules came off as a coarse powder, but an adherent plate of molybdenum about 0.001" thick remained. This is shown in Figure 6. Examination of this photomicrograph clearly shows that the adherent deposit is one grain thick. This is probably the reason that the rest of the deposit was powder, since it is unlikely that an electrodeposit whose grain size is as large as this would hold together. Evidently, a single grain adhered to the cathode but the coherence between grains as large as this was too low to form a sound deposit.

The deposit shown in Figures 7 and 8 is typical of those produced at 100 amp/dm² by the high concentration solution. Figure 7 is a photomicrograph of the molybdenum agglomerates deposited on the cathode. The deposit was scraped off and photographed. Figure 8 shows the same material after grinding lightly in a mortar, washing with water, and drying. Figure 9 shows another deposit produced under the same conditions having a more spheroidal grain structure. The hardness of this deposit was found to be 287 Vickers, not significantly different

from the dendrites. At low current density, an adherent layer was deposited under the powder as described above. The powder deposit appears superficially to be very coherent. An attempt to prepare a photomicrograph of it, however, resulted in its crumbling from the cathode during mounting even when the greatest possible care in this operation was used. Beyond the initial grain deposited, the plate was a well-knit powder deposit. In the belief that this might be a matter of roughness, rather than poor coherence, a number of runs were made using Periodic Reverse Current with the hope that the smoothing effect of this process might give more coherent deposits. The cycles shown in Table VI were used.

TABLE VI. Periodic Reverse Current Cycles

<u>Direct</u>	<u>Time</u>	<u>Reverse</u>	<u>Time</u>
30 amp/dm ²	60 sec.	60 amp/dm ²	10 sec.
40 "	20 "	60 "	6 "
83 "	60 "	166 "	15 "
100 "	60 "	200 "	15 "
66 "	60 "	200 "	15 "

In no case was a coherent deposit produced. There was some increase in smoothness of the powder agglomerate and somewhat better interlocking of the particles, but it still crumbled to powder. It was noted that the powder produced consisted of flat platelets rather than spheroidal granules. A deposit of this type is shown in Figure 10 but the flatness of the particles as compared to the spheroidal form

of those in Figure 9 is not clearly visible except when viewed through a binocular microscope. The hardness of this deposit was 293 Vickers, again not significantly different from the previous ones.

It was noted that the particle size of deposits from fresh baths was usually smaller than the size from baths which had been electrolyzed for some time. Since it has been shown that electrolysis removes oxides from the bath, it was hoped that the addition of a very small amount of an oxygen-containing substance to the bath might act as an addition agent and produce refinement of structure. To test this, a bath which had been well electrolyzed and which had produced good deposits of pure powders was used, and to it were added 35 mg $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (total weight of bath was 133 g). The solution was electrolyzed at 100 amp/dm² and a deposit was obtained with a current efficiency of 96%. The deposit showed no effect of the presence of molybdate. Another run with 175 mg of the molybdate present in the bath resulted in no molybdenum deposit at all. It is clear that addition of oxygenated compounds is detrimental in even small amounts and, although traces might be of some help, their control would be difficult.

Chemical analysis of the deposits showed them to contain 99+% molybdenum. Spectroscopic analyses of four of them are shown in Table VII.

TABLE VII. Spectroscopic Analysis of Electrolytic Molybdenum Powders

<u>Element</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Silver	T	-	-	-
Aluminum	T	T	W	VW
Calcium	T	T	T	T
Cobalt	-	-	-	VW
Copper	VW	VW	T	T
Iron	-	W	VW	VW
Magnesium	T	VW	VW	T
Manganese	-	T	T	-
Molybdenum	VS	VS	VS	VS
Lead	-	-	T	T
Silicon	VW	T	W	VW
*Oxygen				0.068%

VS, very strong \pm greater than 10%

W, weak \pm 0.01 - 0.1%

VW, very weak \pm 0.001 - 0.01%

T, trace \pm 0.0001 - 0.001%

*Not spectroscopic determination

Columns 1 and 2 are for deposits from the intermediate concentration bath; column 3 is for a typical deposit from the high concentration bath; and column 4 is for a deposit from the same bath using periodic reverse plating. Fifty four elements were checked and lines

for only those listed were observed. The relative strength of the lines is indicated in the table. Taking the median values for the concentrations indicated by the symbols, the deposits are apparently 99.9+ $\%$ molybdenum. The oxygen content of the deposit of column 4 was determined by loss of weight in hydrogen at 1060°C (details of method are described below).

Table VIII is a summary of the types of deposits obtained from the bath using the mixture of potassium and sodium chlorides as the halide solvent.

TABLE VIII. Deposits from K_3MoCl_6 - KCl - $NaCl$ Solution

Cone. Mo (Mole %)	Current Density (amp/dm ²)	Plating Time (hr.)	Wt. of Deposit Collected (g)	Type of Deposit	Fig. Ref.	Table VII Ref.
2.0	30	1.0	0.25	Non-metallic Black Powder	3B	-
2.0	100	0.5	-	Non-metallic Black Powder	-	-
3.3	3	1.5	-	Modular superficially coherent Mo deposit overlying thin coherent layer	6	Col. 2
3.3	100	0.5	6.7	Dendritic Mo powder overlying adherent layer	5	Col. 1
4.9	3	1.5	0.86	Superficially coherent modular deposit overlying adherent layer	Similar to Fig. 6	-
4.9	30	1.0	2.8	Powder agglomerates consisting of trees and large multi-faceted crystals of molybdenum over an adherent layer	-	-
4.9	100	0.5	8.5	Granular metallic powder over adherent layer	7,8,9	Col. 3
4.9	Periodic reverse 30 direct 60 reverse	1.0	3.2	Powder consisting of small platelets over about 0.002" of adherent plate	10	Col. 4

All deposits prepared at 900°C

In general, the deposits are rather coarse powders. The typical particles are about 0.01 inch in diameter. The deposits are characteristically powders only, except for a layer of about 0.001 inch which adheres to the cathode. The adherent layer appears to be quite dense, but is limited in thickness to a single metallographic grain. The physical limit to the thickness of coherent deposits from this bath indicated that if the grain size could be reduced, the deposit might build up in an orderly fashion as occurs in aqueous electrolytes. Unfortunately, the temperature of 900°C, which is required for adequate solubility of the molybdenum compound is very close to the recrystallization temperature of molybdenum which is reported to be as low as 890°C with quite rapid recrystallization at 1090°C². It is apparent that even if the grain structure were refined by addition agents, recrystallization might be expected to occur during deposition at 900°C, resulting in deposits of poor physical properties, if not actual unsoundness of structure. In order to materially reduce the temperature of operation, halide solvents which melt lower than the potassium chloride-sodium chloride mixtures were investigated. The eutectic composition of lithium chloride and potassium chloride (41 mole % potassium chloride) melts at 352°C. The minimum melting point for AlCl₃-KCl occurs at 158.4°C with a composition of 34.5 mole % KCl. The minimum melting point for AlCl₃-LiCl occurs at 114.4°C with a composition of 40.1 mole % LiCl. The mixtures shown in Table IX were prepared from anhydrous materials. The halide solvents in each case were very close to the composition indicated above, and the molybdenum compound was present in a concentration of 4 to 5 mole %.

TABLE IX. Composition of Mixtures of K_3MoCl_6 with Low-Melting Halide Solvents.

Component	<u>Solution Number</u>		
	I	II	III
$AlCl_3$		4.3 g	4.0 g
KCl	2.7 g	1.2 g	
$LiCl$	2.3 g		0.8 g
K_3MoCl_6	1.7 g	1.1 g	1.1 g

Each mixture was sealed in an evacuated pyrex tube, heated in steps of $100^\circ C$ and held at the temperatures indicated in Table X for one hour before heating to the next higher temperature. The tubes were agitated intermittently. They were visually examined at each of the indicated temperatures with the results shown in Table X.

TABLE X. Solubility Characteristics of Mixtures of K_3MoCl_6 with Low-Melting Halide Solvents.

Temp.	<u>Solution Number</u>		
	I	II	III
$300^\circ C$	Solid	No solubility of Mo compound. Clear melt above red salt	Same as II
$400^\circ C$	Solid	Melt above solid Mo compound very slightly colored	Clear melt above Mo compound
$500^\circ C$	Deep red liquid mixed with small solid phase	Reddish brown solution with some solid phase	Similar to II but more solid present
$600^\circ C$	Uniform dark red liquid	Same as at $500^\circ C$ with only small solid phase remaining	Similar to II but solid phase larger

Each mixture was allowed to cool to room temperature and removed from the glass tubes. Mixture I was a uniform pink solid. Mixture II was a uniform brown solid with a small amount of red solid as a lower layer. Mixture III contained a light green upper layer and a dark red lower one, each forming about one-half of the total material. These tests show that a concentration of 4 to 5 mole % Mo may be obtained in the LiCl-KCl eutectic composition at about 600°C, while an equivalent concentration can barely be attained in the AlCl_3 -KCl mixture, and cannot be even closely reached in the AlCl_3 -LiCl mixture at the same temperature. Since anhydrous AlCl_3 is very difficult to handle, sublimes easily, fumes in air, is difficult to dehydrate and difficult to keep free of oxy-compounds, the LiCl-KCl eutectic mixture was chosen for investigation of electrolyses at 600°C.

Electrolysis. Electrolyses were run with a solution of the following composition at 600°C.

45.5 g LiCl
54.5 g KCl
33.0 g K_2MoCl_6

The halide solvent corresponded closely to the 41 mole % KCl eutectic composition and the molybdenum was present at a concentration of 4.1 mole %. Great difficulties were experienced in the early runs with this solution due to moisture contamination. Even after electrolyzing the bath, deposits mixed with oxides were produced at low current efficiencies (about 50%). This was undoubtedly due to the high hygroscopicity of the lithium chloride. Even with the precautions used, enough moisture was absorbed during the transfer of materials and the adjusting of electrodes to seriously affect the plating. It

was found, however, that if the solution was heated to 900°C and held there for a short time, a grey sublimate was expelled from the solution. This powder developed a blue color identical with the familiar molybdenum blue as it approached the outlet to the atmosphere and turned white in the open air above the glass envelope of the apparatus. It was apparent that the oxides and oxychlorides formed by the reaction with moisture at lower temperatures, either decomposed at 900°C or reacted with the trivalent molybdenum compound to produce higher valence molybdenum chlorides which are volatile. Because of the above difficulties, the following procedure was used before electrolytic runs: The bath was heated to 900°C at the same time that the argon flow was increased to about 3000 cc per minute. Released moisture and volatile oxy-compounds were thus rapidly driven off and their opportunity to attack the solution was reduced. After 15 to 30 minutes at 900°C , the solution was cooled to 600°C and the argon flow was reduced to the usual value of about 300 cc per minute. The solution was electrolyzed at a low current density until the deposits showed that oxides were not present.

With this combination of thermal and electrolytic purification, the current efficiencies for the production of molybdenum at the cathode shown in Table XI were measured. The cell voltage varied from 300 millivolts at 3 amp/dm² to 2 volts at 100 amp/dm².

TABLE XI. Cathode Current Efficiency of K_3MoCl_6 - KCl - LiCl Solution

<u>Current Density (Amp/dm²)</u>	<u>Current Efficiency (Cathode)</u>
	%
3	99
30	97
100	100

Another difficulty which was encountered, both with these solutions and with those using KCl-NaCl as the halide solvent, was a tendency to stop plating after about 20 ampere-hours had been passed through the solution. When this happened the electrolyte had usually lost its pink color and analysis showed the complete absence of trivalent molybdenum and the presence of only a trace of any molybdenum compound. The cause of this difficulty was eventually found to be due to electrical contact between the molybdenum anode and the graphite crucible. When the anode was separated from the crucible by a sheet of mica, the depletion of the solution stopped. Anode current efficiencies were measured by weight loss from the molybdenum anode during electrolysis, and calculated on the basis of the reaction

$$\text{Mo} \longrightarrow \text{Mo}^{3+} + 3e.$$

The results are shown in Table XII.

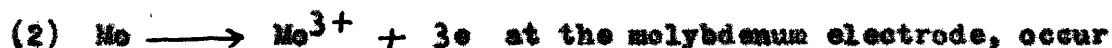
TABLE XII. Anode Current Efficiency of K_3MoCl_6 - KCl - LiCl Solution

Current Density (amp/dm ²)	Current Efficiency (Anode)	
	Anode in contact with graphite crucible	Anode insulated from graphite crucible
7	39	97
70	75	107*
200	-	101

* Values higher than 100% were due to unavoidable loss of anode material as smuts and fine particles.

Usually, when a soluble anode is in contact with an insoluble one, the insoluble anode is inert in the system, because the potential required to decompose the electrolyte at the insoluble anode is much greater than the potential at which the soluble anode goes into solution.

In this case, however, the oxidation of the electrolyte to a higher valence state at the graphite occurred at about the same potential as the solution of the molybdenum anode. That is, the reactions



at about the same potential in this system. x in reaction (1) may be either 1 or 2. In both cases, the corresponding halide is either volatile or unstable and would be expelled from the system at the temperature of operation. This clearly accounts for the observed loss of molybdenum and cessation of plating observed in solutions in which the anode was in contact with the crucible. As confirmation of this, 133 ampere-hours were passed through the 133 g of solution at a current density of 100 amp/dm^2 . Since the plating current was about 15 amperes, this series of runs represented an actual plating time of almost nine hours. Due to the small size of the apparatus this had to be accomplished in seven separate runs, changing the anode and cathode each time, but making no additions to the solution. At the end of this time, with the bath still plating satisfactorily, the series was stopped and the electrolyte was analyzed for trivalent and total Mo. The results were:

Total Mo	2.80%
Trivalent Mo	2.73%

These results indicate that the solution in its steady state contained molybdenum almost entirely in the trivalent state. This fact, coupled with the fact that anode and cathode current efficiencies were both essentially 100% when calculated on the basis of a three electron

reaction for each, conclusively proved that the anode dissolved in the system to form a trivalent ion, that the trivalent ion was reduced at the cathode, and that the trivalent bath was fundamentally stable with respect to both anode and cathode reactions.

It was observed that the final molybdenum content of the bath was one-half the initial value of 5.6% Mo. This loss after 1 ampere-hour per gram of solution has been passed is actually quite negligible and can be easily accounted for by very small and accidental deviations in the system. Further, since seven runs were required, material could have been lost during the thermal purification between each run.

Deposits. The most important characteristic of the solution in which the LiCl-KCl eutectic mixture is used as the halide solvent is the deposition of coherent, continuous, and dense electrodeposits at low current density and low temperature. At high current density very fine-grained powders are produced. At about 3 amp/dm² and 600°C coherent plates up to 0.02" in thickness have been produced in five hours of plating. Figure 11a shows a cross-section of such a deposit on a tungsten cathode (The tungsten base is at the bottom). Some porosity is observed in the deposit but its continuous nature is unquestionable. Figure 11b shows a portion of this deposit at higher magnification, etched to show the grain structure. Some porosity is again evident. The soundness of the grain structure is definite. The hardness was found to be 283 Vickers, about the same as the value obtained for the individual powder particles.

Another deposit was made under very nearly the same conditions, the temperature being 900°C instead of 600°C. The deposit had a thin

layer of dusty powder over a superficially coherent layer of molybdenum. When the powder was brushed off, a macroscopic pore and crack structure was exposed. Metallographic examination showed this deposit to be essentially unswound. Figure 12a shows a cross-section of this deposit. The first observation of note is the thinness of the deposit compared to that produced at 600°C , although they were both run for the same length of time at the same current and with about the same current efficiency. The powder, which was brushed off, comprised more than half the deposited metal. Also noteworthy is the complete network of cracks and pores. Figure 12b shows a portion of this deposit at higher magnification etched to bring out the grain structure. The much larger grain size compared to that at 600°C is evident as is also the lack of continuity in the structure. At 900°C , the deposit was practically a powder deposit with only superficial coherence. It is of interest to compare the two deposits shown in Figures 11 and 12 with that in Figure 6. The deposits shown in Figures 6 and 12 were both produced under the same conditions except for solution composition. The deposit shown in Figure 6 was produced from the KCl-NaCl bath and the deposit shown in Figure 12 was produced from the KCl-LiCl bath. In the former case the entire deposit, except for a portion one grain thick, rubbed off as powder, and the grain-size of the coherent portion is even larger than in the latter. An interesting difference between a coherent deposit and a powder deposit which is only superficially coherent was observed. It may serve as a quick test to distinguish between them. A coherent deposit, when rubbed with a metal burnishing tool or with a file, becomes bright on the rubbed area. A powder deposit merely abrades but does not show any brightness where rubbed.

A molybdenum deposit similar to that shown in Figure 11 was chiseled from the tungsten rod. It came off as large chips and showed no tendency to form powder. It was analysed and found to be 99+ % Mo.

The soundness of the structure of an electrodeposit is best evaluated by removing it from the base metal and examining its properties. This is usually accomplished by plating on a base metal which can be chemically dissolved by a reagent which does not attack the electrode. Attempts to plate molybdenum on either a steel or copper cathode resulted in the cathode dissolving in the solution and an impure sponge of molybdenum powder was precipitated in the crucible. In addition, the solution was practically stripped of dissolved molybdenum salts. It was concluded that both iron and copper chemically displaced molybdenum from solution. This will be discussed further below. A satisfactory cathode was finally made by closing the end of a 1/4" diameter steel tube, giving it a strike plate in a cyanide copper solution and plating it with about 0.001 inch of silver. This plate was buffed down to about 0.0005 inch and then another 0.0005 inch of silver was applied. This silver-plated steel tube was then used as the cathode on which about 0.02 inch of molybdenum was deposited from the LiCl-KCl bath at 600°C and 3 amp/dm². The welded end was cut off to form a tube open at both ends and both the tube and the cup (originally the welded end of the tube) were allowed to stand in 50% hydrochloric acid. The iron was dissolved and the thin silver tube was removed mechanically since its adherence to the molybdenum was poor. The electroformed tube of molybdenum which remained was rough on the surface, but extremely sound in structure. It is shown, with the cup, in Figure 13. It was

about 2 inches long, 1/4 inch diameter and 0.02 inch thick. The tube was hard and tough but somewhat brittle. Its density was measured by comparison of its weight in air and in tetrabromethane of accurately known density. Its density was found to be 9.6, or 94% of the theoretical density of molybdenum metal. Molybdenum produced by powder-metalurgical methods reaches a density of 90 to 92% of the theoretical value after pressing and sintering at a temperature 250°C below its melting point. When sintered at only 25°C below the melting point, the density still is about 92 to 93% of the theoretical value. Higher values can be attained only by swaging the sintered bar⁴⁸. The electro-formed molybdenum tube had a density in the as-deposited condition greater than that reported for pressed and sintered molybdenum.

Periodic reverse current with 6 amp/dm² direct current for 40 seconds and 60 amp/dm² reverse current for 2 seconds was tried. A uniform coherent plate about 0.008 inch thick was obtained in five hours with no improvement in smoothness. It is possible that extremely rapid cycles might decrease the roughness of the coating.

At 6 amp/dm² and 600°C the deposit was a powder. It was very smooth and adhered tightly to the cathode. Microscopic examination of the cathode at 100X magnification showed the deposit to consist of very small individual dendrites with little coherence among themselves.

At 30 and 100 amp/dm² and 600°C, very fine-grained powders were produced. In general, the deposits from this bath were much finer-grained than those from the KCl-NaCl solution and the deposits, even when powders, adhered to the cathode better. The slightly higher

current efficiencies measured in this bath as compared to the KCl-NaCl solution are probably due to this greater coherence and the resultant smaller mechanical loss of deposit rather than to an actual difference in current efficiency.

During part of the life-test described above, which was run at 100 amp/dm² and 600°C, the powder deposits were collected. About 110 grams of molybdenum powder were obtained during five runs. Figure 14 is a photograph of a tungsten cathode with its deposit of powder, and Figure 15 is a photomicrograph of the powder itself. Figure 15 has the same magnification (50X) as Figures 5, 8, 9 and 10. The difference in particle size is readily evident. The range of particle sizes in the batch is quite large, and is shown in Figure 16. The "apparent density" of the powder was 4.8 g/cc. Compacts were prepared from this powder by cold pressing at 30 tons/in² and pre-sintering at 1200-1500°C in argon for 15 minutes. The compacts were completely metallic in appearance, were polished to a high luster, and were very strong. However, they would break in a brittle manner when subjected to a sharp impact, as is characteristic of molybdenum compacts which have had no mechanical working. The density of the compact as measured by weight in air and in tetrabromethane was 8.36. Figure 17 is a photomicrograph showing the cross-section of the compact. The voids, consistent with its density of 81% of theoretical, are apparent. The good welding of the grains and clear grain boundaries are evident. No evidence of impurity segregations appears.

A sample of powder from this large batch was analyzed chemically and found to be 99+% Mo. Oxygen content was determined by drying a 10 gram sample of powder at 110°C and heating it in purified hydrogen for 30 minutes at 1060°C. The weight loss which resulted from the hydrogen treatment was determined and considered as loss of oxygen. The hydrogen was purified by passing through copper turnings at red heat, a Drierite tower, and two magnesium perchlorate towers*. The

* This procedure for determining oxygen in molybdenum powder is that used in the Detroit Laboratories of Climax Molybdenum Company and was kindly communicated to us by Mr. H. E. Hostetter of that company.

oxygen content of the powder was found to be 0.257%. The spectroscopic analysis appears in column 1 of Table XIII. To prepare Table XIII, the spectra of two powders prepared from the LiCl-KCl solution, one powder from the NaCl-KCl solution, a commercial Mo powder, a sample of the Mo anodes used in this work, a sample of specially purified molybdic acid used as a spectroscopic standard, and a sample of molybdenum powder (Hardy) used as a spectroscopic standard, were all flashed on the same photographic plate so that the comparison of individual impurity levels in the various samples would be more accurate.

TABLE XIII. Spectroscopic Analysis of Electrolytic Molybdenum Powders,
Commercial Molybdenum, and Specially Purified Molybdenum
Metal and Compounds.

Element	1	2	3	4	5	6	7
Silver	T	-	-	-	-	-	-
Aluminum	W	VW	VW	VW	VW	-	W
Barium	-	-	-	-	VW	-	-
Calcium	VW	-	T	T	T	T	-
Cobalt	VW	-	VW	VW	VW	-	VW
Chromium	T	-	-	VW	T	-	-
Copper	VW	T	T	VW	VW	VW	T
Iron	W	VW	VW	W	VW	VW	W
Magnesium	VW	T	T	VW	VW	T	T
Manganese	VW	-	-	W	VW	W	VW
Molybdenum	VS	VS	VS	VS	VS	VS	VS
Nickel	VW	-	-	VW	VW	-	VW
Lead	VW	T	T	T	T	-	T
Silicon	W	VW	VW	W	VW	W	W
Tungsten	-	-	-	-	-	W	-
*Oxygen	0.257%	0.026%	0.068%	0.268%			

Col. 1 - part of 110 g batch from LiCl-KCl solution

Col. 2 - sample from LiCl-KCl solution produced with specially purified melt

Col. 3 - sample from NaCl-KCl solution

Col. 4 - Commercial molybdenum powder (Westinghouse Corp.)

Col. 5 - Commercial molybdenum sheet used as anodes (Fansteel Corp.)

Col. 6 - Specially purified MoO₃ used as spectroscopic standard

Col. 7 - Molybdenum powder (Hardy) used as spectroscopic standard

VS, very strong = greater than 10%

W, weak = 0.01 - 0.1%

VW, very weak = 0.001 - 0.01%

T, trace = 0.0001 - 0.001%

*Not determined spectroscopically.

It can be seen that the powders produced electrolytically compare very favorably with commercial materials and even with specially prepared spectroscopic standards.

The powder from the 110 g batch was not prepared under ideal conditions of purity. The system had to be opened five times during the collection of this material. No electrolytic purification and only a little heating above plating temperature was performed between runs. A sample of powder was prepared at 100 amp/dm², 900°C with most rigorous purification of the solution before the run. In this case a nodular deposit was produced, the nodules of which were malleable, i.e., they could be flattened with a hammer without cracking. Figure 18A shows two large nodules as deposited, and Figure 18B shows the same nodules after flattening with a hammer. Figure 18C shows other nodules of this deposit etched to bring out the grain structure. The oxygen content of this powder, 0.0258%, and the spectroscopic analysis (column 2, Table XIII) confirm its very high purity. The hardness of this powder was 245 Vickers, appreciably softer than that of previous runs. Table XIV gives a summary of the types of deposits obtained from the LiCl-KCl solution.

TABLE XIV. Deposits from K_3MoCl_6 - KCl - $LiCl$ Solution

Temp. °C	Current Density (amp/dm ²)	Plating Time (Hr)	Wt. Deposit Collected (g)	Type of Deposit	Figure Reference	Table XIII Reference
600	3	5	2.9	Coherent rough plate, 0.02" thick	11a, 11b 13	-
900	3	5	-	Superficially coherent powder covering about 0.01" of badly cracked and porous plate	12a, 12b	-
600	6	4	-	Powder composed of microscopic dendrites over coherent plate	-	-
600	30	1	5.7	Fine grained powder (5.3 g) over approximately 0.0015" plate (0.43 g)	-	-
600	100	1.75	29.0	Very fine-grain powder	14, 15	Col. 1
900	100	1	17.9	Malleable nodular powder deposit	18a, 18b, 18c	Col. 2

All solutions contained 4.1 mole % Mo.

In determining the purity of deposits, chemical analyses for molybdenum were run, foreign metals were determined spectroscopically, and oxygen was determined by combustion with hydrogen. Since the solutions in which the deposits are prepared are halide solutions, it was thought advisable to check the halide content of a representative deposit, although the salts of the electrolyte are very soluble in the dilute acid in which the deposits are washed. This was done by dissolving 10 g of a deposit produced in the LiCl-KCl bath in 40 cc of 1:1 nitric acid, diluting to 100 ml, adding 40 cc of 1:1 sulfuric acid, and warming (not boiling) until the brown residue was converted to molybdic acid. This was filtered off and the clear filtrate diluted to 500 ml. Silver nitrate was added and only a faint opalescence was observed. The halide content of the deposits is evidently negligible.

Polarization and Potential Measurements

The most important physical quantity associated with an electrode reaction is the potential of the electrode at which it occurs. The potentials which are of interest are of two types, the static or equilibrium potential of an electrode at equilibrium, i.e., at which no net chemical change is occurring and no current is flowing, and the potential of the polarized electrode at which some chemical process is occurring at a definite rate described by the current density. The latter is usually expressed as a polarization curve, a curve of electrode potential vs current density. The equilibrium potential is of value in describing the behavior of an electrode in that it serves as a measure of the tendency of a given reaction to occur at that electrode. Since the equilibrium potential is a thermodynamic quantity directly

derivable from the free energy of a reaction, it has little to do with the actual operation of the electrode when current is flowing through it. The polarization is the quantity most useful in describing the properties of an operating electrode. However, the equilibrium potential is important in setting up the E.M.F. series for a given system and provides information which is valid to the extent that the electrodes operate under reversible conditions.

Reference Electrode. In order to measure an electrode potential of either type, a reference electrode which is constant, reproducible, reversible, and non-polarizable is required. The saturated calomel cell satisfies these requirements admirably in aqueous systems, but is, of course, unsuitable for use with molten salts. Yntema and his students⁴⁹ describe a reference electrode for use in molten salts between 100°C and 200°C which consists of an aluminum rod in a ternary mixture of AlCl_3 - NaCl - KCl . This would not be suitable in the temperature range of 600-900°C in which we are interested, mainly because of the volatility of AlCl_3 . An ideal molten electrolyte for this range of temperature is silver chloride. It melts at 455°C, boils at 1550°C and is easily prepared with high purity. There are no other stable valence states of silver to provide ambiguity of composition and it was found that in the absence of light it undergoes no visible decomposition when heated for long periods of time. Oxide contamination, which is a serious problem in most molten systems, does not occur in silver chloride because silver oxide decomposes at about 300°C, and if formed during the filling of a cell, it would be destroyed when the cell is brought up to temperature. That the $\text{Ag}, \text{AgCl}(l)/\text{cell}$ is reversible and

non-polarizable was shown by Aten, den Hertog, and Westenberg⁵⁰ who report that silver dissolves anodically and deposits cathodically from molten silver chloride at 475°C and that the polarisation voltage is only 0.5 mv at a current density of 1 amp/dm². This was confirmed in tests described below. One important disadvantage of the Ag, AgCl(1) electrode had to be considered in the design of a cell. Since silver is quite noble* in its potential, its presence in the

* In order to avoid the confusion which has resulted from the different conventions regarding the sign of the potential, a terminology which conforms to current usage in publications of the Electrochemical Society will be used in this thesis. If metal A appears below metal B in the E.M.F. series of the elements as it is usually written, i.e. with sodium near the top and gold near the bottom, then metal A will be described as more "noble" than metal B, and B as "base" with respect to A. The standard electrode potentials associated with the elements in the series will be described as becoming more "noble" as one goes down the series.

electrolyte of a base-metal electrode being measured would very seriously change the measured potential. On the other hand, the presence of a foreign electrolyte containing a base-metal ion in the molten AgCl would change its value only as a function of the concentration change of AgCl in the cell. The cell was therefore designed to minimize diffusion and convection, to cause flow, if there was any, to be into the molten silver chloride rather than into the electrolyte, and to have a large amount of silver chloride present so that small impurities

of base-metal electrolyte entering it would cause negligible changes in its potential. The apparatus for measuring potentials is shown in Figure 19, the electrical circuit diagram is shown in Figure 2B, and the reference electrode cell is shown in Figure 20. The reference electrode cell was made of quartz and consists of two tubes (A, D) of 9 mm bore connected by a heavy walled capillary (B) of 1.5 mm bore. Another capillary tube (C) was fitted on one of the larger tubes. The end of this capillary was bevelled to an angle of about 60° and is the equivalent of the Luggin capillary used as a probe for measuring potentials in aqueous solutions. At the point where capillary B enters tube D, there was a constriction which was tightly packed with asbestos. Molten silver chloride was poured into tube A and suction was applied to tube D (while stopping up the opening of C) until a tiny bead of silver chloride was drawn through the asbestos plug. A $1/8$ inch rod of silver was inserted in the molten chloride to within one inch of the bottom of tube A and held in that position by a silver disk fitting over the top of the tube. A silver wire was silver-soldered to the top of the silver rod. The entire cell was rigidly held at the top in an aluminum fixture by spring-loaded set screws. This fixture also held the cathode in contact with the end of capillary, C. A strip of molybdenum sheet, serving as anode was bent to a half-cylinder and placed over the outside of tube A. It was held by a clamp, to which a heavy plastic-insulated wire was attached. This wire was wound as a helix and served as an anode lead. The entire assembly was suspended by the cathode from the electrode connector J (Figure 2A). The anode lead wire and the wire from the silver reference electrode were drawn

through holes in the rubber stopper in the bung, E, (Figure 2A) and the system closed. After the usual procedure for establishment of an inert atmosphere was followed, the electrolyte in the crucible was melted and the electrode assembly was lowered into the crucible. The electrolyte entered tube D, through capillary C, and formed a liquid junction with the silver chloride at the asbestos plug. The levels of the solutions were adjusted so that the level of the electrolyte in D was slightly higher than that of the silver chloride in A. The asbestos plug was tight enough to prevent flow of solution through it except under applied vacuum, as when filling the cell, but the levels were adjusted in this manner so that if flow did occur it would be toward the silver chloride rather than toward the electrolyte. Current was passed through the anode and cathode, (cathode area $\approx 0.1 \text{ dm}^2$) as for plating. The current was set and held at each value for about one minute while the potential between the cathode and reference electrode was measured using a potentiometer and high sensitivity galvanometer. Zero current values were taken before and after each run. The mean difference between the initial and final zero values in eight runs was 7 mv. The largest single difference was 15 mv.

When measuring equilibrium potentials, the anode was not used and the cathode hung above capillary C rather than in contact with it. The same procedure for maintaining an inert atmosphere was followed. Potentials were read at half-hour intervals, and when the potential remained constant within one millivolt for three hours, that value was taken as the equilibrium potential.

The reproducibility and reversibility of the reference electrode was confirmed in the following manner. Silver chloride was poured into both sides of the quartz cell, capillary C was sealed, and silver rods inserted in both legs of the cell. The entire unit was immersed in molten potassium chloride-lithium chloride eutectic mixture which was maintained at 600°C in the usual manner. The immersed area of the electrodes was 0.025 dm^2 . The initial potential difference of 3.0 mv fell in one hour to 0.4 mv at which point the potential difference became constant. This potential difference is probably due to some small asymmetry in the two electrodes, contact potentials, etc. The cell was then polarized by passing current through it for five minute periods, at the end of which the circuit was opened and the potential read.

With 1 ma passing through the cell the 0.4 mv potential was re-established in less than 30 seconds after opening the circuit. With 2.5 ma it took one minute and with 5 ma the cell was permanently polarized, its potential being 1 mv, 30 minutes after the polarizing current was stopped. Since full-scale deflection of the galvanometer used during the measurements corresponded to a current of $0.6 \mu \text{ a}$, the possibility of polarizing the cell while balancing the potentiometer was negligible. That the cell is reversible is demonstrated by the fact that one of the silver rods was anode, and the other cathode during polarization, and up to 2.5 ma the cell reverted rapidly to normal on stopping the polarizing current.

Polarization Measurements. A solution of K_3MoCl_6 in LiCl-KCl eutectic mixture of standard composition (4.1 mole % K_3MoCl_6) was

prepared and purified by thermal and electrolytic means as described previously. The reference electrode cell with molybdenum anode and cathode were inserted into the melt and allowed to stand until the zero current potential value became fairly constant. Readings were taken

at 20 points in the current density range from 0 to 100 amp/dm². Fewer points were taken in the upper than in the lower part of the range because at high current density the nature of the cathode surface changes very rapidly and makes the values obtained less reliable.

Polarization curves were determined at 600°, 700°, 800° and 900°C.

Two runs were made for each temperature, no two runs at the same temperature being done consecutively. In addition, the runs at different temperatures were done in random sequence, so that no time or systematic solution variation effects would be confused with a temperature effect. The average value of the two determinations of cathode potential for each current density and temperature was taken and the isothermal polarization curves plotted. Figure 21A shows these over the entire 0 to 100 amp/dm² range, Figure 21B shows the 0 to 10 amp/dm² range on an expanded scale and Table XV shows the data from which these curves are plotted. The mean average deviation from the mean of eighty pairs of points is ± 8 mv and only three pairs of points had an average deviation greater than ± 20 mv.

Table XV: Data for Polarization Curves of Pure K_2MnCl_6 -KCl-LiCl Solution

I (amp/dm ²)	600°C				700°C				800°C				900°C				
	E ₁ (volt)	E ₂	E _{ave}	A.D.	E ₁	E ₂	E _{ave}	A.D.	E ₁	E ₂	E _{ave}	A.D.	E ₁	E ₂	E _{ave}	A.D.	
0	0.379	0.334	0.349	±0.022	0.430	0.394	0.414	±0.017	0.452	0.464	0.459	±0.008	0.505	0.499	0.501	±0.006	
0	.364	.320			.427	.394			.449	.469			.509	.491			
0.10	.357	.349	.353	.004	.427	.406	.416	.010	.451	.471	.461	.010	.512	.487	.500	.013	
0.32	.383	.393	.388	.005	.430	.407	.419	.012	.459	.473	.464	.009	.510	.488	.499	.011	
0.63	.391	.422	.406	.015	.430	.410	.420	.010	.470	.472	.471	.001	.512	.493	.503	.010	
1.0	.398	.440	.419	.021	.436	.419	.429	.009	.478	.473	.476	.002	.512	.500	.506	.006	
1.6	.423	.450	.436	.013	.448	.426	.437	.011	.481	.475	.478	.003	.515	.506	.511	.005	
2.0	.429	.441	.435.	.006	.453	.423	.438	.008	.487	.478	.483	.005	.515	.506	.511	.005	
2.5	.435	.450	.443	.007	.453	.433	.443	.010	.494	.486	.490	.004	.523	.509	.516	.007	
3.0	.449	.459	.454	.005	.459	.442	.451	.009	.499	.486	.492	.006	.525	.513	.519	.006	
3.5	.462	.469	.466	.004	.462	.450	.456	.006	.507	.492	.500	.008	.530	.519	.525	.006	
4.0	.477	.480	.478	.002	.466	.456	.461	.005	.515.	.494	.504	.010	.531	.524	.528	.004	
4.5	.487	.486	.487	.000	.474	.462	.468	.006	.520	.495	.508	.012	.539	.527	.533	.006	
5.0	.504	.493	.498	.005	.481	.469	.475	.006	.525	.497	.511	.014	.544	.530	.537	.007	
6.0	.520	.508	.514	.006	.489	.483	.486	.003	.532	.507	.519	.012	.549	.541	.545	.004	
8.0	.549	.525	.537	.012	.506	.509	.508	.001	.545	.522	.534	.011	.564	.555	.559	.005	
10	.569	.552	.560	.008	.520	.523	.521	.002	.587	.617	.592	.015	.579	.572	.576	.004	
16	.629	.626	.628	.001	.560	.574	.567	.007	.620	.678	.649	.029	.618	.617	.618	.000	
32	.780	.800	.790	.010	.674	.680	.677	.003	.738	.723	.730	.008	.735	.737	.736	.001	
56	.981	.972	.979	.005	.839	.900	.870	.030	1.061	1.024	1.042	.018	.906	.896	.901	.005	
100	1.323	1.303	1.313	.010	1.081	1.095	1.088	.007	1.197	1.186	1.191	.005	1.161	1.145	1.153	.008	
Mean Ave. Deviation				±0.008					±0.009					±0.010			±0.006

The zero current potentials (equilibrium potentials) range from 0.349 volts to 0.501 volts between 600°C and 900°C with a temperature coefficient of $+5 \times 10^{-4}$ volts/degree. The silver reference electrode is the positive (noble) pole. It was found that another series of polarization curves was obtained with freshly prepared solutions in which the equilibrium potentials ranged from 0.071 volts to 0.034 volts from 600 to 800°C with a temperature coefficient of -2×10^{-4} volts, but on heating the solution at 900°C for some time the potential reverted to the higher values and then stayed at the higher values over the entire temperature range. The solution was then allowed to freeze and was exposed to air over night. The next day the potential was found to be 0.05 volt at 600°C and stayed there even after two hours of heating at 900°C. The solution was then electrolyzed with an auxiliary cathode at 100 amp/dm² for twenty minutes at 900°C, after which the equilibrium potential at 600°C was found to be 0.32 volts. It should be noted that the electrolysis was required only because of the prolonged exposure to air. With slight exposure, heating is sufficient to establish the normal values.

The polarization curves of the air-contaminated solutions are shown in Figure 22A. These results conclusively show that air contamination enables the potential of a molybdenum electrode in the solution by about 0.3 to 0.4 volt.

A solution consisting of 45.5 g LiCl, 54.5 g KCl and 18.5 g K₂MoO₄ (4.1 mole % K₂MoO₄) was prepared and polarization curves were run under an inert atmosphere with the usual precautions for drying the salts. The initial values of equilibrium potentials were highly irreproducible,

varying from 0.75 to 1.25 volts with no reproducibility between the zero current potentials at the beginning and end of the run. The silver electrode was still the positive pole. In any event this unstable potential showed the electrode to be much less noble than in the trivalent molybdenum solution. The solution was then electrolyzed, after which stable equilibrium potentials were obtained. The values were 0.029 volts at 600°C and 0.052 volts at 900°C. The temperature coefficient was $+8 \times 10^{-5}$ volts/degree in this range. These values remained in this range despite heating, electrolysis, or other treatment. The polarization curves for this solution are shown in Figure 22B. The potential values obtained in this solution are not as reproducible as in the uncontaminated trivalent molybdenum solution.

Equilibrium Potential Measurements. Equilibrium potential data were obtained for Zn^{2+} - ZnCl_2 , Fe^{2+} - FeCl_2 , Cu^{+} - Cu_2Cl_2 , and Ag^{+} - AgCl , each in 4.1 mole % solution in the KCl-LiCl eutectic mixture in the absence of air. This was done to obtain some information about the EMF series in this medium at 600°C and particularly to find the position of molybdenum in this series. The solutions were prepared as follows:

Zinc chloride. - CP ZnCl_2 (anhyd.) was held at 400°C for two hours in a stream of dry hydrogen chloride gas. 10.6 g of the molten salt were then poured into 100 g of the molten eutectic mixture of LiCl-KCl and the solution quickly transferred to the inert atmosphere apparatus. Since zinc is molten at 600°C, the potential was measured by adding 250 gm of pure zinc sticks to the crucible containing the electrolyte. This formed a pool on the bottom of the crucible and electric contact was made with it by immersing a seven-inch length of

0.060" diameter tungsten rod over which had been sealed a nonax glass sleeve so that about 1/2 inch of tungsten was bare at each end. The bare end of the rod and some of the glass dipped beneath the zinc-electrolyte interface so that the potential measured was that of the molten zinc electrode.

Ferrous chloride.- C.P. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was held at 400°C for two hours in a stream of dry hydrogen chloride gas. After the FeCl_3 impurity was volatilized, the powder remaining was cooled. 9.82 g of the anhydrous FeCl_2 were then added to 100 g of the molten LiCl-KCl eutectic mixture. The resulting mixture was placed in an inert atmosphere.

Cuprous chloride.- C.P. Cu_2Cl_2 was washed with water until the washings were no longer blue. The stiff aqueous paste was heated at 450°C in a stream of dry hydrogen chloride gas. A colorless melt of Cu_2Cl_2 was obtained. After freezing, 7.66 g of the melt were added to 100 g of the molten eutectic mixture and the resulting mixture was transferred to the inert atmosphere.

Silver chloride.- 13.8 g C.P. AgCl (molten) was added to 125 g of the molten eutectic mixture and the resulting mixture was transferred to the inert atmosphere.

All potential determinations were made with argon flowing through the system using the procedure for determining equilibrium potentials as described above. Table XVI gives the potential values for each of these cells, the silver reference electrode in each case being the positive pole. The sign of E is positive if a representative cell is written as follows:



The first four cells are analogous to Daniel cells. The last cell is a concentration cell in which silver chloride is transferred from the pure state to a concentration of 4.1 mole %.

TABLE XVI. Potential, E , of H Electrode in 4.1 mole % H Chloride Dissolved in KCl - LiCl (Detectic Composition) Against the Ag, AgCl (Pure) Reference Electrode at 600°C.

M	E (Volt)
Zinc	1.277
Iron (ous)	1.033
Copper (ous)	0.626
Molybdenum (trivalent)	0.349
Silver	0.312

The equilibrium potential found for molybdenum at the same concentration in the same electrolyte at the same temperature with respect to the same reference electrode is also included in Table XVI. This Table represents the E.M.F. series for these elements at 600°C at a concentration of 4.1 mole % in lithium chloride-potassium chloride detectic mixture as solvent.

CHAPTER III

DISCUSSION

One of the most important facts demonstrated in this investigation was the inability to obtain a pure molybdenum deposit from solutions containing oxygenated salts or even from solutions of non-oxygenated salts which had been slightly contaminated with air or moisture. Whenever oxy-compounds were present, the current efficiency for molybdenum deposition was reduced and in many cases molybdenum oxides were present in the deposit as X-ray diffraction studies showed.

To determine the cause of this behavior, and to obtain some insight into the electrochemistry of these systems, let us consider the potential measurements with the pure trivalent molybdenum, air-contaminated trivalent molybdenum, and molybdate solutions. It was shown that the equilibrium potential of a molybdenum electrode in an air-contaminated trivalent molybdenum solution is about 0.4 volt lower (more noble) than in a pure trivalent molybdenum solution. A difference of this magnitude indicates that the electrode reactions occurring in the two systems must be entirely different. This conclusion is corroborated by the observation that the temperature coefficient of the potentials in the two systems differs not only in magnitude, but also in sign.

Since the trivalent salt is easily oxidized by air at these temperatures, one of the effects of the contamination must be to produce oxygenated compounds of molybdenum in which the molybdenum has a valence higher than three. The reduction of these intermediate valence

molybdenum compounds to the trivalent oxide evidently proceeds at a much lower potential than does the reduction of trivalent molybdenum to molybdenum metal. Therefore, at low current density one would expect no molybdenum deposit at all, only oxides, and at high current density, when the cathode has become sufficiently polarized to reach the deposition potential for molybdenum metal, one would expect both processes to occur. At 600°C the cathode in a contaminated bath doesn't reach the potential at which molybdenum can co-deposit with the oxide until a current density of 30 to 40 amp/dm² is used. At 900°C it barely reaches it at 100 amp/dm². It appears, therefore, that the higher potential is characteristic of the electrode reaction, $\text{Mo}^{3+} + 3e \longrightarrow \text{Mo}$; and the lower potential is characteristic of a reaction which may be written: $\text{Mo}^{(3+x)+} + xe \xrightarrow{0} \text{Mo}_2\text{O}_3$. It is apparent that oxygen must be absent from the system in order to obtain pure molybdenum.

In the potential measurements on the potassium molybdate solution it was observed that no equilibrium potential at all could be determined with a molybdenum electrode in the solution before it was electrolyzed and that in any event the ambient potential which was observed was more than 0.5 volt higher (less noble) than that for reducing trivalent molybdenum to metal. A possible explanation is that the molybdate solution is actually not in equilibrium with molybdenum; that is, the reaction $\text{MoO}_4^{2-} + 6e \longrightarrow \text{Mo} + 4\text{O}^{2-}$ either does not occur or it never reaches equilibrium. If it did, some stable potential for the MoO_4^{2-} , Mo half-cell should be observed within a reasonable time. In any event, the observed high potential is of no

consequence in the electrode reactions which may be expected, since, after electrolysis for a short while, a stable potential of about the same value as that found with an air-contaminated trivalent solution is observed. This stable potential is almost a volt lower than the initial value and so no reaction characterised by the initial value can possibly occur at reasonable current densities with any efficiency.

The polarization curves of Figure 22B do not reach the value of 0.75 volt even at 100 amp/dm². Breaks in the curve do occur in the vicinity of 0.3 volt at about 30 amp/dm² and these probably represent the beginning of the reduction of trivalent molybdenum to metal. It may be surmised that since the potentials measured in the electrolyzed molybdate solution and in the air-contaminated trivalent molybdenum solution are about the same, the same reaction would be occurring. This is confirmed by the X-ray diffraction data which identifies Mo₂O₃ in the deposit from the molybdate and in the deposit from the trivalent molybdenum solution. The fact that the molybdate solution is observed to turn blue after electrolysis confirms the presence of lower valence molybdenum compounds in the solution and that it is these, rather than the hexavalent molybdenum, which are in equilibrium with the electrode.

Yntema⁵¹ measured the potential of a molybdenum electrode in dilute solutions of K₂MoO₄ and K₃MoCl₆ in AlCl₃-NaCl-KCl mixture at about 200°C and reports that they are both about the same. It has been shown that the electrode reactions in these systems are clearly not the same since one plates pure molybdenum and the other does not. The explanation of Yntema's conclusion is that 1) the solutions were electrolyzed in order to purify them, and 2) they were exposed to air

at all times. Yntema noted that there was^a red condensate on the walls of the vessel containing the K_3MoCl_6 . This could only have been $MoCl_5$ produced by oxidation of the compound by air, since we have shown K_3MoCl_6 to be stable and non-volatile in the absence of air up to at least $600^\circ C$. What Yntema was comparing then, was an electrolyzed molybdate solution and an air-contaminated K_3MoCl_6 solution. We have shown these solutions to be almost identical in their potentials with a molybdenum electrode. Since it has been shown that in either case, the deposit on the electrode is not molybdenum but a mixture of molybdenum and its oxides, it is difficult to associate the measured potential, called "the deposition potential of molybdenum" with any electrode reaction.

The polarization curve which was found by Yntema for both systems at $200^\circ C$ started at a very noble potential and showed a large break near 1 amp/dm^2 for the molybdate solution and near 0.2 amp/dm^2 for the "trivalent" solution at which the potential became less noble by about 1.2 volts. The breaks shown by the polarization curves for the molybdate solution at $600^\circ C$ and $900^\circ C$ occur at a higher current density (30 amp/dm^2) and are not as large as at $200^\circ C$. However, these differences can easily be accounted for by the difference in temperature and solvent at which the two determinations were made.

The potentials measured by Yntema are "deposition potentials" rather than equilibrium potentials. They were obtained by extrapolating a polarization curve to zero current. An examination of the curves for the molybdenum solutions in reference 51 will show the difficulty in performing such extrapolations. "Deposition potentials" have been

used as though they were equilibrium potentials but this can be justified only as a very broad approximation. The equilibrium potential of electrodes in electrolytes may be determined by allowing a purified electrolyte to come to equilibrium with an electrode, and the potential measured. When the electrode reaction which occurs reversibly at that electrode has been clearly established, then this measured value is clearly the equilibrium potential of the reaction in the system measured. For example, it has been shown that molybdenum deposits cathodically with very low overvoltage from a purified K_3MoCl_6 solution in LiCl-KCl solvent and that molybdenum dissolves anodically in the same system to form a trivalent molybdenum compound. A stable potential measured in this system is unequivocally, therefore, the equilibrium potential of the $Mo, [MoCl_6]^{-3}$ half-cell with reference to some arbitrary zero potential assigned to a stable, reversible, reference electrode.

A problem of some importance which arises from this investigation is the explanation of the reasons for the deposition of coherent deposits under some conditions and powders under others. It should be emphasized that the change from one form to the other is not a sudden one, but rather, as the temperature and current density are raised, there is a gradual coarsening and loosening of the structure of the deposit. Yntema finds that in the $AlCl_3$ -NaCl-KCl solvent at $156^\circ C$, the formation of a dendritic deposit is characterized by a higher "deposition potential" than is a smooth plate in the cases of aluminum, copper, cobalt, and zinc, but not in the case of nickel, iron, or manganese⁵². Examination of the isothermal polarization curves in Figure 21B shows that the 600° curve has a very slight change in curvature

at about 3.5 amp/dm^2 , the current density above which the plates become very powdery at 600°C . This is too small a break to consider as significant and a decision on this matter cannot be reached. However, even if this were significant, the change in slope of the polarization curve might be a result of the changed surface of the cathode in going from coherent to powdery plates and not at all related to any electrochemical change in the system.

One significant feature of the polarization curves of Figure 21B is the break at about 0.25 amp/dm^2 which appears in the 600° curve but not in any of the others. Also, the slope of the 600° curve is greater than that of the others over the full range from 0 to 100 amp/dm^2 as well as the low current density range. It must be remembered that coherent deposits were obtained only at 600°C . At higher temperatures no satisfactory coherent plates were obtained at any current density. It is well known that high polarization favors small grain size and coherence of deposits. For example, an aqueous solution of silver nitrate which shows low polarization, deposits isolated silver crystals while the cyanide complex of silver, with high polarization, deposits fine silver plates. There are many other examples of this. It is apparent from Figures 21A and B that the 600° bath undoubtedly shows greater polarization than the others and thus would be expected to favor the deposition of coherent deposits. The origin of this polarization may be indicated by the break at 0.25 amp/dm^2 . This is far below the change from coherent to powder deposits and is not known to be associated with any property of the deposit. The break is large enough, though, for one to be quite certain that a change in reaction

mechanism does occur there. We propose that this represents the point where the slow dissociation of the $[\text{MoCl}_6]^{-3}$ ion becomes the rate-controlling step of the reaction.

It has been shown that K_3MoCl_6 is thermally stable at 600°C . Its high thermal stability may also be predicted from theoretical considerations. The specific magnetic susceptibility of K_3MoCl_6 is given by Gmelin (op.cit. p. 239) as 13.23×10^{-6} emu at 18°C . This corresponds very closely to the value for three unpaired electrons. The electronic structure of trivalent molybdenum indicates that the most likely structure for six covalent bonds with three unpaired electrons in the complex is the octahedral structure of the sp^3d^2 bond type. This bond type is one of very high bond strength and is the same as that of other complex ions of high stability such as ferrocyanide, trivalent cobalt and chromium complexes, and others. At 900°C a very slow and slight sublimation is observed to occur, indicating that at this temperature the dissociation of the $[\text{MoCl}_6]^{-3}$ is sufficiently great to form some of the less stable MoCl_3 which decomposes to produce a brownish yellow sublimate. If one assumes that the rate of dissociation is associated with the observed stability, one would expect this rate to decrease as the temperature is reduced. It has been shown, further, that even in aqueous systems $[\text{MoCl}_6]^{-3}$ is not in equilibrium at room temperature with its component ions. One may therefore conclude that up to a rate of deposition of 0.25 amp/dm^2 the rate of dissociation of the complex is sufficient to maintain the concentration of the molybdenum ions. Above this rate of deposition the concentration of molybdenum ions is seriously depleted and the potential of the electrode rapidly increases. One may consider the solution in the vicinity of the cathode

at this point to have no free molybdenum ions, and that deposition occurs by diffusion of the complex to the cathode where it is directly reduced (or as some believe, the complex dissociates on the surface of the cathode and the free molybdenum ion is simultaneously reduced). The direct reduction of a complex anion is not unreasonable. A strong argument that this occurs in argentocyanide solutions was put forth by Haber as early as 1904⁵³. S. Glasstone also found that dissociation followed by reduction of the free silver ion was an unreasonable mechanism for the argente cyanide system⁵⁵. This explanation of the break observed in the 600° polarization curve, the higher polarization at 600° throughout the full range of current density, and the fact that the most coherent plates are obtained at this temperature are all consistent with the large body of knowledge which associates high polarization with coherent plates. That the plates cease to be coherent at higher current densities is not surprising to anyone who has seen a "burnt" deposit from an aqueous solution.

There are factors other than electrochemical, which also favor coherent deposits at lower temperatures. As indicated earlier, molybdenum recrystallizes at about 900°C and as this temperature is approached a deposit which is initially fine-grained would come out of the solution coarse-grained as a result of recrystallization. In addition, the decreased viscosity and higher diffusion rate at higher temperatures would also tend to give coarser-grained deposits.

It was noted that at all current densities at 900°C, the LiCl-KCl solution gave finer-grained deposits than the KCl-NaCl solution at the same temperature. No adequate explanation has been found for this.

The next matter of interest is the E.M.F. series for this system shown in Table XVI. The first point to note is the noble position of molybdenum in this series. It is not surprising that iron and copper electrodes dissolved in the molybdenum solution and molybdenum sponge precipitated when we realize that molybdenum is noble to them by about 0.7 and 0.3 volt respectively. There has been much confusion with regard to the potential of molybdenum in aqueous systems because the electrode is irreversible. So-called active and passive states have been reported with a difference in potential of 1.4 volts, the "passive" form having a potential noble with respect to the normal hydrogen electrode of 0.66 volts, or 0.14 volt less noble than silver⁵⁵. By a rather indirect method, Russell and Rowell placed the position of molybdenum in the E.M.F. series in aqueous systems near mercury⁵⁶. In this molten salt system, where the reversibility of the electrode was established, the noble potentials, near to silver, are the ones which clearly apply. The potential for the reaction: $\text{Mo} \longrightarrow \text{Mo}^{3+} + 3\text{e}$ (in aqueous acid solution) calculated by Latimer⁵⁷ is about 0.2 volt on the hydrogen scale.

In Table XVII are collected four different E.M.F. series for different systems, all potentials calculated with reference to a silver electrode in a solution of silver salt at the same concentration as the other metals in the series. Column 1 is calculated from the data of Yntema⁵⁸ for one mole percent solutions of salts of the indicated element in $\text{AlCl}_3\text{-KCl-NaCl}$ solvent at about 200°C . Column two was calculated from Lorenz' values⁷ of the potentials of Daniel cells consisting of $\text{M} \mid \text{pure molten chloride of M} \parallel \text{pure molten chloride of N} \mid \text{N}$, where M and N are metals, at 600°C . (The value for Sn is at 350° but the author states that the temperature coefficient of the potential is very small in this case.) Column 3 is the familiar E.M.F. series for 1N electrolytes in aqueous systems 1N in acid, taking the silver instead of the hydrogen electrode as zero. Column 4 is taken from Table XVI, with the potential of silver in 4.1 mole percent AgCl solution taken as zero.

TABLE XVII. E.M.F. Series in Various Systems

Element	E (Volt)			
	1	2	3	4
Zinc	0.42	0.43	1.6	0.97
Lead (ous)	.30	.32	0.92	-
Iron (ous)	.19	-	1.2	.72
Tin (ous)	.17	.07	0.93	-
Copper (ous)	.04	-	0.28	.31
Molybdenum	.35	-	-	.04
Silver	0	0	0	0

The parallelism between the series for $\text{AlCl}_3\text{-KCl-NaCl}$ solvent (Column 1) and for pure electrolytes (Column 2) and the large difference

between these two series and the ones in aqueous systems (Column 3) ^{78.}

and in KCl-LiCl solvent (Column 4) are apparent. The obvious difference between the pure molten salt system and the aqueous system is the absence of solvation in the former (since there is no solvent) and the existence of extensive solvation of the ions by water in the latter. It would appear, that if this is the cause of the differences in the two series, then the salts dissolved in the $AlCl_3$ -KCl-NaCl mixture are in a state very similar to the pure molten state while the salts dissolved in KCl-NaCl mixture are highly solvated. There is ample chemical evidence to expect this to be so. The solvent used by Intema contained 66 mole percent $AlCl_3$. It is well known that molten $AlCl_3$ does not ionize easily; that in fact, near its boiling point, even the vapor is dimeric⁵⁹. In addition, complexes of the $[AlCl_4]^{-1}$ type form easily and are quite stable, the potassium salt of this anion melting at $257^{\circ}C$. The major component of this solvent, therefore, is a material which not only does not give up its chloride ions easily but tends to take on another mole of chloride for each mole of $AlCl_3$ present. The KCl and NaCl, comprising only 34 mole percent of the solvent is not even sufficient to completely convert the $AlCl_3$ itself to the complex. As a result the added metal ions are largely free cations under no greater restraints from the surrounding ions than in the pure molten metal salt. Whatever complexes do form probably form with the aluminum salt whose tendency for forming covalent and coordinate valence bonds with halides is strong.

In the KCl-LiCl solvent, on the other hand, we have a highly ionic material with little or no tendency to form complexes. In this

solvent the added metal ions have ample free chloride ion with which to form complex anions of the type $[MCl_x]^-$. Lorenz has demonstrated the existence of a complex chloroplumbate anion in molten $KCl-NaCl-PbCl_2$ mixtures and in molten $KCl-PbCl_2$ mixtures by transference measurements⁷. The E.M.F. series in the $KCl-LiCl$ solvent shows a much larger range of potential differences, as one compares more and more active metals with silver, than in $AlCl_3$ or pure molten materials. The E.M.F. series in $KCl-LiCl$ approaches the type of series given by the aqueous, alcoholic and similar systems characteristic of high solvation. Just as solvents have been compared as to their relative tendency to accept or donate protons in acid-base phenomena, molten salts may be analogously compared as solvents on the basis of their relative tendency to accept or donate halide or other anions. In this case, $AlCl_3$ is apparently a much weaker halide donor than KCl or $LiCl$. The metal ions, therefore, have a greater tendency to form complex halo-anions in the latter than in the former. This may be of some importance in electrolysis of molten salts because the desirability of plating a metal from a solution of a complex anion rather than the simple cation in order to obtain smooth fine-grained deposits has been demonstrated many times in experience with aqueous solutions.

The magnitude of stable complex formation which may occur even at $600^\circ C$ is given by the following calculation. The potential for the cell: $Zn/ZnCl_2$ (pure) // $AgCl / Ag$ is given by Lorenz as 0.427 at $600^\circ C$ (Ref. 7, Vol. III, p. 123). The potential for the cell: $Zn/ZnCl_2$ (4.1 mole %), $LiCl, KCl$ // $AgCl / Ag$ was found by us to be 1.277 at the same temperature. The difference between the two should be the potential of the cell:



The potential of this last cell can be expressed in terms of the activities (assuming that the difference in the liquid junction potentials of the two Daniel cells is negligible) by

$$E = \frac{-RT}{nF} \ln \frac{a_{\text{soln}}}{a_{\text{pure}}} .$$

where E = potential of the cell = $1.277 - 0.427 = 0.850$ volts

$$n = 2$$

a_{soln} = activity of Zn^{2+} in the solution

a_{pure} = activity of Zn^{2+} in the pure molten state

$$T = 873^\circ\text{K}$$

R and F are the gas constant and the Faraday.

The most convenient standard state for use with molten electrolytes is that of the pure molten salt. By using the pure molten electrolyte as the standard state one can at least compare the molten solutions of electrolytes with the pure molten salts even though the state of the latter is unknown. Taking a_{pure} as 1 and solving the equation for a_{soln} , we find that the activity of the Zn^{2+} in the 4.1 mole % solution is about 10^{-10} in units of mole fraction. Since the concentration is 4×10^{-2} in the same units, the amount of zinc ion present in the same state of freedom as in the pure zinc chloride is negligible.

The extent of solvation or complex formation depends, not only on the solvent, but also on the solute. The potential of the silver concentration cell which was determined, i.e.:



may be expressed by

$$E = \frac{RT}{F} \ln \frac{a_{\text{pure}}}{a_{\text{soln}}}$$

As an approximation, the diffusion potential has been ignored in this concentration cell because the KCl-LiCl mixture present in large excess in one of the solutions may be considered as equivalent to a salt bridge. With $E = 0.312$ (from Table XVI) and $a_{\text{pure}} = 1$ as before, a_{soln} is found to be 0.016 in mole fraction units compared to a concentration of 0.041 in the same units. In this case the extent of solvation is not very large.

R. Suchy⁶⁰ determined the potentials of the following molten electrolyte cells:

Pb / PbCl₂ // AgCl (1.858 N), KCl, LiCl / Ag; $E = 0.127$ volt at 600°C.

Pb / PbCl₂ // AgCl (pure) / Ag : $E = 0.319$ volt at 600°C.

The difference between these values of E , 0.192 volt, represents the potential of the concentration cell,

Ag / AgCl (1.858 N), KCl, LiCl // AgCl (Pure) / Ag.

Unfortunately, Suchy does not give the composition of his AgCl - KCl - LiCl mixture except to indicate that the normality was calculated from the specific gravity of the mixture according to a method which was to be published later. A careful search revealed no publication on the matter. In an attempt to get an approximate comparison, the density of the 4.1 mole % solution used in our work was calculated from the densities of pure LiCl, KCl and AgCl at 600°C assuming no volume change on mixing. The details of this calculation will be found in the appendix. The "normality" of the 4.1 mole % solution

turned out to be 1.163. Taking the mole fraction as approximately proportional to the normality, Suchy's 1.858 N solution would be about seven mole %. The activity of the silver ion in this solution was calculated as above from the potential, $E = 0.192$ volt, which in turn was calculated from Suchy's data for the two Daniel cells. A value of 8 mole % is obtained for the activity of the silver ion in Suchy's solution. Considering the approximations which were made, one may infer that, if any complex formation occurs in this system, it certainly is not large. The fact that the chlorosilver complex is found to be more stable at high temperature than the chloro-silver complex is consistent with the postulated bond types by which these ions form complexes. The sp^3 bond of the tetrahedral zinc complex does have greater bond strength than the sp bond of the two-coordinate silver complexes⁶¹.

CHAPTER IV

SUMMARY AND CONCLUSIONS

In this study of the electrolysis of molybdenum compounds in fused salts it has been shown that a solution of potassium hexachloromolybdate (III) dissolved in a mixture of alkali halides can be electrolyzed in an inert atmosphere to produce deposits of pure molybdenum at the cathode. It has also been shown that this cannot be accomplished with oxygenated compounds of molybdenum because of the preferential deposition of highly stable oxides at the cathode which resist further reduction to metal. The recommended compositions for the deposition of pure molybdenum are:

I	KCl	50 g	and II	KCl	54.5 g
	NaCl	50 g		LiCl	45.5 g
	K ₃ MoCl ₆	33 g		K ₃ MoCl ₆	33 g

Solution I was operated at 900°C with a rotating cathode at any current density up to 100 amp/dm². No information at higher current densities has been obtained. Under these conditions deposits of 99.9+ % molybdenum powder were obtained at current efficiencies closely approaching 100% over the entire range. The powders were bright metallic coarse granules which adhered tightly to the cathode and were easily separated from adhering electrolytes by washing with dilute acid. With a lower concentration of molybdenum, the powder was deposited as long dendrites rather than granules.

From solution II, when operated at 600°C and 3 amp/dm², with a rotating cathode, coherent dense deposits of molybdenum up to 0.02"

thick have been produced. In the as-deposited condition, these plates have a density of 94% of the theoretical density of molybdenum. They are strong and hard, but brittle and somewhat rough on the surface. We believe that this is the first reported instance of the production of coherent massive electrodeposits from fused inorganic salts. From the same solution, when operated at higher current densities and temperatures between 600° and 900°C, fine-grained pure molybdenum powders of at least equal purity to that from Solution I have been produced. The powders can be compacted by ordinary powder metallurgy methods. The current efficiency for deposition of molybdenum is approximately 100% up to 100 amp/dm². No information was obtained above this current density.

A study of the electrolytes shows them to be electrochemically stable. Molybdenum anodes dissolve in them with 100% efficiency to form the same trivalent ion from which the molybdenum metal deposits at the cathode. Polarization studies have shown that the cathode polarization is small at the higher temperatures, but somewhat greater at 600°C. There is also some evidence that the reaction mechanism at 600°C differs from the mechanism at higher temperatures. It is believed that the production of coherent deposits resulted from the higher polarization involved in plating from a stable complex anion of molybdenum and from the fact that the operating temperature was well below the recrystallization temperature of molybdenum.

The relative position of zinc, iron, copper, molybdenum, and silver in the E.M.F. series in molten lithium chloride-potassium chloride eutectic mixture as solvent at 600°C has been established.

Molybdenum has been shown to be more noble than all but silver. The values for the potentials obtained indicate that these metals tend to form complexes in this solvent and are present mainly as the chloro-metal anion. The use of potential measurements such as these in determining solvation or complex-formation in molten electrolyte solvents has been explored.

A new reference electrode for measuring potentials in molten salts has been described. It consists of silver in pure molten silver chloride contained in a suitable cell to reduce contamination of the electrolytes due to diffusion and convection. The reference electrode has been shown to be stable, constant, and reversible. It is easy to prepare and may be used over a wide range of temperature.

A simplified method for the preparation of potassium hexachloromolybdate (III) and a new method for the preparation of molybdenum dichloride has been described.

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Dr. A. Brenner, Chief, Electrodeposition Section, National Bureau of Standards, under whose supervision this work was done, and to Dr. W. J. Swirbely, Professor of Chemistry, University of Maryland, for their advice, suggestions, and encouragement throughout the course of this investigation.

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APPENDIX

Electrodeposit from Aqueous Molybdate Solution

An attempt to produce a deposit from the solution described by Keycki and Yntema on page 55 of their article¹⁹ produced only a black non-adherent powder over what appeared to be a discolored cathode. Samples were then plated for us on gold cathodes by Sister Keycki and sent to us for examination. The cathodes were 3.8 cm x 6.4 cm. They were plated on both sides, one with 4.45 mg of deposit, the other with 19.06 mg of deposit. This represented a deposit thickness of 0.1 and 0.4 microns respectively (assuming a density of 10 for the deposit). Spectroscopic analysis of the bare gold and of the gold plus deposit showed the deposit to have molybdenum, 0.1 to 1% Cu, and traces of Fe and Mg. The deposit was then stripped from the cathode by solution in nitric acid. Molybdenum was determined colorimetrically and gravimetrically on each sample and copper was determined colorimetrically.

The results are listed in Table XVIII.

TABLE XVIII. Analysis of Deposit from Aqueous Molybdate Solution

	1	2
Weight of deposit stripped from cathode	4.45 mg	19.06 mg
Molybdenum % (colorimetric)	74	78
Molybdenum % (gravimetric)	74	81
Copper %	1.3	0.8

It should be noted that pure MoO_2 contains 75% Mo.

An electron diffraction pattern was also run on one of the deposits (No. 2). Three lines were seen as diffuse halos which were difficult

to measure. It was possible however that two of them corresponded to two of the strongest lines of molybdenum.

It was suggested that the deposits might have oxidized in transit and so Sister Kaycki analyzed similar deposits plated on gold as soon as they were produced. In an unpublished communication she states that "some deposits contain more than 90% molybdenum". It should be noted that a deposit consisting of 60% molybdenum and 40% MoO_2 would contain 90% Mo by analysis.

Calculation of Current Efficiency

According to Faraday's Law, 96,500 coulombs of electricity will deposit one gram-equivalent of metal when the deposition of metal is the only reaction occurring at the cathode. When other reactions occur at the electrode, the yield of metal will be that fraction of a gram-equivalent corresponding to the fraction of the total current used for metal deposition. The current efficiency for a reaction is defined as the percent of the total current which is used for that reaction. In the case of the electrodeposition of a metal at a cathode, the current efficiency is expressed by:

$$\text{C.E.} = \frac{g}{ite} \times 9.65 \times 10^6, \text{ where C.E.} = \begin{matrix} \text{current efficiency} \\ \text{in percent} \end{matrix}$$

g = weight of the deposited metal in grams

e = equivalent weight of the metal in grams

i = current in amperes

t = time in seconds

For the reaction, $\text{Mo}^{3+} + 3e \longrightarrow \text{Mo}$, the equivalent weight of molybdenum is one-third of its atomic weight, or 31.98 g. In a typical run

in the LiCl-KCl bath at 900°C , 6.0 g of molybdenum powder was produced in 20 minutes with a current of 15 amperes. Therefore, in this case, $g = 6.0$, $i = 15$, and $t = 1200$. On substituting these values in the equation, it is found that the current efficiency was 100%. When coherent plates were obtained, their weight was determined by cutting off that part of the cathode which contained the deposit and weighing it. The molybdenum deposit was then dissolved in 1:1 nitric acid and the bare tungsten cathode was reweighed. The difference was taken as the weight of the molybdenum deposit.

Calculation of the "Normality" of the 4.1 mole % AgCl Solution
in the Molten KCl-LiCl Mixture

In order to calculate the "normality" of the above solution (i.e. the number of moles of silver chloride per liter of solution) it is necessary to know the volume of the solution. An approximate value of the volume can be obtained from the density of each of the components, if one assumes no volume change on mixing. The data in Table XIX is taken from the International Critical Tables.

TABLE XIX. Density of Molten Halides

<u>Substance</u>	<u>Density at $T^{\circ}\text{C}$.</u>	<u>Temperature Range ($^{\circ}\text{C}$)</u>
LiCl	$1.762 - 4.32 \times 10^{-4} T$	626 to 985
KCl	$1.971 - 5.8 \times 10^{-4} T$	789 to 958
AgCl	$5.267 - 9.2 \times 10^{-4} T$	628 to 783

In Table XX, the second column gives the weight of each substance in the solution. The third column is the density of each substance at 600°C calculated from Table XIX. The fourth column gives the volume calculated from the second and third columns.

TABLE XX: Volume of 4.1 mole % AgCl Solution

<u>Substance</u>	<u>Weight (g)</u>	<u>Density (g/cc)</u>	<u>Volume (cc)</u>
LiCl	56.8	1.503	37.8
KCl	68.1	1.623	42.0
AgCl	13.8	4.715	2.9
Total Volume			82.7

Since 0.0962 mole AgCl was present in the solution,

$$N_{\text{AgCl}} = \frac{0.0962}{82.7} \times 1000 = 1.163 \text{ Normal}$$

ILLUSTRATIONS

FIGURE 1

Apparatus for Electrolysis of Fused Salts



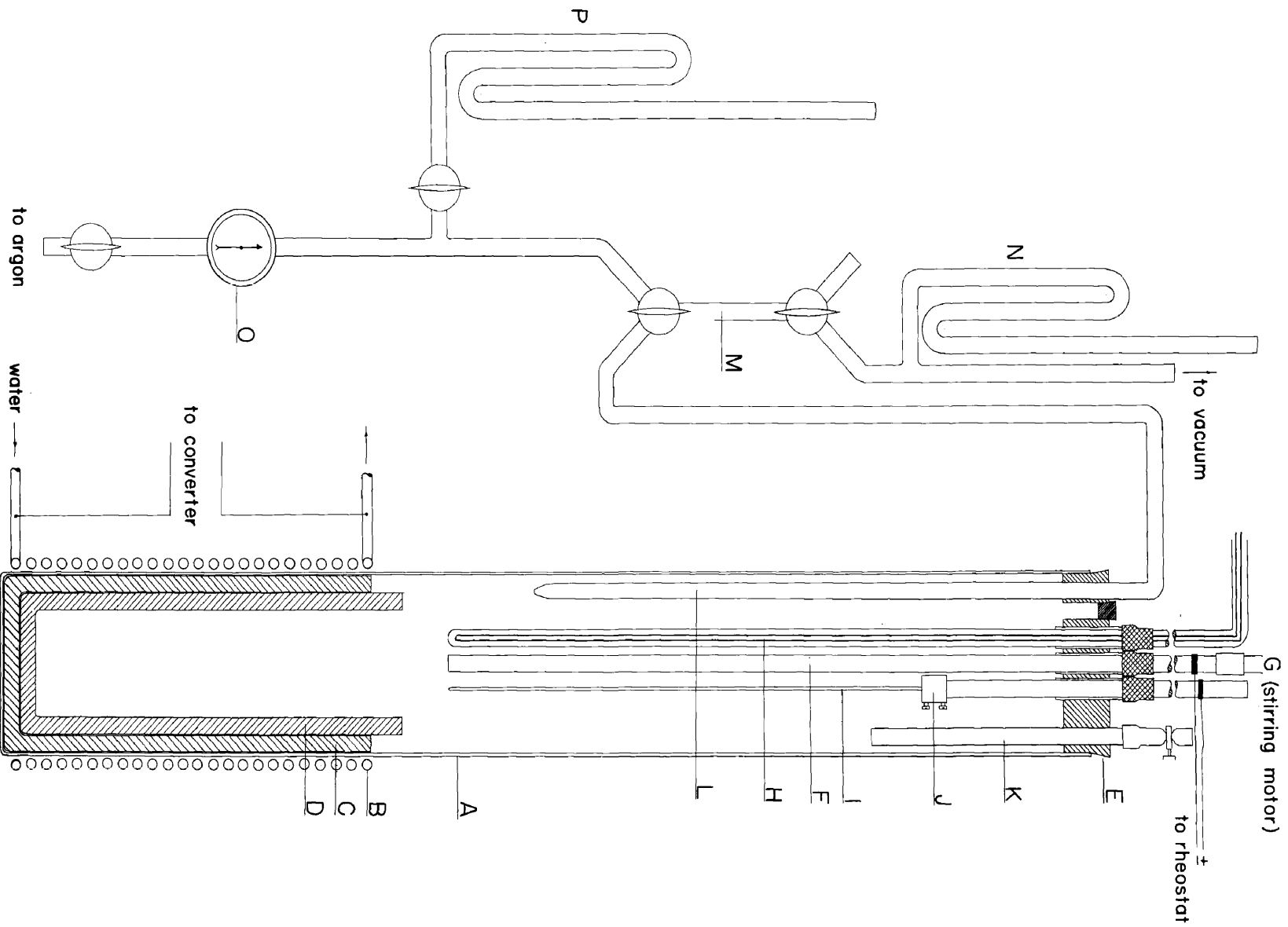


FIGURE 2A

Schematic Diagram of Electrolysis Cell and Auxiliary Equipment

FIGURE 2B

Electrical Circuit Diagram

DPDT	Double Pole Double Throw Switch
A	Ammeter
V	Voltmeter
POT.	Potentiometer
G	Galvanometer
SC	Standard Cell
RE	Reference Electrode
Cell	Electrolysis Cell

Resistors

1	10 ohms
2	10 ohms
3	0.5 to 50 ohms
4	0 to 1000 ohms

The portion enclosed by the broken line was used only for potential and polarization measurements.

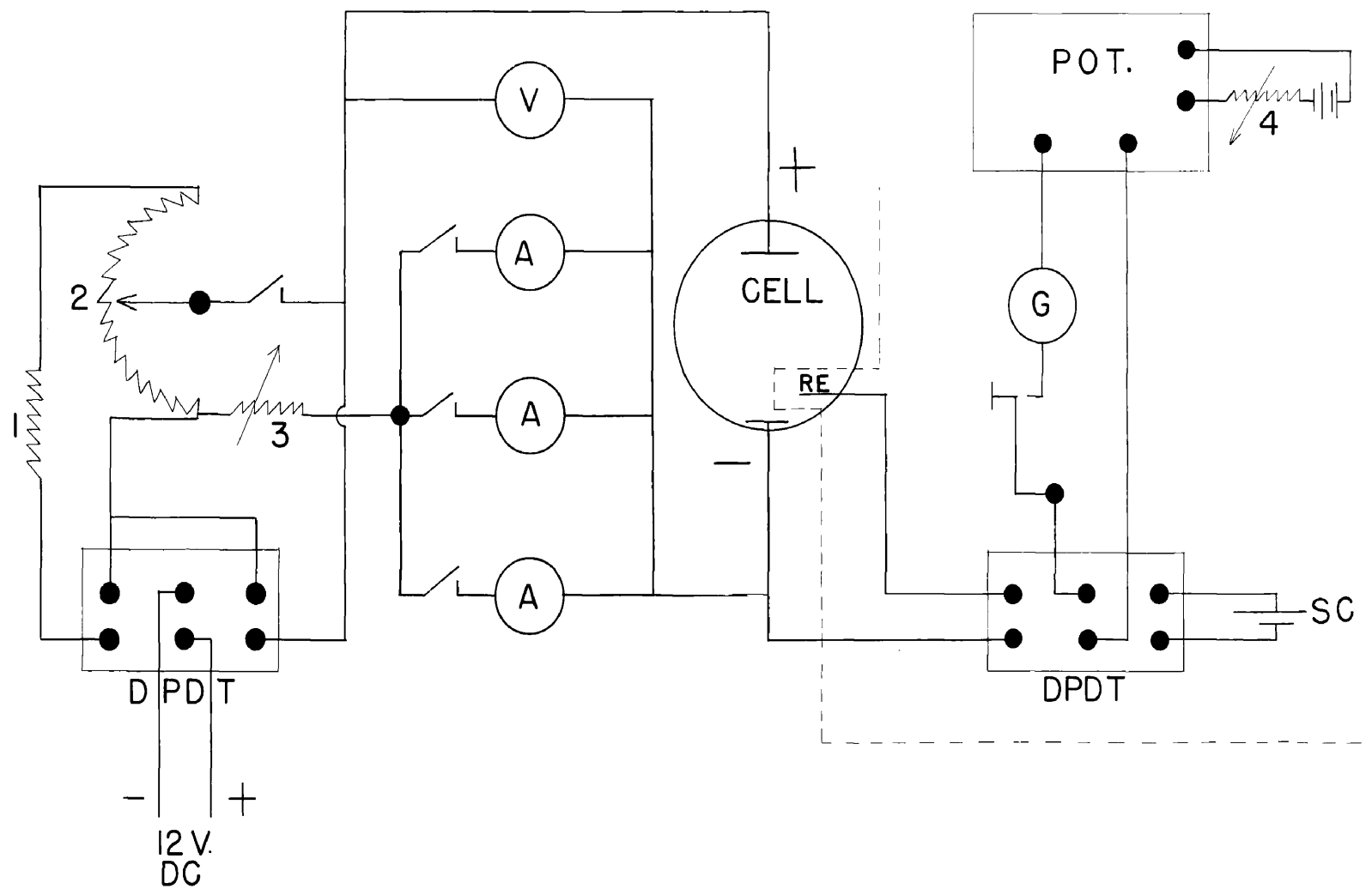


FIGURE 3

X-Ray Diffraction Patterns of Impure Deposits from Various Solutions

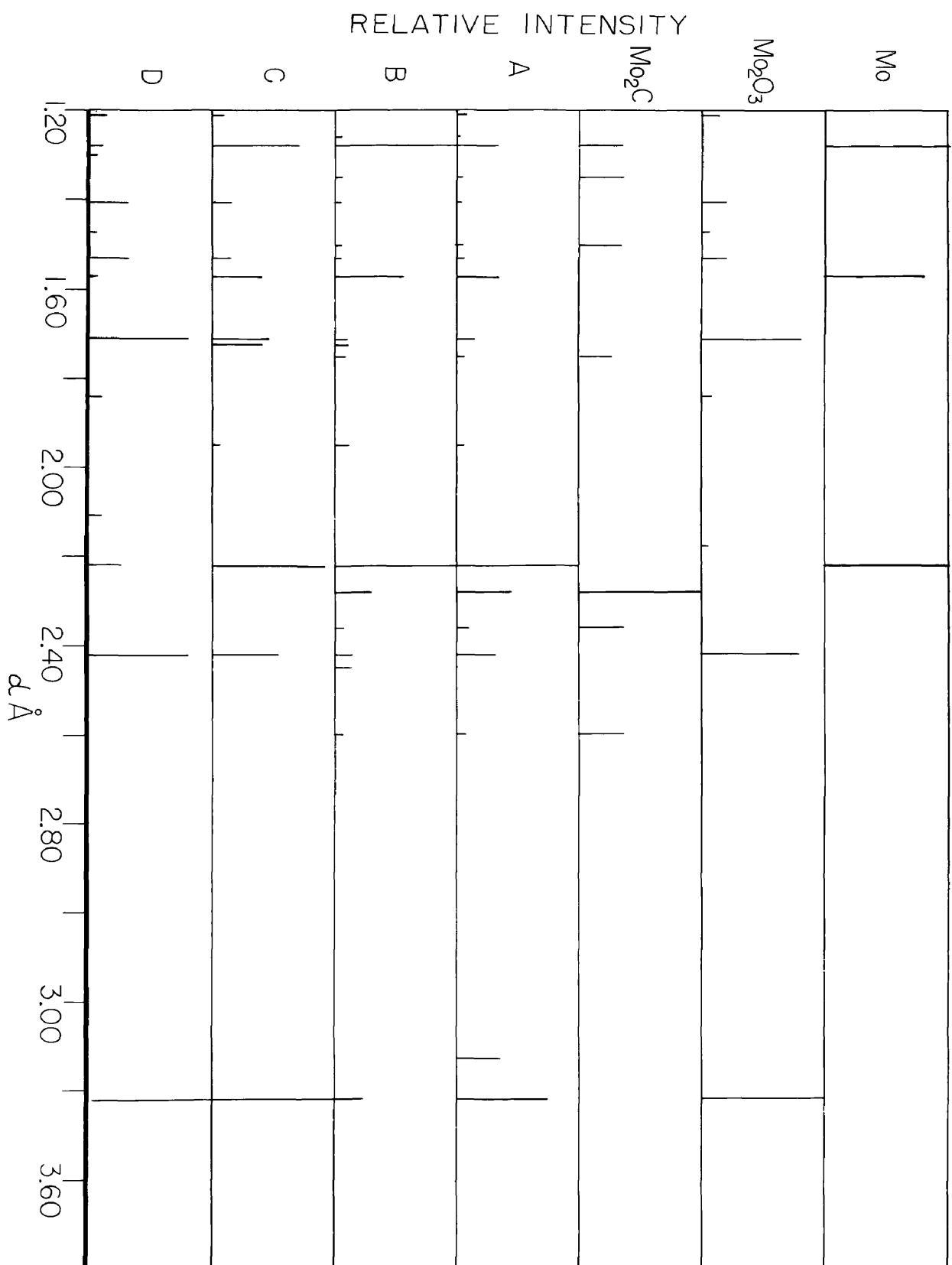
The patterns for the pure compounds are taken from the A.S.T.M. card file.

A - Cathode Deposit from Molybdate Solution

B - Cathode Deposit from Low-Concentration Trivalent Molybdenum Solution

C - Impurity in Cathode Deposit from Contaminated Trivalent Molybdenum Solution

D - Impurity in Electrolyte of Contaminated Trivalent Molybdenum Solution



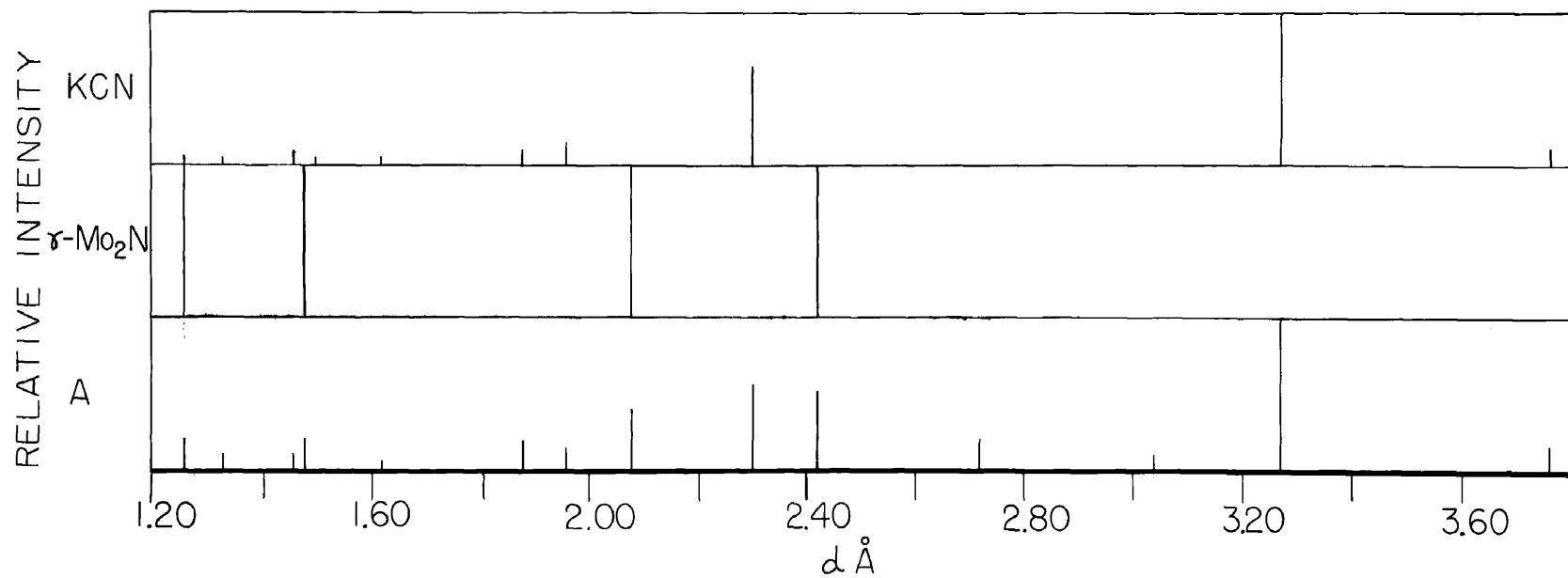


FIGURE 1

X-Ray Diffraction Pattern of Thermal Decomposition Product of $K_4Mo(CN)_8$.

The patterns of the pure compounds are taken from the A.S.T.M. card file.

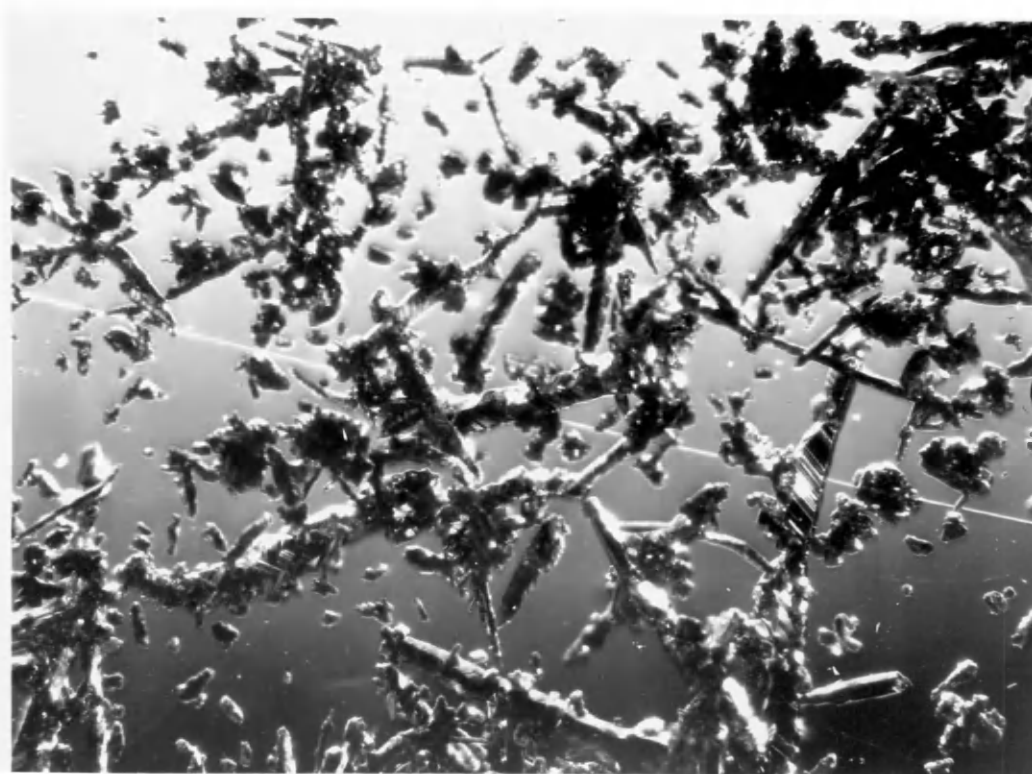


FIGURE 5

Dendritic Molybdenum Powder 50X

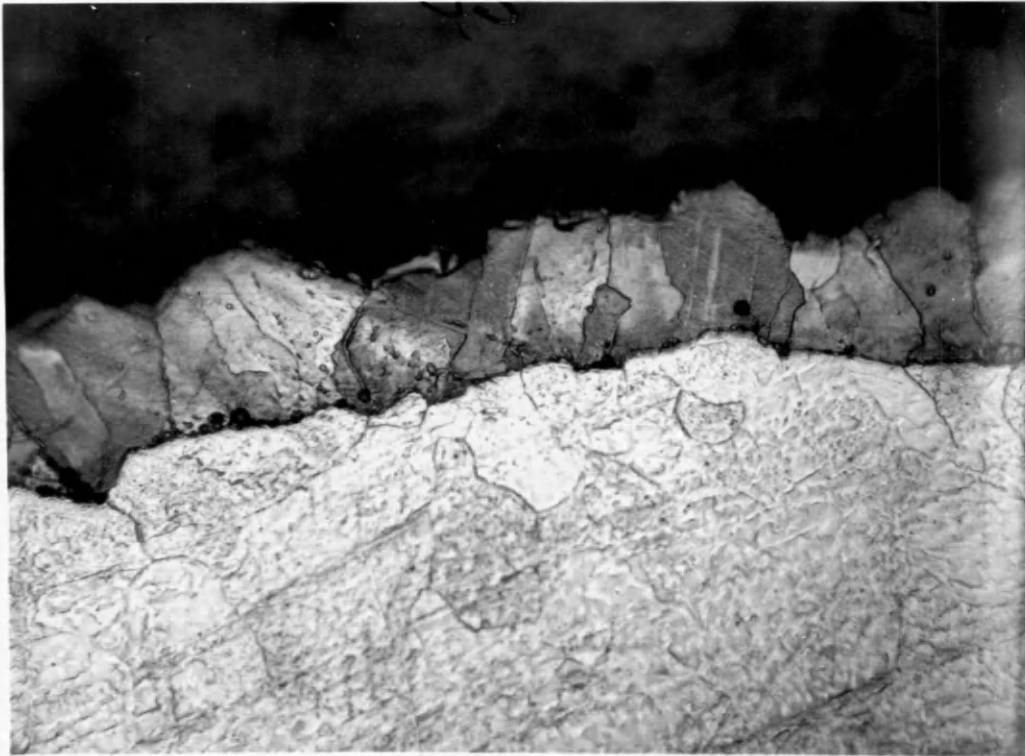


FIGURE 6

Cross-section of Adherent Molybdenum Layer after Removal of Overlying Powder

500X

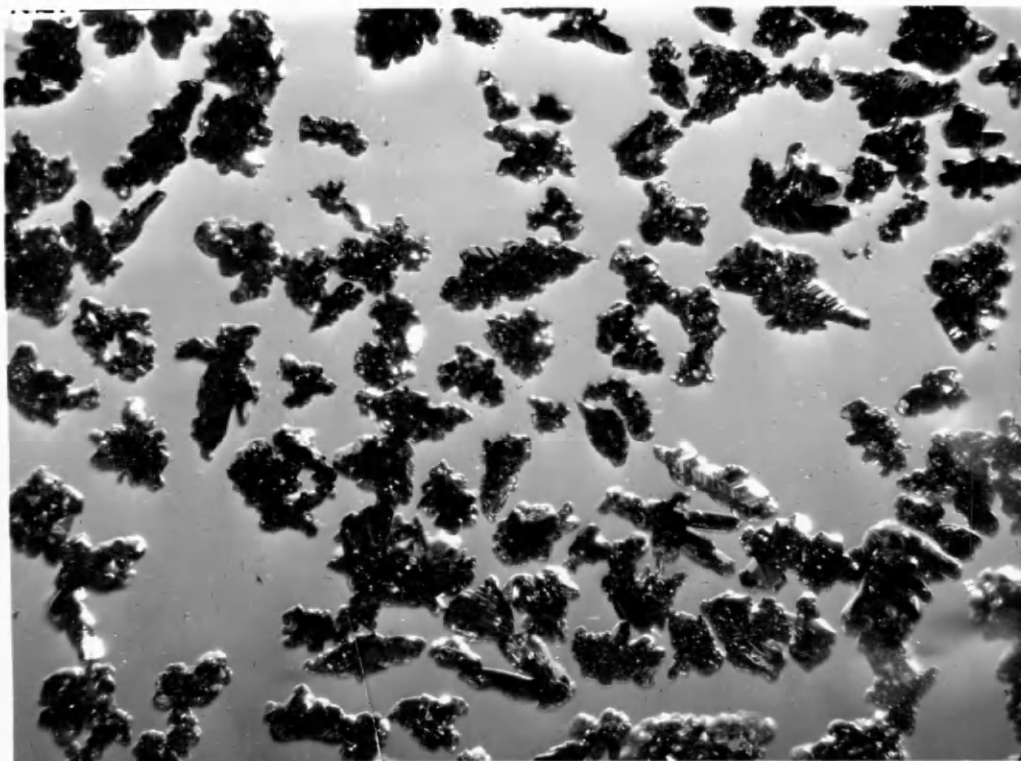


FIGURE 7

Agglomerates of Polyhedron Powder from Concentrated Solution

50X

As-Deposited Condition



- FIGURE 8

Deposit of Figure 7 after Washing and Grinding 50X

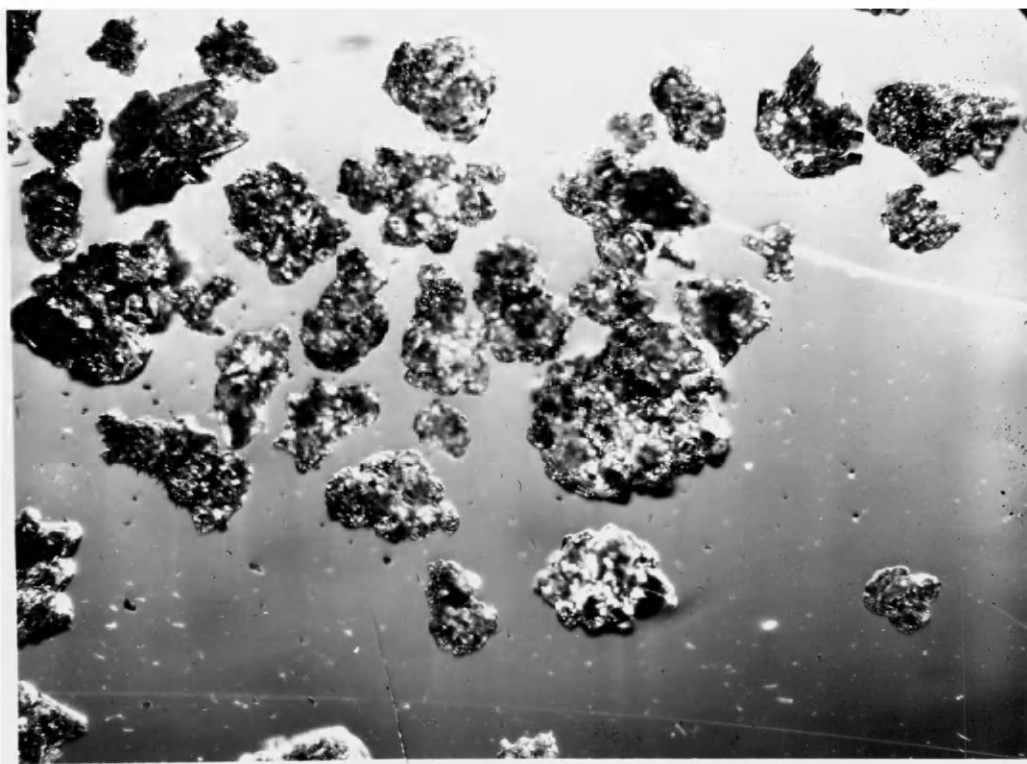


FIGURE 9

Molybdenum Deposit in the Form of Spheroidal Granules 50X



FIGURE 10

polyphenyl powder deposit Resulting from Periodic Reverse Plating 50%

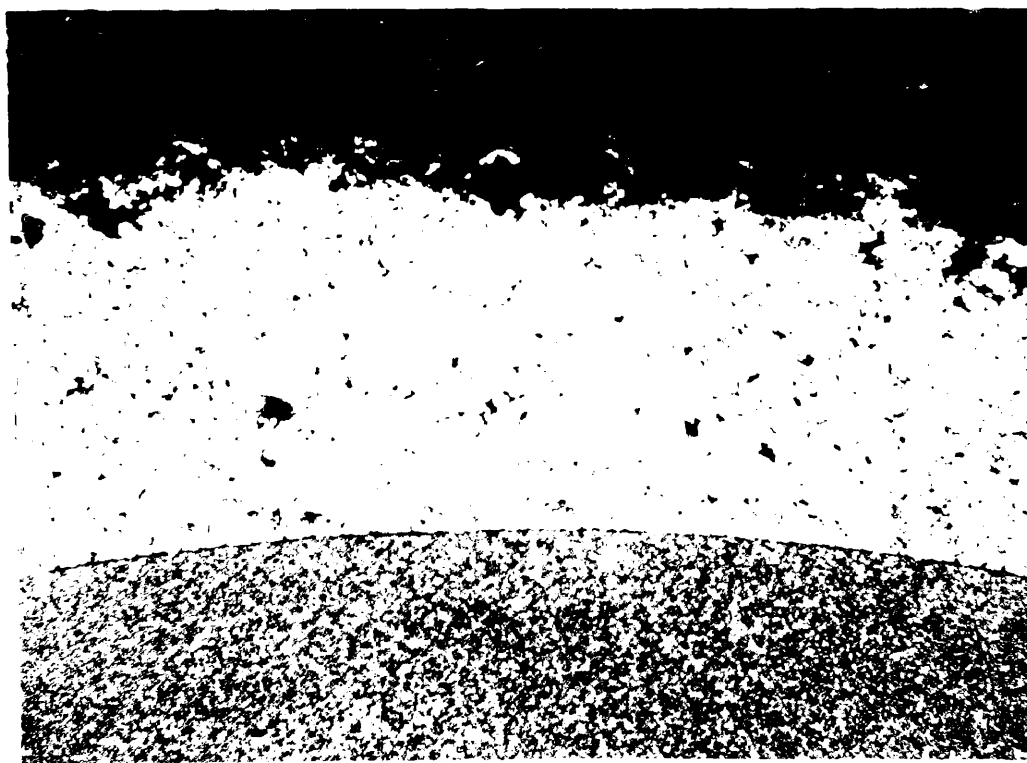


FIGURE 11A

Cross-section of Coherent Epitaxial Deposit from $\text{LiCl}-\text{KCl}$ solution, 600°C

100X

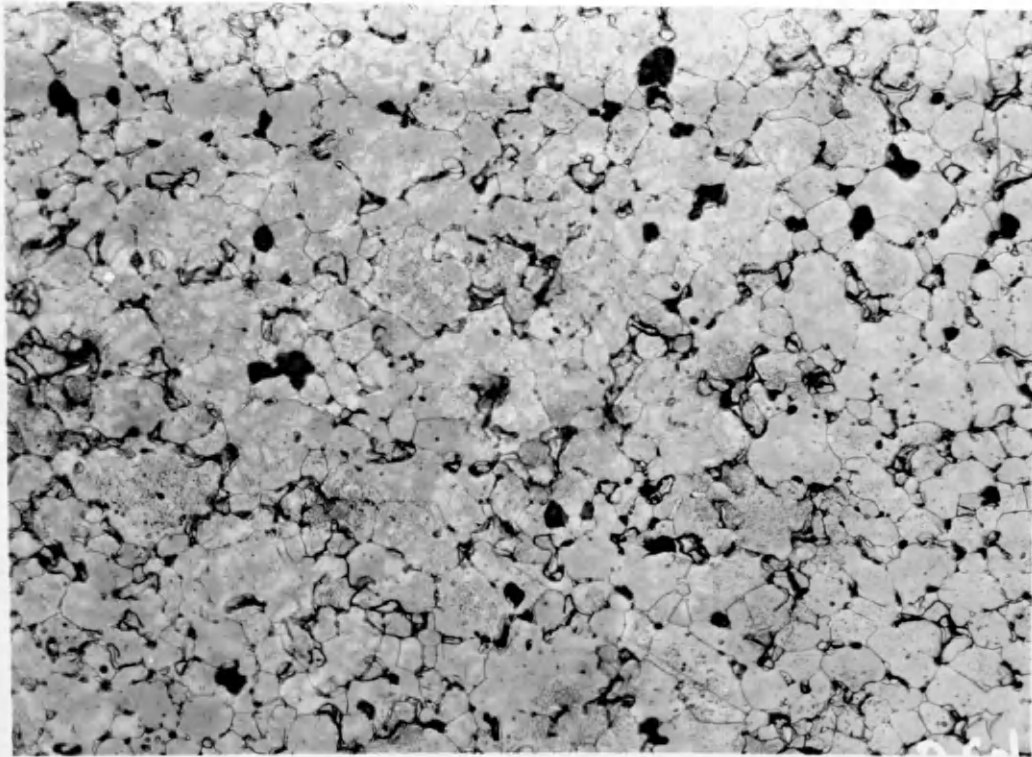


FIGURE 11B

Same Deposit as Figure 11A, Etched to Show Grain Structure 500X

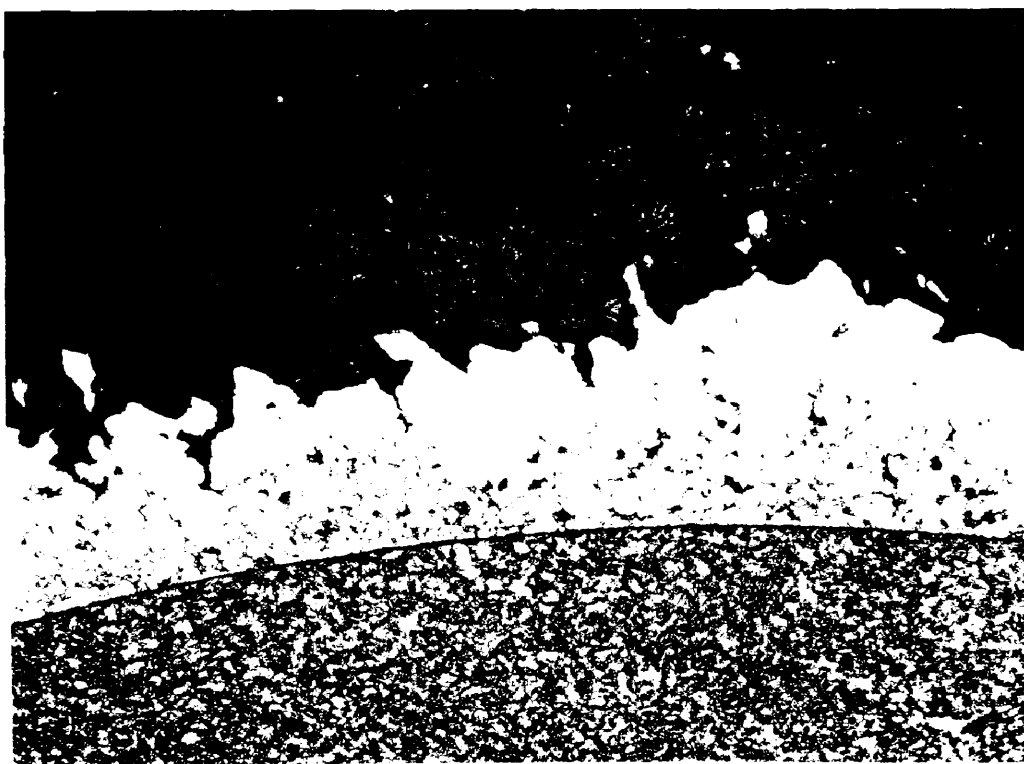


FIGURE 12A

Cross-Section of Molybdenum Deposit from LiCl-KCl Solution, 900°C 100X

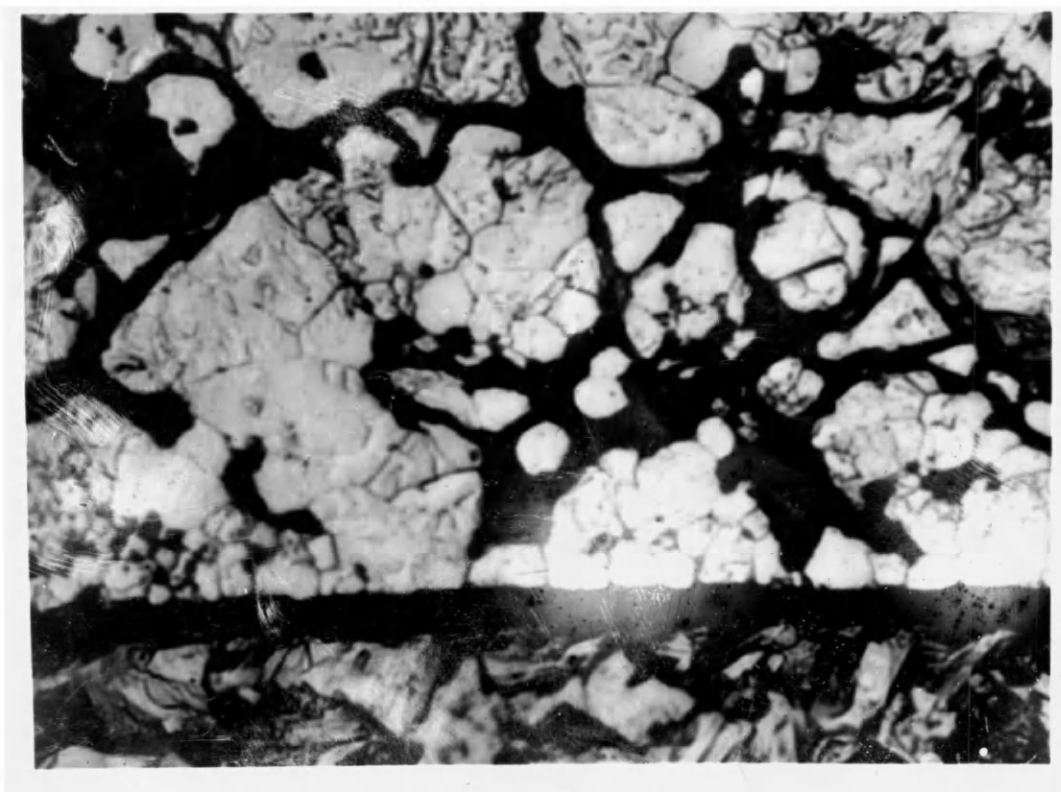


FIGURE 12E

Same Deposit as Figure 12A, Etched to Show Grain Structure 500X



FIGURE 13

Electroformed Molybdenum Tube and Cup

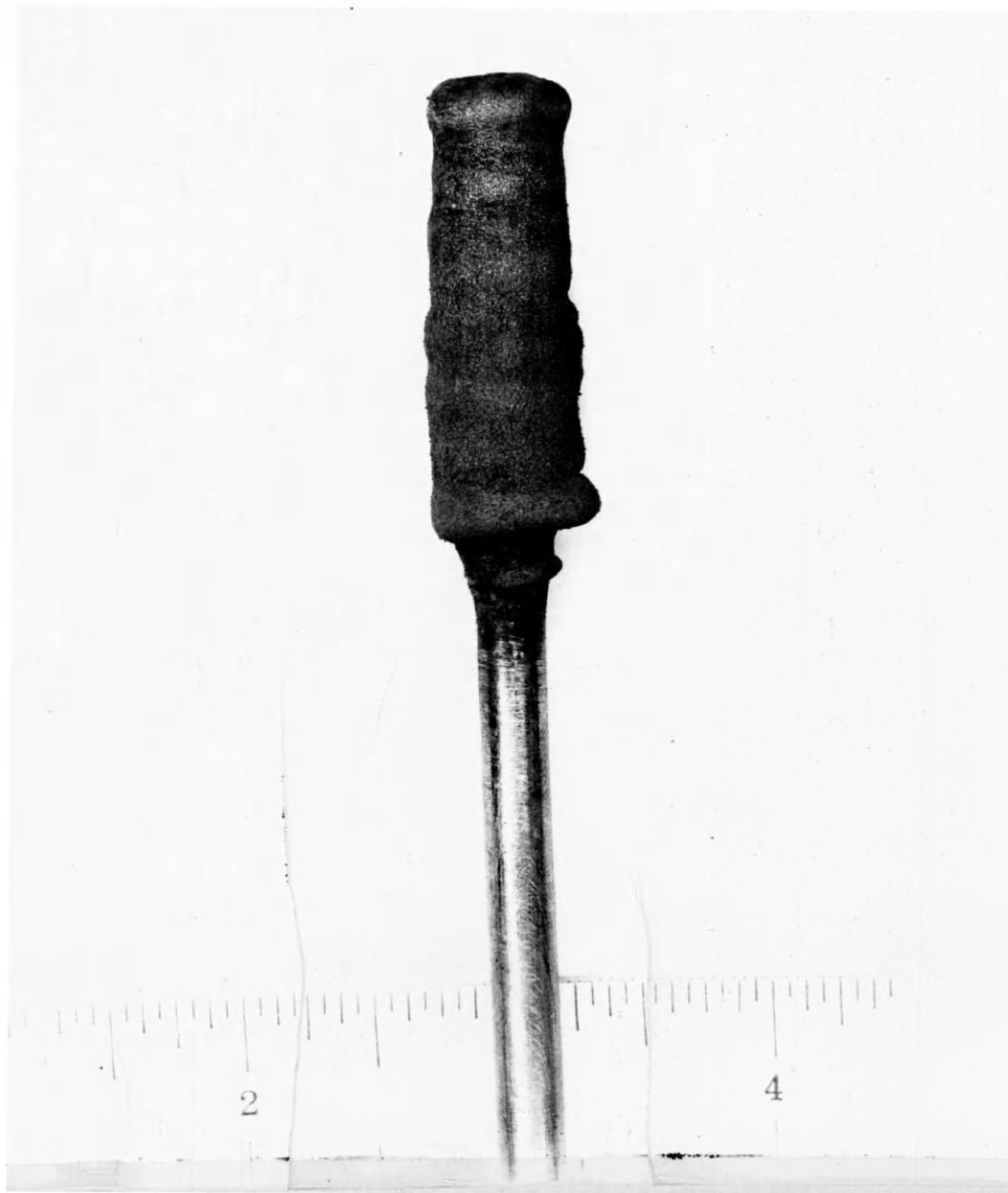


FIGURE 14

Molybdenum Powder Deposit on Cathode, as it Appears after Immersion
in Dilute HCl to Dissolve Adhering Electrolyte

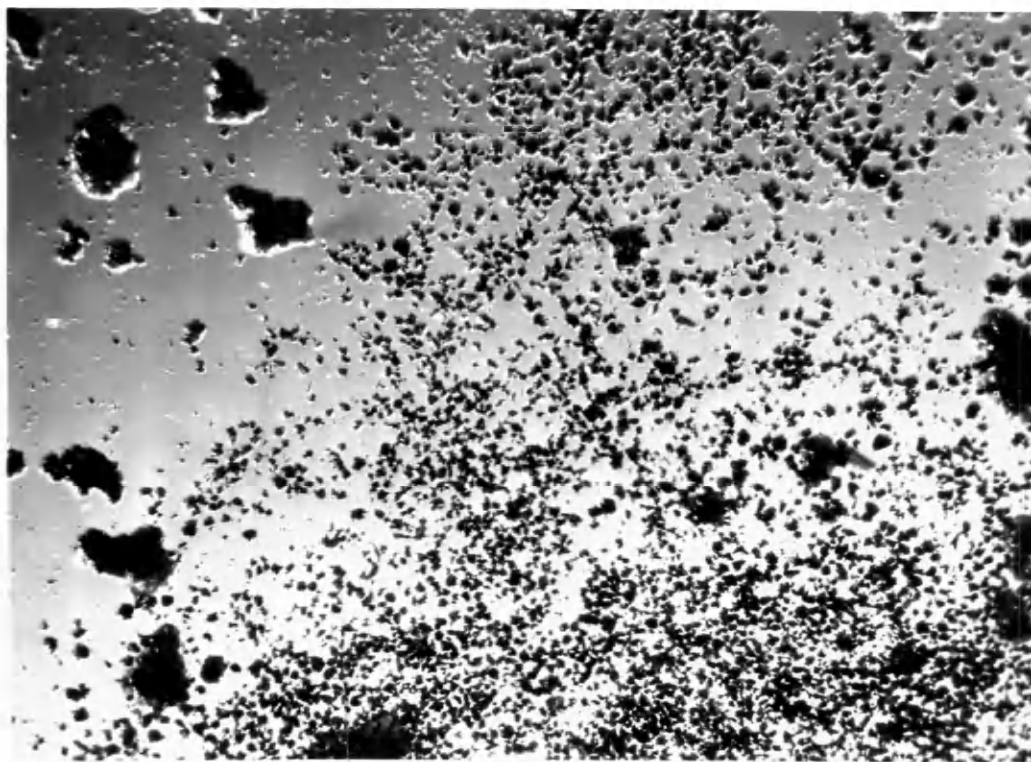


FIGURE 15

Molybdenum Powder from 100 g Batch Produced at 600°C from LiCl-KCl Solution

50X

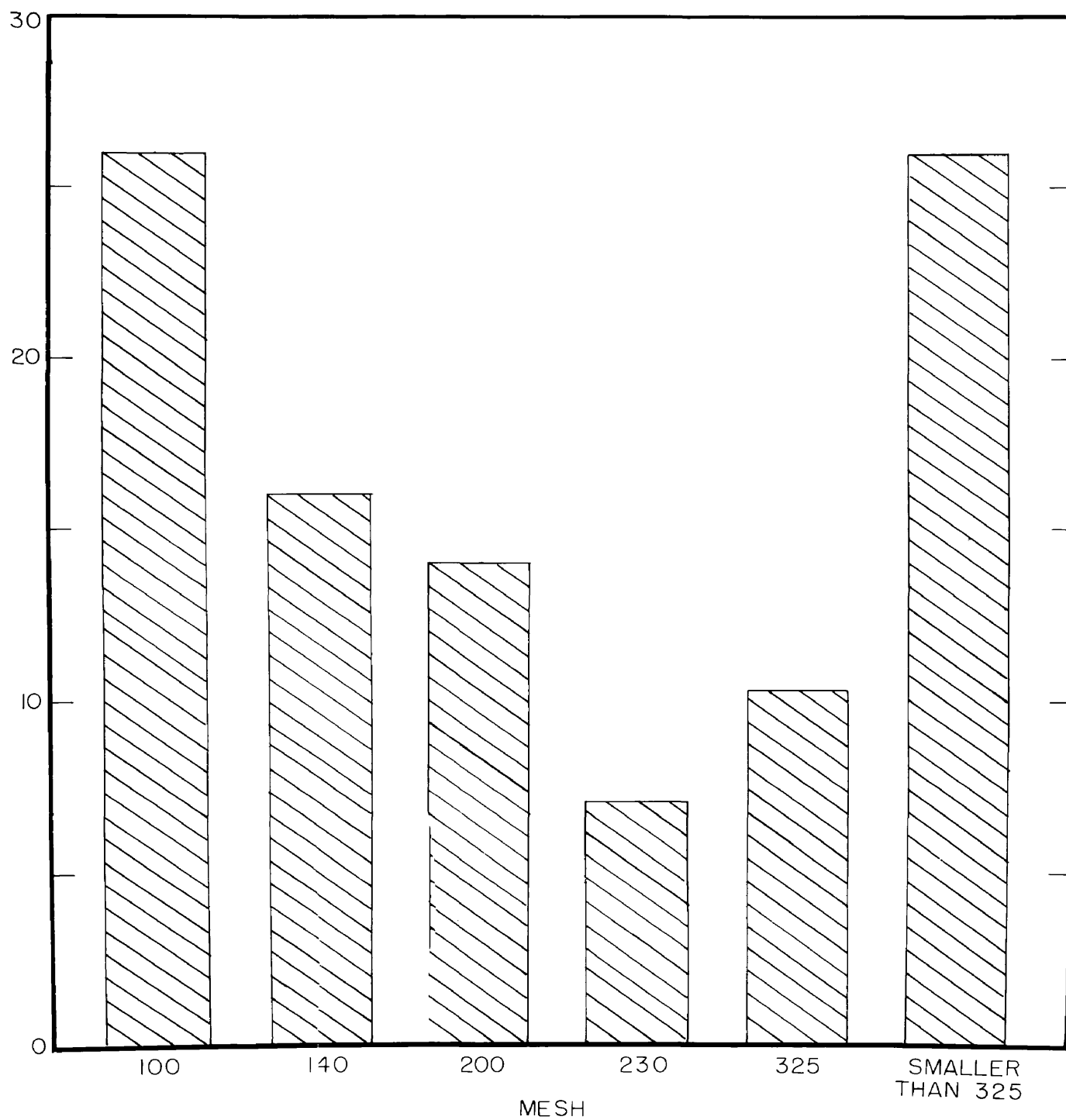


FIGURE 16

Particle Size Distribution of Molybdenum Powder in 100 g Batch

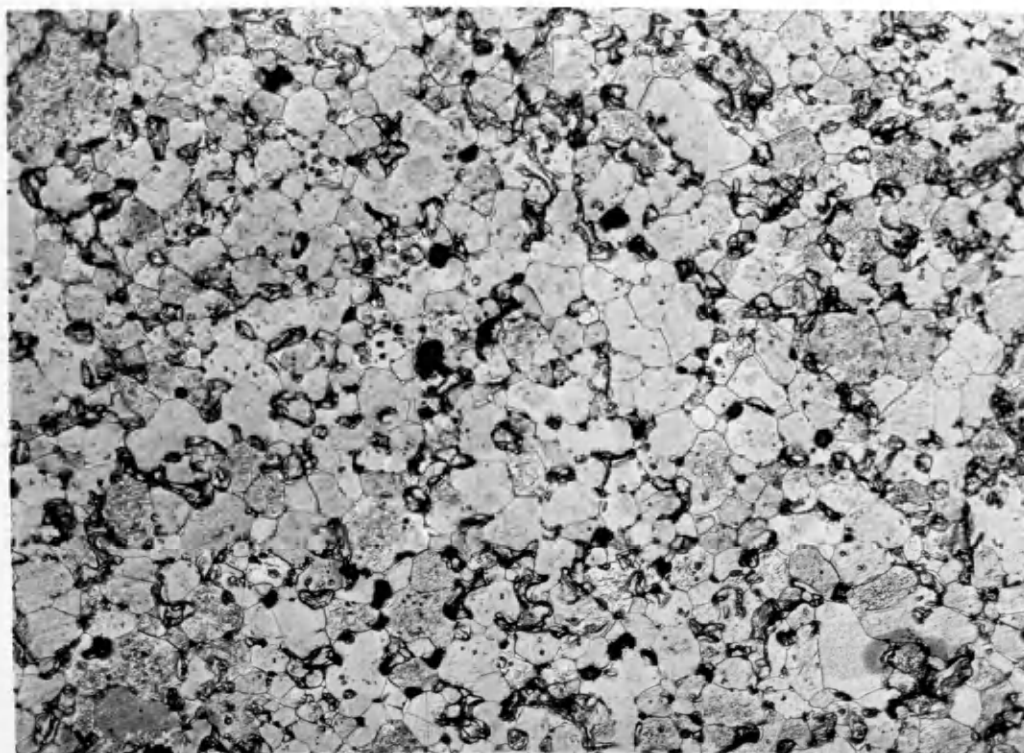


FIGURE 17

Cross-section of Compacted and Presintered Molybdenum Bar Prepared from
Electrolytic Molybdenum Powder 100X



FIGURE 18A

Large Nodules of High-Purity Molybdenum Powder, As-Deposited

50X

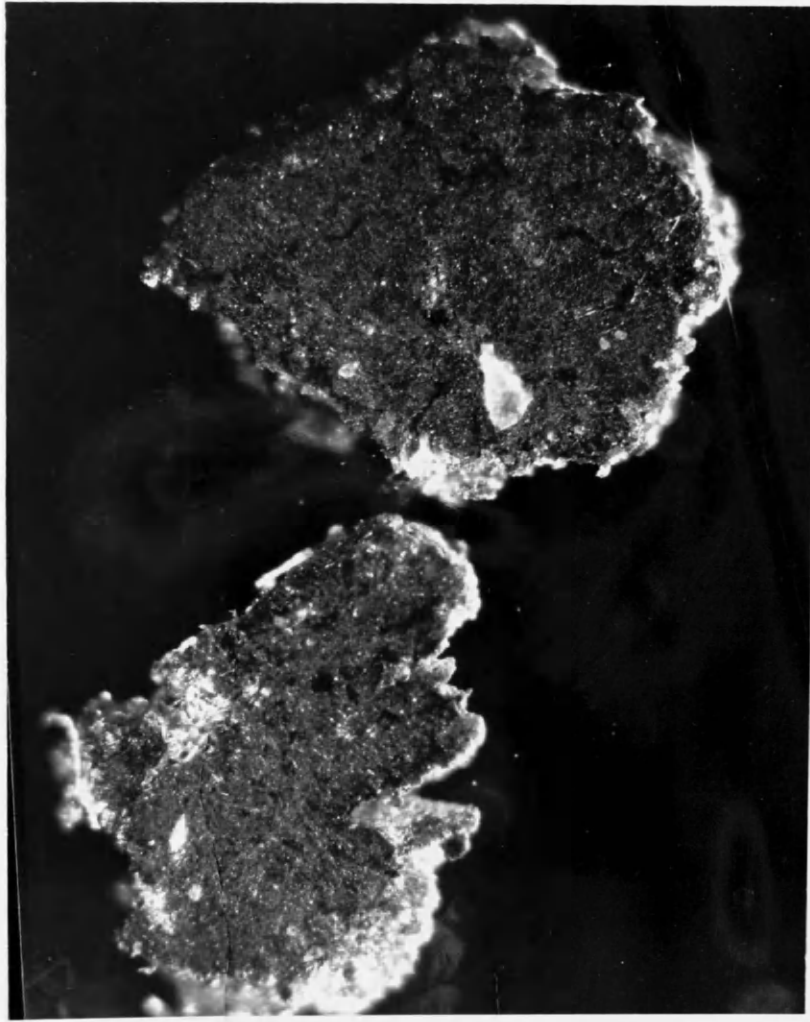


FIGURE 18B

Same Nodules Shown in Figure 18A after Flattening

50X

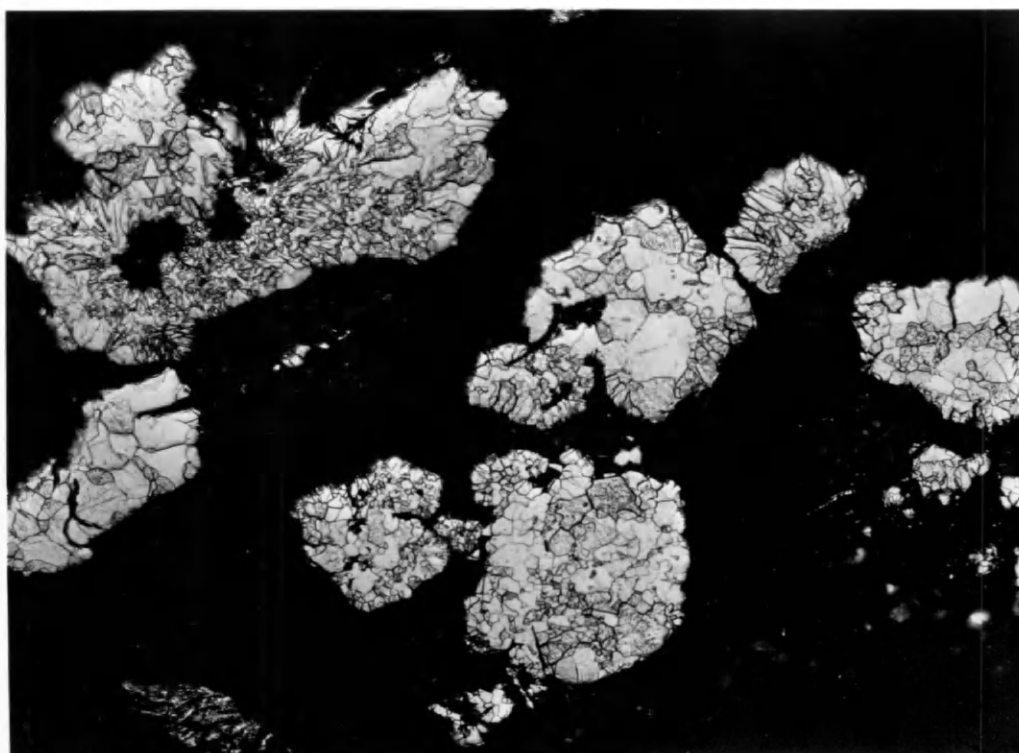


FIGURE 18C

Nodules of Same Deposit as Figure 18A, Etched to Show Grain Structure 100X

FIGURE 19

Apparatus for Polarization and Potential Measurements



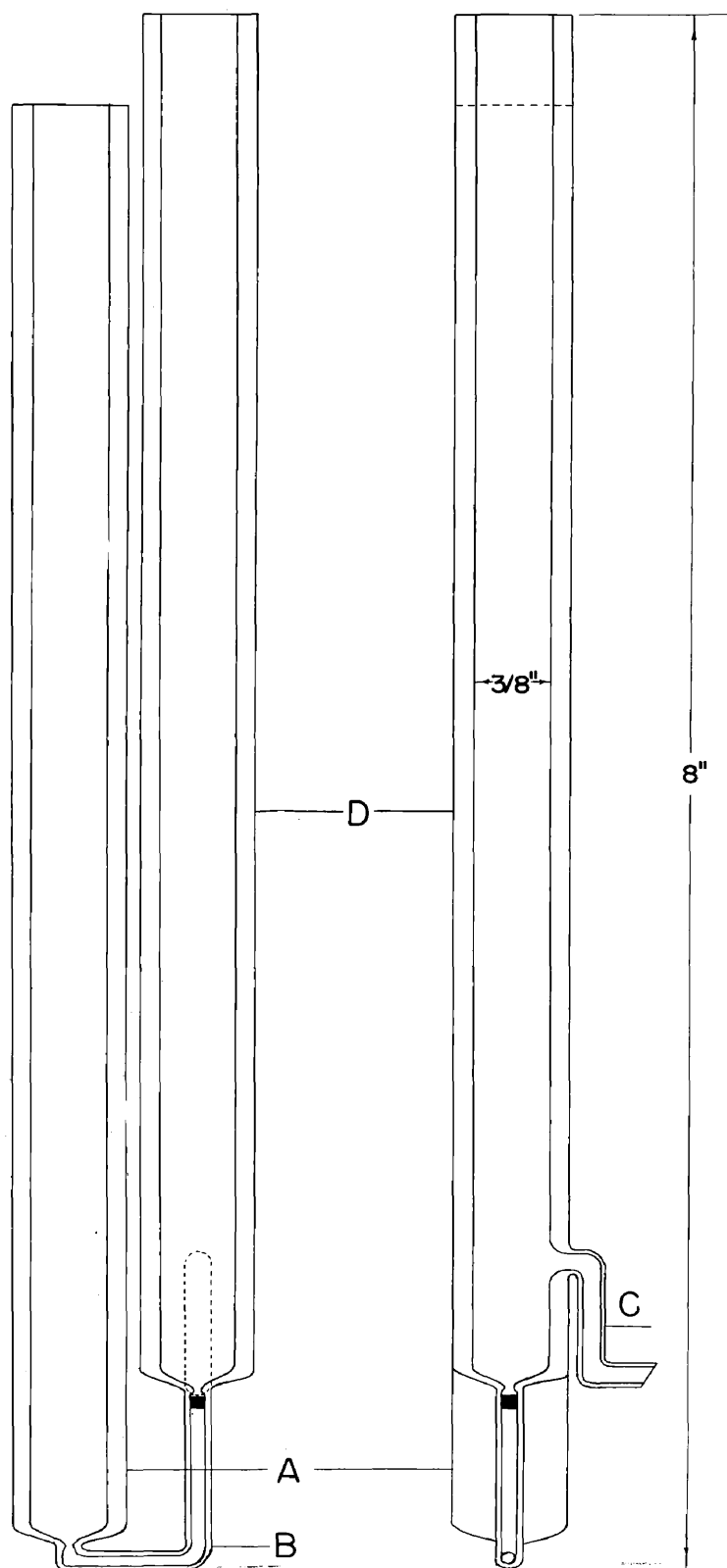


FIGURE 20

Detail of Reference Electrode Half-Cell

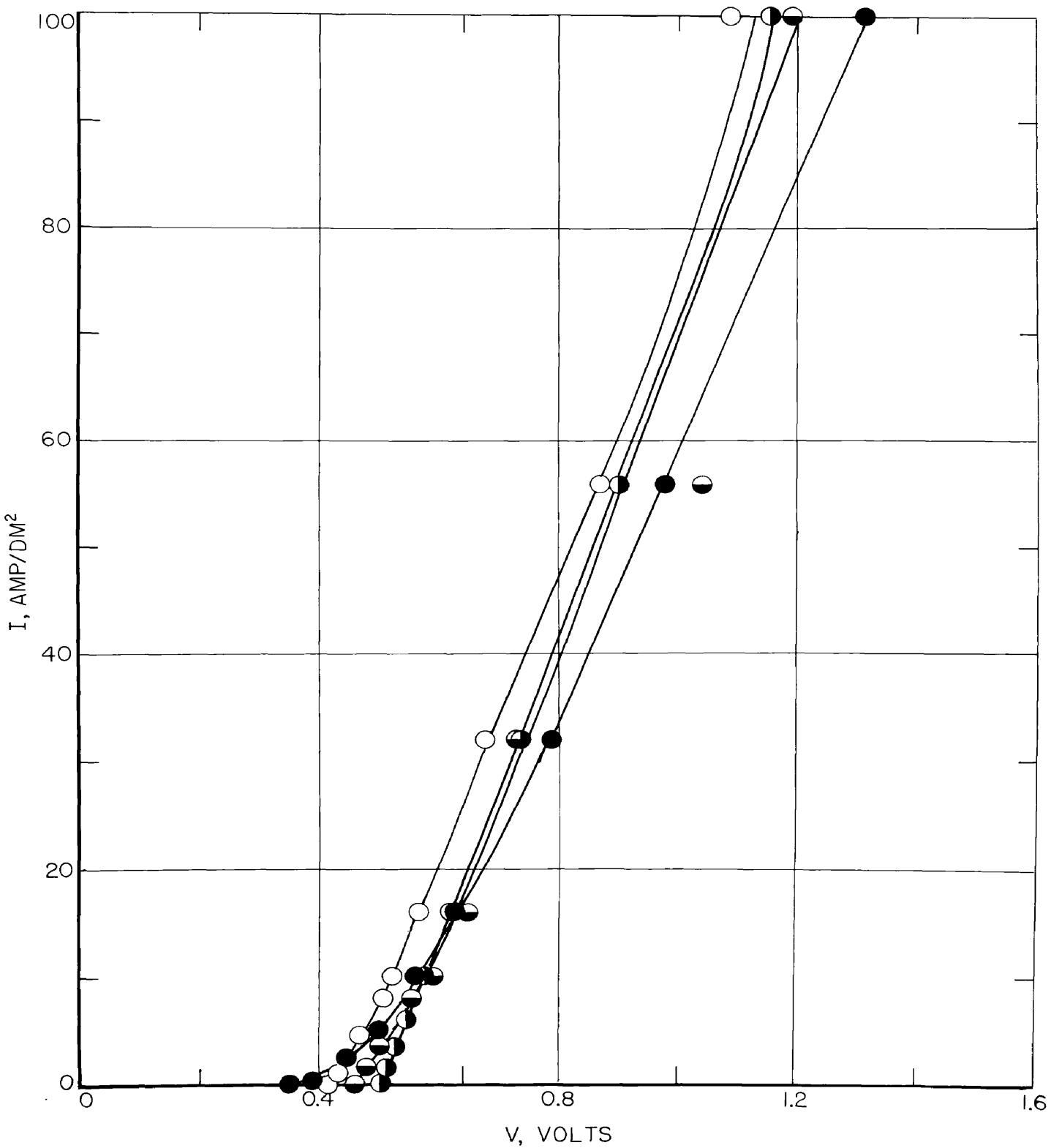


FIGURE 21A

Polarization Curves for Solution of K_3MoCl_6 in $LiCl-KCl$ (0 to 100 amp/dm²)

● 600°C, ○ 700°C, ◐ 800°C, ◑ 900°C

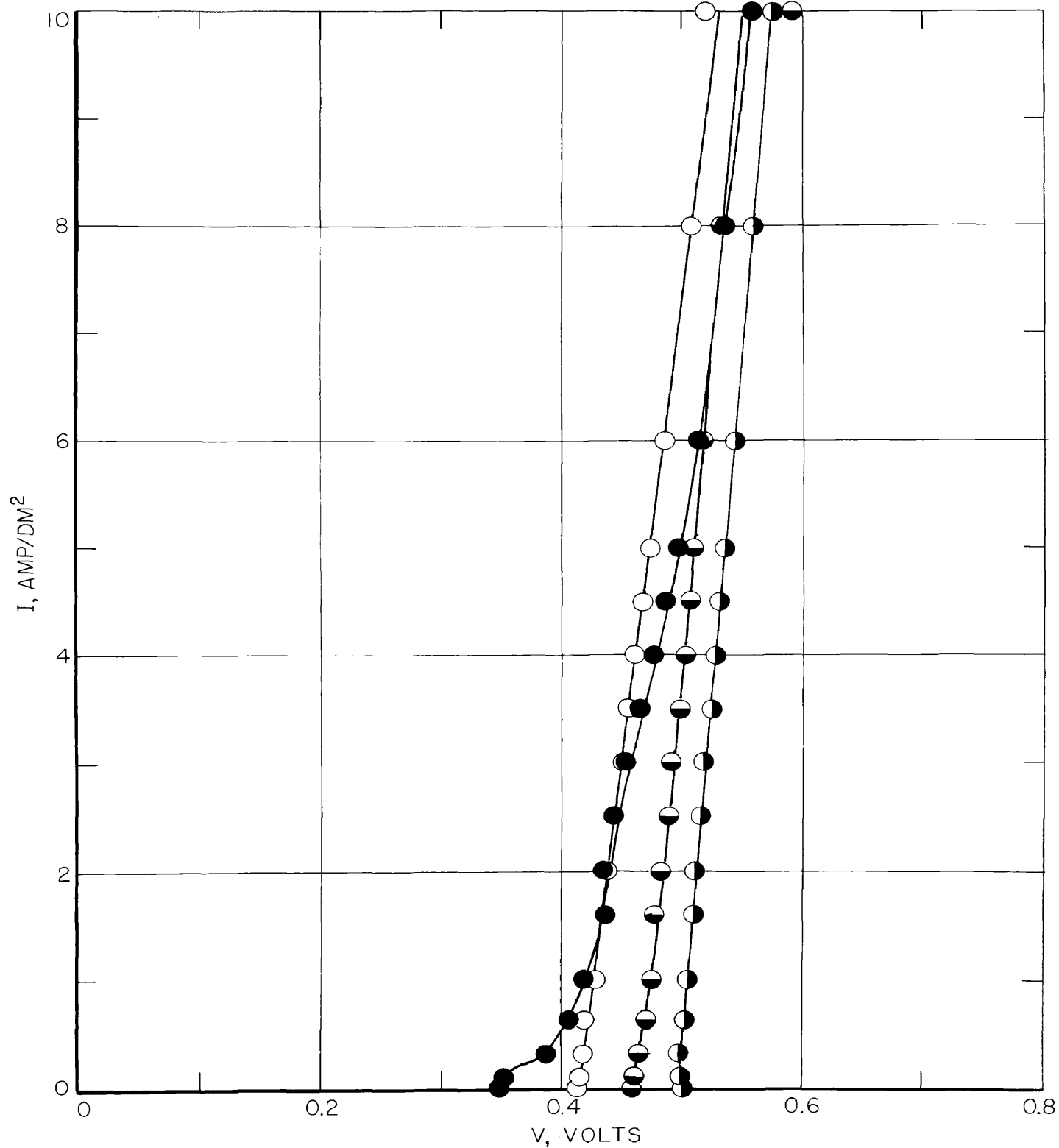


FIGURE 21E

Low Current Density Portion of Curves in Figure 21A (0 to 10 amp/cm²)

● 600 °C, ○ 700 °C, ◐ 800 °C, ⊙ 900 °C

FIGURE 22

Polarization Curves for Oxygenated Solutions of Molybdenum Salts

A - Air-Contaminated Solution of K_2MoCl_6 in LiCl-KCl

● 600 °C,

○ 700 °C,

◐ 800 °C

B - Solution of K_2MoO_4 in LiCl-KCl

● 600 °C,

◐ 900 °C

