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 $K_2\text{MoCl}_6$ in a 1:1 mixture (by weight) of KCl and NaCl at current densities of 3 to 100 amp/dm$^2$ and a temperature of 900°C resulted in the deposition of course powders of pure molybdenum at the cathode. The optimum concentration range of the molybdenum salt was 3 to 5 mole %.

The electrolysis of a solution of $K_2\text{MoCl}_6$ in the eutectic mixture of KCl and LiCl at current densities of 3 to 100 amp/dm$^2$ and temperatures between 600°C and 900°C resulted in the deposition of pure molybdenum in various forms at the cathode. At 3 amp/dm$^2$ 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 to 100% 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 $K_2MoCl_6$ 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 $K_2MoCl_6$ in the alkali halide mixture occurs with very low polarization in the temperature range of 700° to 900°C but with somewhat higher polarization at 600°C. There is some evidence that the reaction mechanism at 600°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 MoCl₂ and an improved method of preparation of K₃MoCl₆ are described.
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THE ELECTROLYTIC PREPARATION OF MOLYBDENUM FROM FUSED SALTS

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THE ELECTROLYTIC PREPARATION OF MOLYBDENUM FROM FUSED SALTS

By
Seymour Senderoff

Thesis submitted to the Faculty of the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy

1952

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22. Polarization Curves for Oxygenated Solutions of Molybdenum Salts in LiCl-KCl
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 (vitalium, 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 ores.\(^1\)

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. Parke.\(^2\)

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 by-passing 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

<table>
<thead>
<tr>
<th>Material</th>
<th>Price (per pound of molybdenum contained)</th>
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<tr>
<td>Molybdenite ore concentrate</td>
<td>$1.00</td>
</tr>
<tr>
<td>Molybdenic oxide (Technical)</td>
<td>1.14</td>
</tr>
<tr>
<td>Molybdenum metal powder</td>
<td>3.25</td>
</tr>
<tr>
<td>Molybdenum wire</td>
<td>9.00</td>
</tr>
<tr>
<td>Molybdenum sheet (rolled)</td>
<td>13.50 - 25.00</td>
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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 molybdenum 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 operation. 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 described 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 deposits 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 hydroxide. 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 Lilliedahl 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. Chismotti 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 no far none has been forthcoming. A patent
on the electrodeposition of molybdenum from alkaline molybdate solutions, an article on the use of molybdic acid in sulfuric acid for this purpose, two Russian patents 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 baths 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 Intema 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 MoO₂ 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 solutions. Deposits of somewhat lower Mo content alloyed with iron or cobalt can be obtained from concentrated alkali solutions. 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% Mo\textsuperscript{22}. The phase diagram for Fe-Mo has a eutectic temperature near 1500°C and no solid solution stability below 89% Mo\textsuperscript{23}. The phase diagram for Co-Mo has a eutectic temperature near 1400°C and no solid solution stability below 96% Mo\textsuperscript{24}.

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. Wolf\textsuperscript{25} 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 acetone\textsuperscript{26} is claimed to give a molybdenum deposit on electrolysis. Molybdenum pentachloride in liquid ammonia\textsuperscript{27} 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 Gmelin\textsuperscript{28} with references to two review articles\textsuperscript{29}, 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 Gin\textsuperscript{30}. Another process recommends a mixture of calcium molybdate and molybdenum carbide dissolved in bauxite\textsuperscript{31}, while still another recommends the electrolysis of molten calcium molybdate\textsuperscript{32}. Krathy and Brushner\textsuperscript{33} 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. Forland\textsuperscript{34} 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 volatilisation 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\textsuperscript{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 Pecharsky which exhaustively covers the literature on the chemistry of molybdenum and its compounds up to about 1926.
Chapter II

Experimental
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 electrolysces 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 AGR* 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 McDaniell refractory thermocouple protection tube, (glazed) (M), 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 stabilised 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.
General Procedure

The action system was passed through the transducer (N)
and the system arranged to a process of about 41. The feed on the
due to the pressure and of the pressure (PM) were properly adjusted.
The feed F was adjusted for some time. The apparatus was then trans-}

done. This was continued until all bubbles ceased and the metal re-

The procedure began with the "whale tooth". The next step was performed in a manner described above.

The material was passed through the transducer or concentration by air.

The material was passed through the transducer or a mixture of air and a solvent of methylcyclohexane. The material

The general procedure used in the work consisted

General Procedure

upon the speed and to the torque at which the mixer or diffuse

In Figure 2, the loads were attached to the mode rod by a

ammeters and to 12 volt voltmeter. The ammeters are shown

gaged with 0 to 500 milliamperes, 0 to 5 amperes and to 0 amperes

and measured by an ohmmeter and a test meter. These ammeters were

The practice current was supplied by 27-10Y 200 amperes rectifiers.
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 stopcock 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 electrefining, 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 Method and a few were performed using the gravimetric method of precipitation in acid solution with \( \alpha \)-benzoin oxime. 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 sulfuric 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 Vansteel 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 cathode. 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 MoO₃, i.e., 75%. The cathode deposit of powder was scraped off and analyzed by X-ray diffraction method. Figure 3A summarizes the diffraction pattern obtained. The deposit clearly contains molybdenum metal, Mo₂O₃ and Mo₂C. A quantitative estimation is difficult since the cubic structure of the molybdenum would normally give more intense
below

will be obtained from the polarization of the molten metal at low temperature. Further, a secondary effect which results from the secondary current increases the molybdenum content in the melt, and does not decrease the molybdenum content in the melt.

It is certain that the electrodeposition of the molybdenum compounds

at 3 amp/dm² proceeds on deposits at all of the cathode. A similar electrodeposition occurs in the anodic solution. It is certain that the same electrodeproces of the molybdenum oxides in the anodic solution and at the anode depend on the same appearance of the same compounds at the same electrode, as described above. The molybdenum oxides are formed on the cathode in an inert atmosphere under the same conditions.

12. Sodium molybdate is reduced in water, the water is removed,

and was deposited there.

The carbide electrode formed at the anode with the cathode.

have some from the electrode which was not in contact with the anode.

Solf. c The presence of the carbide at the electrode interface is not more than

postion would probably be a molybdenum metal content of no more than

Three then the other compounds, but a faster approach than that of the com-
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 electrolyse this compound in a solution of molten cyanides.

**Preparation.** The compound was prepared according to the directions of Bucknall and Wardlaw with some modifications. 40 g K₂MoCl₆ (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 H₂SO₄ and 5 ml concentrated HNO₃. This was done to be certain that the tetravalent molybdenum was oxidized to the hexavalent state.
The yellow product gave a yellow precipitate with water. 

Powder

Ammonium hydroxide was added to the reaction mixture with methanol. The reaction mixture was filtered and the precipitate was washed with methanol. In the aqueous layer, 2.2 g of precipitate was present. A yellow precipitate formed in the aqueous layer. This precipitate was filtered and washed with methanol.

In order to determine the nature of the precipitate, it was heated.

The yellow precipitate had a yellow color. The product was collected and dried at 110°C after being washed with methanol. The yellow precipitate was filtered, washed with methanol, and dried at 110°C. The precipitate was then dried in water.

The percentage of the Ag in the precipitate was 72.0 ± 3.0%.

The compound was then shown to contain Ag. The compound was recrystallized from water, and the precipitate was washed with methanol. The same compound was obtained. Only Ag was present in the preparation. Further, it is suggested by permanence of the found results (Ag was not reduced by deaeration and further, it is evidenced by our experience). The formation of a compound, the precipitation of AgCl, is not reduced.

According to Graham's Handbook, the precipitation of AgCl is not reduced.
observed that a high gas pressure had built up in the tube as a result and it was allowed to cool to room temperature. When it was opened it was KNO₃. The pure salt (I) remained solid, and turned black. The tube contents of the KNO₃-NH₄OH system does not reach 600°C until it contains 90% KNO₃. The melting point of the contents in composition (II) are a mixture of KNO₃-NH₄OH

\[
\begin{array}{ccc}
\text{KNO₃(NH₄)₄} & \text{KNO₃} & \text{NH₄OH} \\
33.6^\circ & 35.2^\circ & 37.8^\circ \\
96.4^\circ & 98.2^\circ & 100^\circ \\
\end{array}
\]

**TABLE II. COMPOSITION OF KNO₃(NH₄)₄ - KNO₃ - NH₄OH Mixture.**

... and both tubes were heated to 620°C. The pure perchlorate tube and both tubes were heated to 620°C... The mixture of composition II shown in Table II was cooled in another sample of the pure salt was sealed in an evacuated perchlorate tube... In order to determine the properties of high temperature...
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-Mo$_2$N and
KCN are present and represent about 25 to 50% of the total sample.
A trace of KCN or K$_2$MoO$_4$ may be present and the rest of the sample
may be amorphous carbon and therefore not identifiable by X-ray analysis.
Gmelin's Handbuch$^{42}$ states that γ-Mo$_2$N 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, Mo$_3$Cl$_6$ or Mo$_6$Cl$_{12}$.
Preparation. The best method of preparation in the literature appeared to be that of K. Lindner, et. al.\textsuperscript{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 Quill\textsuperscript{44}, a method was devised which proved quite successful. According to Quill, the reaction:

\begin{align*}
(1) \text{MoCl}_3(s) & \longrightarrow \text{MoCl}_4(g) + \text{MoCl}_5(g) + \text{MoCl}_2(s) \\
\text{reaches equilibrium with MoCl}_4 \text{ at a partial pressure of 0.7 atm. and MoCl}_5 \text{ at a partial pressure of 0.3 atm. at 340°C. Further, at 330°C the reaction:} \\
(2) 2\text{Mo(s)} + 3\text{MoCl}_5(g) & \longrightarrow 5\text{MoCl}_3(s) \\
\text{goes practically to completion (at atmospheric pressure). Lastly, the reaction:} \\
(3) \text{MoCl}_2(s) & \longrightarrow \text{MoCl}_4(g) + \text{Mo(s)} \\
\text{does not begin until a temperature of 530°C is reached and at 600°C the equilibrium pressure of MoCl}_4 \text{ is only one atmosphere.}
\end{align*}

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\textsubscript{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\textsubscript{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 MoCl₂ 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 MoCl₅ (4.6 g MoCl₅ 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, (MoCl₂)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 MoCl₂ is 57.4%. The slight excess of molybdenum in the product was undoubtedly due to free molybdenum metal formed by decomposition of the MoCl₂. 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, MoCl₂·XH₂O, from which the water could not be removed without decomposing the salt. The MoCl₂ was slightly soluble in alcohol, but an alcoholate, MoCl₂·XC₂H₅OH was formed. Attempts to drive off the alcohol resulted in decomposition.

A sample of the MoCl₂ was mixed with a portion of a eutectic mixture of lithium chloride and potassium chloride (41 mole % KCl, melting point ≥ 352°C) which had been previously fused and ground. The mixture had the composition given in Table III.

| TABLE III. Composition of MoCl₂ - LiCl - KCl Mixture |
|-----------------|---------|--------|
|                  | Wt %    | Mole % |
| MoCl₂           | 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 red bright/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 "treeed" deposit of molybdenum was obtained. The deposit was collected and weighed. The current efficiency was found to be 37% based on Mo²⁺ → Mo and 55% based on Mo³⁺ → 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 "treeed" 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 oxidised 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 oxidised 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 electro-deposits.

**Preparation.** The compound was originally prepared according to the directions of Bucknell et al\(^45\). 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 Chiossotti\(^46\). 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, molybdate 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 electrolysed 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 61°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 K₃MoCl₆ 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 analysed. The analysis is given in Table IV.

TABLE IV. Analysis of K₃MoCl₆

<table>
<thead>
<tr>
<th>Found</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>22.6%</td>
</tr>
<tr>
<td>Cl</td>
<td>50.2%</td>
</tr>
</tbody>
</table>

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 $\text{MoCl}_6^{2-}$ ion approaches what Bilts calls a penetration complex rather than a normal complex. 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, K₃MoCl₆ precipitates. i.e.,

\[
\text{Reduced catholyte} + \text{HCl} \xrightarrow{20^\circ \text{C}} \xrightarrow{80^\circ \text{C} \text{ heat}} \xrightarrow{0^\circ \text{C} \text{ cool}} \text{KCl (white ppt.)} \xrightarrow{\text{K}_3\text{MoCl}_6 (red ppt.)}
\]
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 \( \text{Mo}^{3+} + 6\text{Cl}^- \rightarrow [\text{MoCl}_6]^{-3} \) occurs and \( \text{K}_3\text{MoCl}_6 \) precipitates. On cooling the mother liquor from this precipitation more \( \text{K}_3\text{MoCl}_6 \) separates but \( \text{KCl} \) does not because most of the \( \text{K}^+ \) has been removed in the precipitation of the complex salt. If \( [\text{MoCl}_6]^{-3} \) were in equilibrium with \( \text{Mo}^{3+} \) and \( \text{Cl}^- \) 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.

\( \text{K}_3\text{MoCl}_6 \) 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 \( \text{K}_3[\text{MoCl}_6\text{H}_2\text{O}] \) may precipitate. The water cannot be removed from this compound by heating without decomposing the compound. \( \text{K}_3\text{MoCl}_6 \) 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 \( \text{MoCl}_3 \) is unstable above 340°C, and that at 650°C it is completely decomposed to \( \text{MoCl}_2 \) and \( \text{Mo} \) metal. This further demonstrates that the \( [\text{MoCl}_6]^{-3} \) ion is a highly stable one with little tendency to dissociate. 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$_3$MoCl$_6$ 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$_3$MoCl$_6$ were dissolved in 100 g of the halide solvent and electrolyzed at 3, 30, and 100 amp/dm$^2$ 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$_3$MoCl$_6$ 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-electrolyze a freshly prepared solution at low current density (about 5 to 6 amp/dm²) for about 3 amperes-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

<table>
<thead>
<tr>
<th>Current Density (amp/dm²)</th>
<th>Current Efficiency (Cathode)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>98%</td>
</tr>
<tr>
<td>40</td>
<td>95%</td>
</tr>
<tr>
<td>100</td>
<td>96%</td>
</tr>
</tbody>
</table>

The current efficiency was calculated on the basis of the reaction, Mo³⁺ + 3e → 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 MoO₃ 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 MoO₃ 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.

Deposit. The deposit from the most dilute baths (i.e.
13.3 g K₂MoO₄ in 100 g KCl-NaCl) was analyzed and, in spite of its
non-metallic appearance was found to contain 96% Mo. An X-ray diffrac-
tion pattern for a sample of this deposit (Figure 3B) showed that
it contained about 85% Mo metal, with the remainder MoO₃ and Mo₂C.
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
the deposit was found to be 28\% Pt, 72\% Fe. The
harmonics of this deposit were measured at 0.5 to 1 mm long. Any of the needs are not the needs are about
from the plates of intermediate concentration of the depositpro-
the oxides and the entire deposit appeared non-metallic.
intermetallic mixed with the oxides that it could not be separated from
In no case were a coherent deposit produced. These were some

<table>
<thead>
<tr>
<th>TABLE VI. Periods Reverse Current Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (min)</td>
</tr>
<tr>
<td>15</td>
</tr>
<tr>
<td>15</td>
</tr>
<tr>
<td>15</td>
</tr>
<tr>
<td>15</td>
</tr>
<tr>
<td>20</td>
</tr>
</tbody>
</table>

shown in Table VI were used. The oven was put in process first. The better current with the hope that the smoking made without period reversed current with the regular mixture of rancidity, rather than poor coherence, a number of times were a well-known powder deposit. In the better that the width of the plate operation was needed. Beyond the initial blank deposit, the plate cathode during mounting even when the greatest possible care in this a photograph the flip of the powder, however, resulted in the a simultaneous from the appearance suggested to be very coherent. An attempt to prepare deposits under the powder was described above. The powder deposit from the cathode, as you current density, an adherent layer was

36
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 Na₂MoO₄·2H₂O (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

<table>
<thead>
<tr>
<th>Element</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>T</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Aluminum</td>
<td>T</td>
<td>T</td>
<td>W</td>
<td>VW</td>
</tr>
<tr>
<td>Calcium</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T</td>
</tr>
<tr>
<td>Cobalt</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>VW</td>
</tr>
<tr>
<td>Copper</td>
<td>VW</td>
<td>VW</td>
<td>T</td>
<td>T</td>
</tr>
<tr>
<td>Iron</td>
<td>-</td>
<td>W</td>
<td>VW</td>
<td>VW</td>
</tr>
<tr>
<td>Magnesium</td>
<td>T</td>
<td>VW</td>
<td>VW</td>
<td>T</td>
</tr>
<tr>
<td>Manganese</td>
<td>-</td>
<td>T</td>
<td>T</td>
<td>-</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>VS</td>
<td>VS</td>
<td>VS</td>
<td>VS</td>
</tr>
<tr>
<td>Lead</td>
<td>-</td>
<td>-</td>
<td>T</td>
<td>T</td>
</tr>
<tr>
<td>Silicon</td>
<td>VW</td>
<td>T</td>
<td>W</td>
<td>VW</td>
</tr>
</tbody>
</table>

*Oxygen 0.068%

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 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+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>
<thead>
<tr>
<th>Conc. No.</th>
<th>Current Density (amp/dm²)</th>
<th>Plating Time (hr.)</th>
<th>Wt. of Deposit (g)</th>
<th>Type of Deposit</th>
<th>Fig. Ref.</th>
<th>Table VII Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>30</td>
<td>1.0</td>
<td>0.25</td>
<td>Non-metallic Black Powder</td>
<td>3B</td>
<td>-</td>
</tr>
<tr>
<td>2.0</td>
<td>100</td>
<td>0.5</td>
<td>-</td>
<td>Non-metallic Black Powder</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.3</td>
<td>3</td>
<td>1.5</td>
<td>-</td>
<td>Modular superficially coherent Mo deposit overlying thin coherent layer</td>
<td>6</td>
<td>Col. 2</td>
</tr>
<tr>
<td>3.3</td>
<td>100</td>
<td>0.5</td>
<td>6.7</td>
<td>Dendritic Mo powder overlying adherent layer</td>
<td>5</td>
<td>Col. 1</td>
</tr>
<tr>
<td>4.9</td>
<td>3</td>
<td>1.5</td>
<td>0.86</td>
<td>Superficially coherent nodular deposit overlying adherent layer</td>
<td>Similar to Fig. 6</td>
<td>-</td>
</tr>
<tr>
<td>4.9</td>
<td>30</td>
<td>1.0</td>
<td>2.8</td>
<td>Powder agglomerates consisting of trees and large multi-faceted crystals of molybdenum over adherent layer</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4.9</td>
<td>100</td>
<td>0.5</td>
<td>8.5</td>
<td>Granular metallic powder over adherent layer</td>
<td>7,8,9</td>
<td>Col. 3</td>
</tr>
<tr>
<td>4.9</td>
<td>Periodic reverse 30 direct 60 reverse</td>
<td>1.0</td>
<td>3.2</td>
<td>Powder consisting of small platelets over about 0.002&quot; of adherent plate</td>
<td>10</td>
<td>Col. 4</td>
</tr>
</tbody>
</table>

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°C. 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$_3$MoCl$_6$ with Low-Melting Halide Solvents.

<table>
<thead>
<tr>
<th>Solution Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
</tr>
<tr>
<td>AlCl$_3$</td>
</tr>
<tr>
<td>KCl</td>
</tr>
<tr>
<td>LiCl</td>
</tr>
<tr>
<td>K$_3$MoCl$_6$</td>
</tr>
</tbody>
</table>

Each mixture was sealed in an evacuated pyrex tube, heated in steps of 100°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$_3$MoCl$_6$ with Low-Melting Halide Solvents.

<table>
<thead>
<tr>
<th>Solution Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp.</td>
</tr>
<tr>
<td>300°C</td>
</tr>
<tr>
<td>400°C</td>
</tr>
<tr>
<td>500°C</td>
</tr>
<tr>
<td>600°C</td>
</tr>
</tbody>
</table>
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 AlCl₃-KCl mixture, and cannot be even closely reached in the AlCl₃-LiCl mixture at the same temperature. Since anhydrous AlCl₃ 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 K₃MoCl₆

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 K₂MoO₄ - KCl - LiCl Solution

<table>
<thead>
<tr>
<th>Current Density (Amp/dm²)</th>
<th>Current Efficiency (Cathode)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>99</td>
</tr>
<tr>
<td>30</td>
<td>97</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
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 amperes-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
\[ \text{Mo} \rightarrow \text{Mo}^{3+} + 3e. \]
The results are shown in Table XII.

TABLE XII. Anode Current Efficiency of K3MoCl6 - KCl - LiCl Solution

<table>
<thead>
<tr>
<th>Current Density (amp/dm²)</th>
<th>Anode in contact with graphite crucible</th>
<th>Anode insulated from graphite crucible</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>39%</td>
<td>97%</td>
</tr>
<tr>
<td>70</td>
<td>75%</td>
<td>107%*</td>
</tr>
<tr>
<td>200</td>
<td>-</td>
<td>101%</td>
</tr>
</tbody>
</table>

* 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

1. \[ \text{Mo}^{3+} \rightarrow \text{Mo}^{(3+x)+} + xe \] at the graphite electrode, and
2. \[ \text{Mo} \rightarrow \text{Mo}^{3+} + 3e \] at the molybdenum electrode, occur 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/cm\(^2\). 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
post mortem. Any posterior defect that does not show a true pattern may require a powder de-
or with a grid becoming apparent on the dipped area. A reaction dependent a metal or a
between them. A coherent deposit, when dipped with a metal part
hermetically observed. If any cavity is found, it often sup-
coherent deposit and a powder deposit where the "interface" is
shown larger than in the latter. An interesting difference between a
supplied off as powder, and the extent of the coherent portion is
the former case the entire deposit, except for a portion one tenth
in the deposit shown in Figure 6 was produced from the KCl-HCl bath. In
the deposit shown in Figure 6 was produced from the KCl-NO3 bath and
both produced under the same conditions except for solution com-
were produced in Figure 6. The deposit shown in Figure 6 and 7 is 
which that in Figure 6. The deposit shown in Figure 6 and 7 is
or not to compare the two deposits shown in Figure 11 and 12 
was produced with a powde r deposit with any substantial coherence. If
are the lacr or confinement in the stratum. At 900°C, the deposit
The much larger stratum was compared to that at 600°C to contrast an
the higher magnetization obtained to bring out the stratum structure.
Figure 12 shows a portion of the deposit
of cracks and pores. Figure 12 shows a cross-section of the deposit
half the deposited metal. Also noteworthy is the complete network
of the powder, which was produced off, compared to more than
length of time at the same current and with about the same current
to that produced at 600°C, although they were both run for the same
The chief observation is not in the thinness of the deposited compared
essentially unreacted. Figure 12 shows a cross-section of the deposit.
where the powder was produced off, a macroscopic pore and crack structure
layer of dusty powder over a superimposed green stratum structure.
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 analyzed and found to be 99+½ 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 electroplate. 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.
when powders, directed to the cathode better, were used. At room temperature, the cathode, and the deposits, were formed than those from the KCNO-KOH solution and the deposits, were produced. In general, the deposits from this bath were much thinner. At 50 and 100 amp/dm² and 600°C, very fine-grained powders were

resulted.

Surface energy of the powders decreases the roughness of the contact. Rapid solvent mixing decreases the roughness. It is possible that the experiment

hours with no improvement in smoothness is the possible that the experiment

uniformly coherent plate about 0.05 mm thick were obtained in the presence of 6 amp/dm² reacting current for 2 seconds were tried. A periodic reverse current with 6 amp/dm² direct current for 40 seconds than that reported for pressed and sintered molybdenum.

Greater than that reported for pressed and sintered molybdenum.

formed molybdenum tube had a density in the as-deposited condition. The accuracy can be attained only by some of the sintered powder. Higher density of the theoretical value. Higher melting point. When sintered at only 25°C below the melting point, the weight after pressure and sintering at a temperature 250°C below the melting point, the weight after pressure and sintering at a temperature 250°C below the

metallurgical methods require a density of 90 to 95% of the theoretical.

KOH-powder produced by powder.
No evidence of impurity segregation appears.

Good wetting of the grains and other grain boundaries are apparent. The consistency with the density of API and the theoretical, are apparent. The photomicrograph showing the cross-section of the compact. The words, "Figure 16" by weight in air and in tetrachloroethylene were 6.36%.

The density of the compact was measured to have had no mechanical working. The character of the compact was compatible with a sharp tap. They would break in a brittle manner when subjected to strong impact. However, they would break in a brittle manner when subjected to a high impact and were very mottled in appearance, were polished to a high surface, and were very smooth.

1200-1500°C in argon for 25 minutes. The compact was compatible from the powder by cold pressing at 30 tons/in² and pre-pressuring at 4000 psi. Compacts were prepared from the powder. The density of the compact was 96.7% and the shown in Figure 16. The stability in particle size is readily evident. The range of particle

The same magnification (50X in Figure 15, 9, and 10, 25X in Figure 15, and Figure 15 is a photomicrograph of the powder. Figure 15 is a photomicrograph of a junction cavity with the deposit of powder. The extent of the junction powder were operated during the run. Figure 15 shows the powder deposits were collected about 100 rpm/°C and 600°C, the powder deposits were collected above, which was ran at

The current efficiency

In current efficiency,

manner mechanical loss of deposits rather than to an actual difference solution are probably due to the greater coherence and the resultant current efficiencies measured in this batch as compared to the KOH-M1.
It would be more accurate to state that the measurements were taken at the same photographic plate so that the comparison of all stages would be made under the same conditions. The powder used was a product of American Powder Company, and a standard of the same size and shape of the powder used in this work was prepared from the powder used in the preparation of the samples presented in column 1 of Table XIII. The results are as follows:

XIII. The results of the powder prepared from the powder used in the preparation of the samples presented in column 1 of Table XIII. The results are as follows:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxygen Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.27%</td>
</tr>
<tr>
<td>2</td>
<td>0.30%</td>
</tr>
<tr>
<td>3</td>
<td>0.25%</td>
</tr>
<tr>
<td>4</td>
<td>0.28%</td>
</tr>
<tr>
<td>5</td>
<td>0.32%</td>
</tr>
</tbody>
</table>

The procedure for determining oxygen in powder was as follows:

1. Heat a platinum crucible and the sample in a muffle for one hour at a red heat. Pass the hydrogen through the crucible at a rate of one liter per minute.
2. Remove the sample from the muffle and cool it in the presence of hydrogen for 30 minutes at 1000°C. The water loss which resulted from the hydrogen treatment was determined and corrected to 100°C.
3. Remove the sample from the muffle and cool it in the presence of hydrogen for 30 minutes at 1000°C. The water loss which resulted from the hydrogen treatment was determined and corrected to 100°C.
4. Remove the sample from the muffle and cool it in the presence of hydrogen for 30 minutes at 1000°C. The water loss which resulted from the hydrogen treatment was determined and corrected to 100°C.
5. Remove the sample from the muffle and cool it in the presence of hydrogen for 30 minutes at 1000°C. The water loss which resulted from the hydrogen treatment was determined and corrected to 100°C.

The results are as follows:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxygen Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.27%</td>
</tr>
<tr>
<td>2</td>
<td>0.30%</td>
</tr>
<tr>
<td>3</td>
<td>0.25%</td>
</tr>
<tr>
<td>4</td>
<td>0.28%</td>
</tr>
<tr>
<td>5</td>
<td>0.32%</td>
</tr>
</tbody>
</table>
TABLE XIII. Spectroscopic Analysis of Electrolytic Molybdenum Powders, Commercial Molybdenum, and Specially Purified Molybdenum Metal and Compounds.

<table>
<thead>
<tr>
<th>Element</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>T</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Aluminum</td>
<td>W</td>
<td>VW</td>
<td>VW</td>
<td>VW</td>
<td>VW</td>
<td>-</td>
<td>W</td>
</tr>
<tr>
<td>Barium</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>VW</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Calcium</td>
<td>VW</td>
<td>-</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>-</td>
</tr>
<tr>
<td>Cobalt</td>
<td>VW</td>
<td>-</td>
<td>VW</td>
<td>VW</td>
<td>VW</td>
<td>-</td>
<td>VW</td>
</tr>
<tr>
<td>Chromium</td>
<td>T</td>
<td>-</td>
<td>-</td>
<td>VW</td>
<td>T</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Copper</td>
<td>VW</td>
<td>T</td>
<td>T</td>
<td>VW</td>
<td>VW</td>
<td>VW</td>
<td>T</td>
</tr>
<tr>
<td>Iron</td>
<td>W</td>
<td>VW</td>
<td>VW</td>
<td>W</td>
<td>VW</td>
<td>VW</td>
<td>W</td>
</tr>
<tr>
<td>Magnesium</td>
<td>VW</td>
<td>T</td>
<td>T</td>
<td>VW</td>
<td>VW</td>
<td>T</td>
<td>T</td>
</tr>
<tr>
<td>Manganese</td>
<td>VW</td>
<td>-</td>
<td>-</td>
<td>W</td>
<td>VW</td>
<td>W</td>
<td>VW</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>VS</td>
<td>VS</td>
<td>VS</td>
<td>VS</td>
<td>VS</td>
<td>VS</td>
<td>VS</td>
</tr>
<tr>
<td>Nickel</td>
<td>VW</td>
<td>-</td>
<td>-</td>
<td>VW</td>
<td>VW</td>
<td>-</td>
<td>VW</td>
</tr>
<tr>
<td>Lead</td>
<td>VW</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>-</td>
<td>T</td>
</tr>
<tr>
<td>Silicon</td>
<td>W</td>
<td>VW</td>
<td>VW</td>
<td>W</td>
<td>VW</td>
<td>W</td>
<td>W</td>
</tr>
<tr>
<td>Tungsten</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>W</td>
<td>-</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.257%</td>
<td>0.026%</td>
<td>0.068%</td>
<td>0.268%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 K3MoCl6 - KCl - LiCl Solution

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Current Density (amp/dm²)</th>
<th>Plating Time (Hr)</th>
<th>Wt. Deposit Collected (g)</th>
<th>Type of Deposit</th>
<th>Figure Reference</th>
<th>Table XIII Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>3</td>
<td>5</td>
<td>2.9</td>
<td>Coherent rough plate, 0.02&quot; thick</td>
<td>11a, 11b</td>
<td>13</td>
</tr>
<tr>
<td>900</td>
<td>3</td>
<td>5</td>
<td>-</td>
<td>Superficially coherent powder covering about 0.01&quot; of badly cracked and porous plate</td>
<td>12a, 12b</td>
<td>-</td>
</tr>
<tr>
<td>600</td>
<td>6</td>
<td>4</td>
<td>-</td>
<td>Powder composed of microscopic dendrites over coherent plate</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>600</td>
<td>30</td>
<td>1</td>
<td>5.7</td>
<td>Fine grained powder (5.3 g) over approximately 0.0015&quot; plate (0.43 g)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>600</td>
<td>100</td>
<td>1.75</td>
<td>29.0</td>
<td>Very fine-grain powder</td>
<td>14, 15</td>
<td>Col. 1</td>
</tr>
<tr>
<td>900</td>
<td>100</td>
<td>1</td>
<td>17.9</td>
<td>Malleable modular powder deposit</td>
<td>18a, 18b, 18c</td>
<td>Col. 2</td>
</tr>
</tbody>
</table>

All solutions contained 4.1 mole % Mo.
In determining the purity of deposits, chemical analyses for molybdenum were run, foreign metals were determined spectrophotically, 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-ECl 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 students 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 AlCl₃-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 AlCl₃. 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 Ag, AgCl(1)/is reversible and
non-polarizable was shown by Atten, den Hertog, and Westenberg [50] who report that silver dissolves anodically and deposits cathodically from molten silver chloride at 475°C and that the polarization voltage is only 0.5 mV at a current density of 1 amp/cm². This was confirmed in tests described below. One important disadvantage of the Ag, AgCl 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
value was taken as the equilibrium potential.

Potential measurements were made at half-hour intervals, and when the
potential remained constant within one millivolt for three hours, that
value was recorded. The procedure for maintaining an inert atmosphere was fol-
lowed. The same procedure for maintaining a purger gas at a steady level
in the cathode room above the purger apparatus was not need
when measuring equilibrium potential, the mode was not need.

In each run, the largest single difference was 1%. The mean difference between the initial and final zero values
in all runs were taken before and after each
measurement. Zero current values were taken before and after each
measurement.

A electrode was measured using a potentiometer and high sensory
one minute while the potential between the anode and reference
was for platinum. The current was set and held at each value for about
20 minutes. A 0.1 g electrode was passed through the anode and cathode, (cathode area = 0.1 cm²) and
toward the latter electrode. Rather than toward the electrode. Current
were measured in this manner so that if the cell were exposed to
except under applied voltage, as when filling the cell, but the readings
were repeated to prevent flow of current through it. A electrode was placed over the tube of the electrode
in which the electrode was exposed to the air. The electrode
of the anode, after the purger gas was allowed into the orifice. The
was metered out and the electrode assembly was lowered into the orifice. The
inert atmosphere was followed, the electrode in the crucible was
the system closed. After the usual procedure for establishment of an
through holes in the rubber stopper in the pipe. E (figure 2).

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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 dm². 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 µa, 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 K₂MoCl₆ in LiCl-KCl eutectic mixture of standard composition (4.1 mole % K₂MoCl₆) 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/dm$^2$. 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$^\circ$, 700$^\circ$, 800$^\circ$ and 900$^\circ$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/dm$^2$ range, Figure 21B shows the 0 to 10 amp/dm$^2$ 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 $\pm 8$ mv and only three pairs of points had an average deviation greater than $\pm 20$ mv.
<table>
<thead>
<tr>
<th>Project</th>
<th>Time</th>
<th>Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Task 1</td>
<td>100</td>
<td>1.2</td>
</tr>
<tr>
<td>Task 2</td>
<td>200</td>
<td>2.4</td>
</tr>
<tr>
<td>Task 3</td>
<td>300</td>
<td>3.6</td>
</tr>
</tbody>
</table>

*Table for project progress.*
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 x 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 x 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 overnight. 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 ennobles 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 \( \text{Zn}^{2+}-\text{ZnCl}_2 \), \( \text{Fe}^{2+}-\text{FeCl}_2 \), \( \text{Cu}^{+}-\text{Cu}_2\text{Cl}_2 \), and \( \text{Ag}^+-\text{AgCl} \), 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 \( \text{ZnCl}_2 \) (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. FeCl$_2$•4H$_2$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$_2$Cl$_2$ 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$_2$Cl$_2$ 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:

$M / MCl_x (4.1 \text{ mole\%}), \text{KCl, LiCl} \parallel/\parallel \text{AgCl (Pure liquid)} / Ag$
concentration of 4.1 mole % in nitric nitric-nitrogen chloride

Table I. Reference Electrode Relative to the Same Electrode at the Same Temperature with Respect to the Same Electrode (NaCl) Reference Electrode at 600°C.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Potential (V vs. AgCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.312</td>
<td>BRIER</td>
</tr>
<tr>
<td>0.349</td>
<td>Molybdenum</td>
</tr>
<tr>
<td>0.626</td>
<td>Copper (one)</td>
</tr>
<tr>
<td>1.023</td>
<td>Iron (one)</td>
</tr>
<tr>
<td>1.277</td>
<td>Zinc</td>
</tr>
</tbody>
</table>

The Table above is not complete and does not show the concentration of 4.1 mole %.

The first four cells are analogous to dental cells. The last cell is

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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,

\[ \text{Mo}^{3+} + 3e^- \rightarrow \text{Mo} \text{;} \]

and the lower potential is characteristic of a reaction which may be written:

\[ \text{Mo}^{(3+x)+} + xe^- \rightarrow \text{Mo}_2\text{O}_3. \]

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

\[ \text{MoO}_4^{2-} + 6e^- \rightarrow \text{Mo} + 40^2 \]

either does not occur or it never reaches equilibrium. If it did, some stable potential for the \( \text{MoO}_4^{2-} \) 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 characterized 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.

Yntema 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 $K_2MoCl_6$. This could only have been $MoCl_5$ produced by oxidation of the compound by air, since we have shown $K_2MoCl_6$ to be stable and non-volatile in the absence of air up to at least 600°C. What Yntema was comparing then, was an electrolyzed molybdate solution and an air-contaminated $K_2MoCl_6$ 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°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°C and 900°C occur at a higher current density (30 amp/dm$^2$) and are not as large as at 200°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 \( \text{K}_3\text{MoCl}_6 \) 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 \( \text{Mo} \mid [\text{MoCl}_6^{3-}] \) 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. Intama finds that in the \( \text{AlCl}_3-\text{NaCl-KCl} \) solvent at \( 156^\circ \text{C} \), 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 manganese. Examination of the isothermal polarization curves in Figure 21B shows that the 600\(^\circ\) 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$^\circ$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$^\circ$ curve but not in any of the others. Also, the slope of the 600$^\circ$ 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$^\circ$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$^\circ$ 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
interester. One may consider the situation of a body of water heated and the particles are then forced to move at a steady rate. Above this rate of movement the conduction of the body is no longer effective and the particles tend to move at a faster rate.

If one assumes that the rate of movement of the body is the same as that at the temperature of the liquid, the motion is observed to occur. In 1900, a very low and stable substance with high stability such as a coolant, is treated and one of very high bond strength and in the same way that of other compounds is treated. The coolant is then used to secure the system of the type shown. The bond type is the coolant structure of the type studied. For the coolant bonds with three unpaired electrons in the compound, the electronic structure of the treatment motif is determined that the most likely structure is the energy as the value for three unpaired electrons. The electronic spectrum is given (opposite p. 239) at 130°C in 100 cm at 1800. The correlation corresponds to the spectra of the coolant. The spectra were used to predict from the theoretical consideration. It has been shown that the K2OCl6 in the medium stable at 600°C.

The conduction step of the reaction

where the show deactivation of the K2OCl6 that the proposed that the reaction mechanism does occur there.
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 1904\textsuperscript{53}. S. Glasstone also found that dissociation followed by reduction of the free silver ion was an unreasonable mechanism for the argentocyanide system\textsuperscript{55}. This explanation of the break observed in the 600\textdegree polarisation curve, the higher polarisation at 600\textdegree 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 polarisation 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\textdegree 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\textdegree 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 silver\(^{55}\). By a rather indirect method, Russell and Rowell placed the position of molybdenum in the E.M.F. series in aqueous systems near mercury\(^{56}\). 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: \(\text{Mo} \rightarrow \text{Mo}^{3+} + 3e^-\) (in aqueous acid solution) calculated by Latimer\(^{57}\) 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 Yntema for one mole percent solutions of salts of the indicated element in AlCl₃-KCl-NaCl solvent at about 200°C. Column two was calculated from Lorens' values of the potentials of Daniel cells consisting of M∥pure molten chloride of M∥pure molten chloride of N∥N, where M and N are metals, at 600°C. (The value for Sn is at 350°C 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**

<table>
<thead>
<tr>
<th>Element</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>0.42</td>
<td>0.43</td>
<td>1.6</td>
<td>0.97</td>
</tr>
<tr>
<td>Lead (cus)</td>
<td>0.30</td>
<td>0.32</td>
<td>0.92</td>
<td>-</td>
</tr>
<tr>
<td>Iron (eus)</td>
<td>0.19</td>
<td>-</td>
<td>1.2</td>
<td>0.72</td>
</tr>
<tr>
<td>Tin (eus)</td>
<td>0.17</td>
<td>0.07</td>
<td>0.93</td>
<td>-</td>
</tr>
<tr>
<td>Copper (eus)</td>
<td>0.04</td>
<td>-</td>
<td>0.28</td>
<td>0.31</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.35</td>
<td>-</td>
<td>-</td>
<td>0.04</td>
</tr>
<tr>
<td>Silver</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The parallelism between the series for AlCl₃-KCl-NaCl solvent (Column 1) and for pure electrolytes (Column 2) and the large difference
some material with little or no tendency to form complexes. In this

case, the term "complex" refers to a molecule or ion that forms an intermolecular bond with another molecule or ion, which is different from the term "complexation" used in chemistry to denote the formation of a new substance (a complex) from two or more substances.

When the pure material melts, the fluid complex decomposes into two or more separate substances. The greater the rate of decomposition, the lower the melting point of the pure material. As a result, the added material does not interfere with the complex formation and does not even sufficiently to complex the added material. The NCI and HCl complexes of the ACN-O type are not detected. In addition, complexes of the NCI-NCI-O type are not detected in the KCl-NaCl mixture. The ACN-O complexes are not detected.

It could appear that this is the cause of the difference in the ACN-NCI-O, but the absence of substantial differences in the KCl-NaCl mixture can be attributed to the greater rate of decomposition of the ACN-O complexes. In contrast, there is no evidence for the presence of substantial differences between the KCl-NaCl and the aqueous systems (column 3).
so 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 chloroplatinate anion in molten KCl-NaCl-PbCl₂ mixtures and in molten KCl-PbCl₂ mixtures by transference measurements. 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 AlCl₃ 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, AlCl₃ is apparently a much weaker halide donor than KCl or LiCl. The metal ions, therefore, have a greater tendency to form complex halide-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°C is given by the following calculation. The potential for the cell: Zn/ZnCl₂ (pure) // AgCl / Ag is given by Lorenz as 0.427 at 600°C (Ref. 7, Vol. III, p. 123). The potential for the cell: Zn/ZnCl₂ (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:
\[ \text{Zn} / \text{ZnCl}_2 (4.1 \text{ mole } \% \text{ KCl, LiCl} \parallel \text{ZnCl}_2 \text{ (pure)} / \text{Zn} \]

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 \( \approx 1.277 - 0.427 = 0.850 \) volts

\( n = 2 \)

\( a_{\text{soln}} \) = activity of \( \text{Zn}^{2+} \) in the solution

\( a_{\text{pure}} \) = activity of \( \text{Zn}^{2+} \) in the pure molten state

\( T = 873^0\text{K} \)

\( R \) 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 \( a_{\text{pure}} \) as 1 and solving the equation for \( a_{\text{soln}} \), we find that the activity of the \( \text{Zn}^{2+} \) in the 4.1 mole \% solution is about \( 10^{-10} \) in units of mole fraction. Since the concentration is \( 4 \times 10^{-2} \) 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.,

\[ \text{Ag} / \text{AgCl} (4.1 \text{ mole } \%), \text{KCl, LiCl} \parallel \text{AgCl} / \text{Ag} \]
may be expressed by

\[ E = \frac{RT}{\gamma} \ln \frac{a_{\text{pure}}}{a_{\text{soln}}} \]

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, \( a_{\text{soln}} \) 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. Suchy \(^6\) determined the potentials of the following molten electrolyte cells:

\[
\begin{align*}
Pb / PbCl_2 &// AgCl (1.858 N), KCl, LiCl // Ag; E = 0.127 \text{ volt at 600°C.} \\
Pb / PbCl_2 &// AgCl (pure) / Ag; E = 0.319 \text{ volt at 600°C.}
\end{align*}
\]

The difference between these values of \( E, 0.192 \text{ volt}, \) 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 M 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 chlorosinate 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 complexes.61
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
  K₂MoCl₆  33 g  K₂MoCl₆  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 hexachloro-

molybdate (III) and a new method for the preparation of molybdenum dichloride has been described.
ACKNOWLEDGMENTS

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APPENDIX

Electrodeposits from Aqueous Molybdate Solution

An attempt to produce a deposit from the solution described by Kseyeki and Yntema on page 55 of their article 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 Kseyeki 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>
<thead>
<tr>
<th>TABLE XVIII. Analysis of Deposit from Aqueous Molybdate Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of deposit stripped from cathode</td>
</tr>
<tr>
<td>4.45 mg</td>
</tr>
<tr>
<td>Molybdenum % (colorimetric)</td>
</tr>
<tr>
<td>Molybdenum % (gravimetric)</td>
</tr>
<tr>
<td>Copper %</td>
</tr>
</tbody>
</table>

It should be noted that pure MoO₂ 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 Keycki 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% MoO₂ 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-equiv-
alent 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 ex-
pressed by:

\[ C.E. = \frac{g}{e \cdot i t/e} \times 9.65 \times 10^6 \]

where \( C.E. \) = current efficiency in percent

\[ g \] = 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, \( \text{Mo}^{3+} + 3e \rightarrow \text{Mo} \), the equivalent weight of molyb-
denum 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**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Density at T°C.</th>
<th>Temperature Range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>( 1.762 - 4.32 \times 10^{-4} ) T</td>
<td>626 to 985</td>
</tr>
<tr>
<td>KCl</td>
<td>( 1.971 - 5.8 \times 10^{-4} ) T</td>
<td>789 to 958</td>
</tr>
<tr>
<td>AgCl</td>
<td>( 5.267 - 9.2 \times 10^{-4} ) T</td>
<td>628 to 783</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Substance</th>
<th>Weight (g)</th>
<th>Density (g/cc)</th>
<th>Volume (cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>56.8</td>
<td>1.503</td>
<td>37.8</td>
</tr>
<tr>
<td>KCl</td>
<td>68.1</td>
<td>1.623</td>
<td>42.0</td>
</tr>
<tr>
<td>AgCl</td>
<td>13.8</td>
<td>4.715</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Total Volume 82.7</td>
</tr>
</tbody>
</table>

Since 0.0962 mole AgCl was present in the solution,

$$n_{AgCl} = \frac{0.0962}{82.7} \times 1000 = 1.163 \text{ Normal}$$
ILLUSTRATIONS
FIGURE 1

Apparatus for Electrolysis of Fused Salts
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$_4$Mo$_2$(CN)$_8$.

The patterns of the pure compounds are taken from the A.S.T.M. card file.
FIGURE 5

Dendritic Molybdenum Powder — 50X
Cross-section of adherent polytetrafluoroethylene layer after removal of overlying powder.
Agglomerates of polyethylene powder from concentrated solution 50X

As-Deposited Condition
Deposit of Figure 7 after Washing and Grinding  50x
Molybdenum Deposit in the Form of Spheroidal Granules 50X
Figure 10
Polyphenyl powder deposit resulting from periodic reverse floating 50x
FIGURE 11A

Cross-section of Coherent Upheavals Deposition Pair, 20°C-10°C solution, 300°F

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
Same Deposit as Figure 12A, Etched to Show Grain Structure  500X
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 100

Nodules of Same Deposit as Figure 10A, 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 $\text{K}_2\text{MoCl}_6$ in LiCl-KCl (0 to 100 amp/dm$^2$)

- $600^\circ \text{C}$,  
- $700^\circ \text{C}$,  
- $800^\circ \text{C}$,  
- $900^\circ \text{C}$
Figure 21B

Low Current Density Portion of Curves in Figure 21A (0 to 10 amp/dm²)

- 500°C
- 700°C
- 800°C
- 900°C
FIGURE 22

Polarization Curves for Oxygenated Solutions of Molybdenum Salts

A - Air-Contaminated Solution of $K_3MoO_4$ in LiCl-KCl

- $600 \degree C$
- $700 \degree C$
- $800 \degree C$

B - Solution of $K_2MoO_4$ in LiCl-KCl

- $600 \degree C$
- $900 \degree C$