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EQUILIBRIA BETWEEN MoO_2 AND LIQUID

MOLYBDENUM OXIDE

BY

PRAKASH BAKHRU, 1945-

A THESIS

Presented to the Faculty of the Graduate School of the

UNIVERSITY OF MISSOURI-ROLLA

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MASTER OF SCIENCE IN METALLURGICAL ENGINEERING

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Approved by

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ABSTRACT

The oxygen pressure over solid molybdenum dioxide in equilibrium with liquid molybdenum oxide was determined by transpiration and solid electrolytic galvanic cell methods at 950°C and 900°, 950° and 1000°C respectively. The results were compared to those expected from thermodynamic data on the Mo-O system.

Possible reactions between MoO_2 and SiO_2 were studied at different oxygen pressures up to 1550°C. No compound formation or solid solution between MoO_2 and SiO_2 was detected by x-ray diffraction techniques.

The phase boundary between MoO_2 and liquid molybdenum oxide was checked by microscopic examination of quenched samples. Equilibration runs were carried out in silica and platinum capsules.

ACKNOWLEDGEMENTS

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I. INTRODUCTION

Molybdenum is a refractory metal, with a melting point of 2617°C. However, the ease with which molybdenum is oxidized limits its use, a fact which has stimulated many studies of its oxidation. The thermochemical conditions that prevail during the oxidation of molybdenum are quite complex, since several oxide species are found. The oxides can exist as solids, liquids and gases.

Despite these studies, several questions remain unanswered, regarding the composition of condensed oxides, the thermodynamic properties and degree of polymerization of the gaseous species of the oxides, and the partial pressure of oxygen over various phase assemblages of the molybdenum oxides.

The complete determination of the thermodynanics of the Mo-O system is beyond the scope of this thesis. The present work was limited to finding the partial pressure of oxygen in equilibrium with solid MoO_2 and liquid molybdenum oxide at 900°, 950° and 1000°C, according to the equation:

$$MoO_{2(s)} + \frac{x}{2}O_2 \rightarrow MoO_{2+x} \text{ (liquid oxide)}.$$
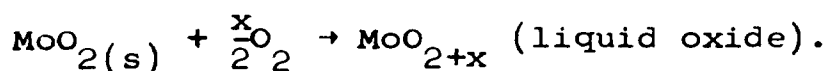
Transpiration and solid electrolytic galvanic cell methods were chosen for the investigation.

An attempt was also made to detect any reactions or solid solutions between SiO_2 and MoO_2 at several pO_2, from 1200-1550°C. The phase boundary between solid MoO_2 and liquid molybdenum oxide was also determined by microscopic study of quenched samples.

II. REVIEW OF LITERATURE

The literature on molybdenum oxides will be reviewed under two general headings. There are (A) Phase Equilibria and (B) Thermodynamics of Oxide Species of Molybdenum.

A. Phase Equilibria

1. Mo-O Binary System

The Mo-O phase diagram has been most recently studied by Phillips and Chang,[1] by equilibration of powders in sealed platinum capsules in the temperature range 873-1973°K. Their phase diagram has been redrawn and is shown as Fig. 1. Four stable oxides exist below about 1093°K: MoO_2, MoO_3 and two intermediate phases very close to Mo_4O_{11} and Mo_9O_{26} in composition. Two modifications of Mo_9O_{26} exist but are not shown on Fig. 1. MoO_2 was found stable to at least 1973°K, the uppermost temperature at which their investigation was made. It is the only solid oxide that is stable above 1093°K. Kubaschewski and Hopkins[2] give the eutectic between MoO_2 and MoO_3 at 1051°K, and the melting point of MoO_3 at 1068°K.

Molybdenum oxides other than those shown by Phillips and Chang[1] are believed to exist, mostly below about 1023°K. It is possible that these oxides are intermediate reaction products and not thermodynamically stable. Information on these oxides has been summarized by Elliott.[3] The solubility of oxygen in solid molybdenum has been determined by Few and Manning[4] to be 0.006 weight percent at 1873°K. The solubility is reported to decrease linearly to about 0.004 weight percent at 1373°K.

2. Non-Stoichiometry of MoO_2

MoO_2 crystallizes in the rutile structure. It exhibits
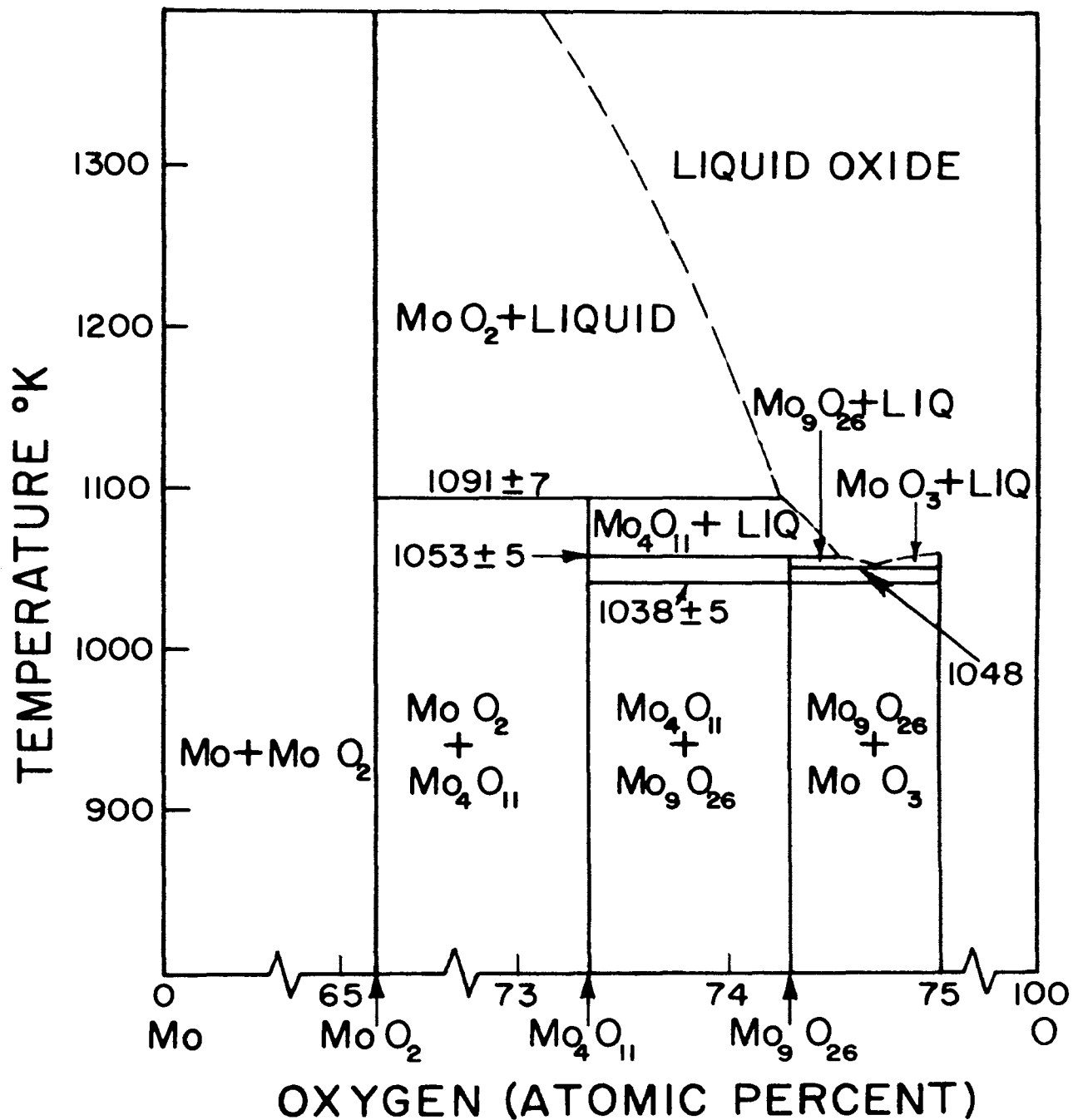
Figure 1. Condensed Phase Relations in the
System Mo-O as Established
by Phillips and Chang.[1]

both oxygen deficient and oxygen excess deviation from the stoichiometric composition.[5] Deviation from stoichiometry of MoO_{2+x} was measured by Zador and Alcock[5] and by Zador[6], by means of a high temperature galvanic cell. X was found to vary from -0.01 to +0.05, however these numbers are somewhat uncertain due to the scatter in their data. The X-ray diffraction pattern obtained by Zador and Alcock[5], for oxygen deficient and oxygen excess MoO_2 were identical except for a very small shift in the lattice parameters. The departure from stoichiometry of MoO_2 is not significant for the purposes of this work.

B. Thermodynamics of Oxide Species of Molybdenum

1. Polymeric Gaseous Species of Molybdenum Oxides

The polymeric species of MoO_2 and MoO_3 that have been reported in significant amount are $MoO_2(g)$ and $(MoO_3)_{n(g)}$, where n varies from 1 to 5. Jaeger and Germs[7] were probably the first to note the polymerization of the MoO_3 molecule in the gas phase. Feiser[8] made an indirect determination of vapor pressure in equilibrium with solid and liquid MoO_3, covering the temperature range 610-1155°C. His attempts to determine the vapor pressure of MoO_3 were based on boiling point determinations of MoO_3, the rule of Ramsey and Young, and by rate of evaporation measurements of sublimed MoO_3. The considerable discrepancy in his vapor pressure data, as obtained by the different methods, could be explained if the molecular species vaporizing was polymeric, i.e. $(MoO_3)_n$. His data yielded an average value of n= 3.774.

Blackburn et al.[9] and Horbe et al.[10] used the
Knudsen effusion method to determine the vapor pressure of
solid molybdenum trioxide. They obtained an enthalpy of
sublimation of 79.74 Kcal/mole of vapor and 88.6 Kcal/mole
of vapor respectively at 900°K. This difference may be
explained by the fact that they selected different propor-
tions of polymeric gaseous species of MoO_3 in making their
calculations. To determine the degree of polymerization
and the vapor pressure of MoO_3, Zelikman et al.[11] used
the boiling point and transpiration methods from 820° to
1000°C. The vapor pressure data calculated by them accord-
ing to the flow method (assuming the monomer gaseous species
alone) was 2.5 to 3.7 times higher than that obtained by the
boiling method, thus confirming the polymerization of gaseous
molecules of MoO_3. The data of Zelikman is given in Table I.

Table I   Vapor Pressure Determined by
Transpiration, and by the
Boiling Point Method.[11]

Temperature °C	Vapor Pressure, mm Hg		$\dfrac{P_{Transpiration}}{P_{Boiling}}$
	According to Transpiration Method, Assuming Monomer Only	According to Boiling Point Method	
820	62	16.6	3.73
860	103	28.8	3.58
900	126	51.3	2.45
950	280	94.8	2.96
1000	515	167.5	3.07

Zelikman et al.[11] concluded that if the data at 900°C is disregarded the degree of polymerization decreases with rise in temperature. Most probably at 950-1000°C the molecules in the vapor are predominantly of the type $(MoO_3)_3$.

Berkowitz et al.[12] have determined the vapor species using the mass spectrometer method. The trimer, $(MoO_3)_3$ was found to be the main gaseous species for the temperature range of 600-700°C. Smaller quantities of $(MoO_3)_4$, $(MoO_3)_5$ and the dimer and monomer were also present. The results of Berkowitz et al.[12] when extrapolated to the liquid region by means of the measured heat of fusion for $MoO_{3(s)}$, predict that $(MoO_3)_4$ predominates in the vapor phase.

Brewer and Elliott[13] attempted to find the vapor density at 1200°C and concluded that the average vapor formula was less than $(MoO_3)_{1.5}$, and the polymerization is less important at this temperature.

There has been substantial disagreement among molybdenum trioxide vapor pressure data obtained by Knudsen effusion method,[12, 14] transpiration measurements,[11, 15, 16] and by the rate of evaporation method.[8] Ackermann et al.[16] presented a comparison of vapor pressure data of these investigators, which showed the large extent of the difference between the investigations. Gulbransen et al.[17] treated the same and later data by recalculating the average molecular weight of the polymeric species. This greatly narrowed the existing differences in vapor pressure data, as shown in Fig. 2, which is taken from his paper.[17]

TEMPERATURE °C

B. P. 1428°K

D

M. P. 1068°K ⟵ 0.015 atm

—·— EXTRAPOLATED

A. GULBRANSEN et. al[17]

B. HÖRBE et al[10]

C. BLACKBURN et al[9]

D. Mo $O_3(\ell)$ HÖRBE et al[10]

Based on Data of

FEISER[8] and

ZELIKMAN et al[11]

1000/T °K

Figure 2. Vapor Pressure Curves,
Solid and Liquid MoO_3.

The data for liquid molybdenum oxide is shown as curve D. At the melting point, the vapor pressure of molybdenum oxide is given as 0.015 atm. The extrapolated part of the curve is constructed on the basis that at the melting point, the vapor pressure of solid and liquid molybdenum trioxide should be the same. The Clausius-Clapeyron equation for the vaporization of $MoO_3(s)$ as determined by Gulbransen et al.[17] is:

$$4.576 \log p(MoO_3)_{\bar{n}} = \frac{-75,400}{T} + 62.3 \pm 0.2$$

Where p is in atmospheres and $\bar{n}$ is the average molecular evaporation number. $\Delta H_{s \to g}$ is 75.4 ± 1 Kcal/mole of $MoO_3(n)$. The corresponding equation for vaporization of three moles of the liquid oxide is:

$$4.576 \log p(MoO_3)_3 = \frac{-35,200}{T} + 24.60$$

Gulbransen et al.[17] reports that the difference in heat of vaporization of solid and liquid molybdenum trioxide is 40.2 Kcal/mole of $(MoO_3)_n$, or 12.4 Kcal/mole for the heat of fusion of $MoO_3(s)$. Cosgrove and Snyder[18] found 12.6 Kcal/mole as the latent heat of fusion of MoO_3. The agreement gives further evidence for the existence of the trimer and tetramer species in the vapor state, at least near the melting temperature of $MoO_3(s)$.

Burns et al.[19] studied the importance of polymers in the vapor over solid MoO_2 by a mass spectrometer in the temperature range 1500-1780°K. The most important polymeric species were found to be $MoO_3(g)$, $(MoO_3)_2(g)$, $(MoO_3)_3(g)$ and $MoO_2(g)$. In addition small peaks of Mo_2O_5, Mo_2O_4 and Mo_3O_8 were found. It was found that $MoO_2(g)$ is of considerably less importance than concluded

by Blackburn et al.[19] and that $MoO_{3(g)}$ is of more importance than their estimate.

2. Graphical Interpretation of the Mo-O System

Gulbransen et al.[20] analyzed thermochemically the surface oxides formed on molybdenum during oxidation, and the nature of the volatile species, for a wide variety of oxidation conditions. He expressed the data as a "thermochemical diagram", by plotting log $p(MoO_x)$ vs log pO_2 under isothermal conditions. Vertical lines on his diagram represent dissociation pO_2 of the solid and liquid oxide phases. Horizontal lines represent volatility curves which are independent of oxygen pressure. The remaining curves represent the effect of oxygen pressure on the volatile oxide pressure.

In Fig. 3 a thermochemical diagram for the Mo-O system at 950°C has been plotted, using the same variables as did Gulbransen et al.[20] The thermochemical data for solid, liquid and gaseous molybdenum oxides were taken from Gulbransen.[21] The data are essentially the same as those in the JANAF[22] tables. Lines in the Mo metal region in the Fig. 3 relate to equilibria such as:

$$Mo_{(s)} + \tfrac{1}{2} O_2 \rightarrow MoO_{2(g)}.$$

Lines in the $MoO_{3(\ell)}$ region represent relations such as:

$$MoO_{3(\ell)} \rightarrow MoO_{2(g)} + \tfrac{1}{2} O_2.$$
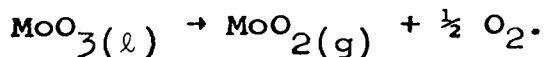
The lines in the region of $MoO_{2(s)}$ represent equilibria such as:

$$MoO_{2(s)} + \tfrac{1}{2} O_2 \rightarrow MoO_{3(g)}.$$
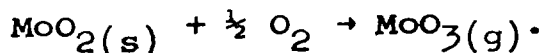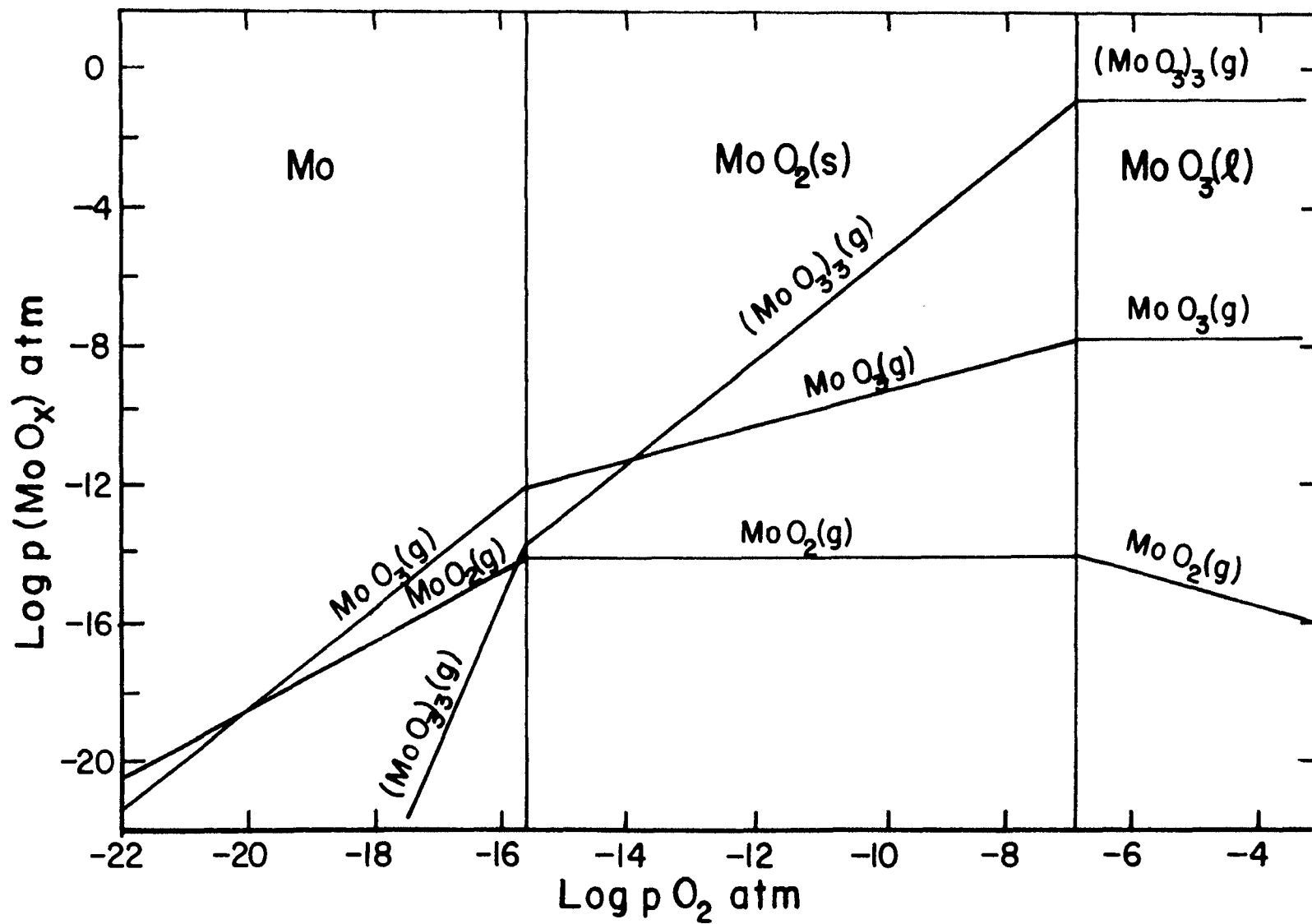
Figure 3. Thermochemical Diagram for the Mo-O System at 950°C.[21]

Over solid MoO_2, the equilibrium partial pressure of $(MoO_3)_{n(g)}$ increases with an increase in pO_2. Over $MoO_{3(\ell)}$, the equilibrium pressure of $(MoO_3)_n$ is independent of oxygen pressure. All vapor species exist at their maximum pressure at the oxygen partial pressure corresponding to coexistence of solid MoO_2 and $MoO_{3(\ell)}$.

Gulbransen et al.[20] assumed that liquid molybdenum oxide has the composition MoO_3, even at pO_2 where the liquid oxide is in equilibrium with $MoO_{2(s)}$. But in reality the composition of liquid molybdenum oxide changes with pO_2. For example, at $950°C$ the composition of liquid molybdenum oxide in equilibrium with $MoO_{2(s)}$ is about $MoO_{2.85}$, (estimated from Phillips and Chang.[1]) and the pO_2 is about 10^{-7} atm. (estimated from Gulbransen [21]). Thus the vertical phase boundary drawn by Gulbransen for $MoO_2/MoO_{3(\ell)}$ equilibria is based on the thermodynamic properties of $MoO_{3(\ell)}$, rather than the properties of actual liquid oxide present. (This is also true of the same boundary drawn in Fig. 3). Thus the correct position of the $MoO_{2(s)}/$liquid molybdenum oxide boundary should actually be somewhat to the left of the boundary drawn in Fig. 3, (i.e. at lower pO_2). The location of the position of this boundary is one of the objectives of this work.

Another consequence of variation in composition of liquid molybdenum oxide with pO_2 is that the $p(MoO_x)_{(g)}$ lines will be slightly curved, rather than straight, in the $MoO_{3(\ell)}$ region. Unfortunately no reliable data are available at $950°C$ to show the position of gaseous species other than $MoO_{2(g)}$, $MoO_{3(g)}$ and $(MoO_3)_{3(g)}$. Apparently the effect of pO_2 on the composition of

liquid molybdenum oxide, and the resulting effect on its vapor pressure, have not been appreciated in earlier vapor pressure studies. The vapor pressure studies have been made under conditions where the pO_2 was not fixed. This may account for some of the discrepancies in reported vapor pressure data.

3. Effect of Moisture on Vapor Pressure of Molybdenum Oxide

The effect of water vapor on the volatility of MoO_3 was first reported by Millner and Neugebauer.[23] Glemser and Volz[24] reported that negligible weight loss was obtained by passing a nitrogen-water vapor mixture over MoO_3 at 923°K. MoO_3 was volatilized in an oxygen-water vapor mixture however, and the pressure of MoO_3 increased linearly with the partial pressure of water vapor. Brewer and Elliott,[13] and Belton and Jordan [25] point to the existence of $MoO_3 \cdot H_2O$ as the vapor species, when MoO_3 is volatilized in the presence of water vapor by the reaction:

$$MoO_3(s) + H_2O(g) \rightarrow MoO_3 \cdot H_2O(g).$$
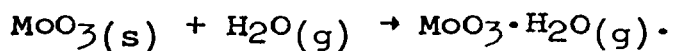
At constant temperature, the pressure of the hydrated compound is directly proportional to the water vapor pressure.

III. EXPERIMENTAL METHODS

A. General

The equilibrium oxygen pressure over solid MoO_2 and liquid molybdenum oxide was determined by a transpiration technique at $950°C$ and by a solid electrolytic galvanic cell technique at $900°$, $950°$ and $1000°C$. Possible reactions between MoO_2 and SiO_2 were studied by x-ray diffraction of quenched samples. Some samples were equilibrated in a sealed silica capsule in the presence of molybdenum foil. Other samples were equilibrated at different oxygen partial pressures, higher than those for equilibrium with Mo metal. The phase boundary between solid MoO_2 and liquid molybdenum oxide was studied by a sealed capsule technique and phase identification was by microscopic examination of quenched samples.

B. Transpiration Method

Transpiration is an important and commonly used technique to determine the vapor pressure of many substances. The literature[11,15,16,26-28] contains many examples of the application of the method, in which a known volume of gas is passed over the material under study, and the weight loss is proportional to the vapor pressure and molecular weight of the species. The transpiration method is considered most useful over a pressure range from about 10^{-6} to 10^{-1} atm.

At very low flow rates of carrier gas, the weight loss of material is higher than that corresponding to an equilibrium vapor pressure, due to thermal diffusion and segregation of vapor and carrier gas.[26] At very high flow rates, the gas is not saturated, and the vapor density (weight loss/unit volume of carrier gas) is too low.

It is therefore important to obtain data at flow rates on the "plateau"; that is, where the vapor density is independent of flow rate. [26,27]

Studies of Alcock and Hooper[27] on vapor pressure measurements of silver and gold have shown that when the vapor pressure is high, the unsaturation of the carrier gas begins at lower flow rates. This results in a plateau that exists over a relatively small range of carrier gas flows. A vapor density vs. flow curve for transpiration of molybdenum oxide is shown in the experimental results section.

C.   Solid Electrolytic Galvanic Cell Method

Most of the thermodynamic properties for oxides available in the literature have been calculated from enthalpies and heat capacities measured calorimetrically or from gas-solid equilibria. More recently, thermodynamic data has been obtained from electrochemical measurements with a solid electrolytic galvanic cell. Such cells theoretically can be used to measure the thermodynamic properties of solid, liquid and gaseous oxides. Kuikkola and Wagner have discussed[29] and demonstrated[30] various applications of solid electrolytes. In particular, their work concerned electrochemical measurements of oxygen activities using a cell incorporating the solid oxide electrolyte calcia stabilized zirconia.

Pure zirconia exists in the monoclinic crystalline form at room temperature but transforms into a tetragonal structure when heated to high temperature; the transformation is accompanied by a seven percent volume change.[31] However, when CaO is mixed with ZrO_2 and sintered a solid solution is formed, and the presence of Ca^{++} cations on the cation sublattice causes the formation of anion vacancies to preserve electrical neutrality.[32] The

resulting increase in oxygen ion conductivity leads to exclusively ionic conduction within certain ranges of temperature and pressure.

A solid electrolyte should be chemically stable even under severe oxidizing and reducing conditions. Any chemical reaction between the electrode and electrolyte may cause corrosion of the electrolyte and will disturb the equilibrium at the electrode. The cell voltage may thus continually decrease with the passage of time.

The galvanic cells used for the determination of thermodynamic properties of the metal oxides are essentially oxygen concentration cells. The two different oxygen pressures at the two electrodes could be obtained by using gas mixtures of different oxygen potential, e.g. pure O_2, air, CO_2/CO, H_2O/H_2 etc. Another way of fixing the oxygen pressure at one or both sides of the cell is to use metal-metal oxide mixture compacts like Ni-NiO, $Cu-Cu_2O$ etc. The choice of reference electrode as close in oxygen potential as possible to the unknown electrode is desirable to give the most accurate value of μO_2 for the unknown electrode.[33]

Under the conditions of essentially exclusive ionic conduction, the voltage $\mathscr{E}$ of a galvanic cell involving the $Zr_{0.85}Ca_{0.15}O_{1.85}$ electrolyte may be related to the free energy change of the virtual cell reaction by the expression[30]

$$\mu'O_2 - \mu''O_2 = \eta \mathscr{F}\mathscr{E}$$

Where $\mu'O_2$ and $\mu''O_2$ are the chemical potentials of oxygen at the anode and cathode respectively. In the present investigation, the reference pO_2 was at the cathode and the

unknown pO_2 was at the anode.

In the concentration cells involving oxygen, the expression for the reversible cell reaction

$$\Delta G^\circ = -n \mathscr{F} \mathscr{E}$$

could be written as

$$\mathscr{E} = \frac{RT}{n\mathscr{F}} \ln \frac{p''O_2}{p'O_2} \ .$$

Where n = number of electrons involved in the cell reaction; n = 4 for 1 mole of O_2. $\mathscr{F}$ = Faraday constant, 23063 cal/volt. $\mathscr{E}$ = e.m.f. in volts. The symbols $p''O_2$ and $p'O_2$ refer to the equilibrium partial pressure of oxygen at the cathode and anode respectively. So

$$\mathscr{E} = 4.97 \times 10^{-5} \ T \ \log \frac{p''O_2}{p'O_2} \ .$$

D.   Sealed Capsule Technique

In order to obtain reliable data on phase relations, where the vapor pressure of the oxide is appreciable, a sealed capsule technique can be used. In this way, the overall composition of mixtures of oxides is fixed at the original composition charged to the capsule. In the present work, the sealed capsule was fused silica. An inner crucible of molybdenum or platinum foil was used in some cases.

IV. EXPERIMENTAL PROCEDURES

A.   Furnaces and Temperature Control

Four furnaces were used in this investigation. A Marshall "wire wound" horizontal tube furnace with 36 mm bore and 35 cms heated length was used for the transpiration experiment. A horizontal fused silica tube of 16 mm I.D. and 91.5 cms long was used as the reaction chamber. Fig. 4 shows a sketch of the apparatus. Baffles were placed on either side of the sample boat, which acted as radiation shields and helped maintain laminar flow of gas.

The second furnace was a nichrome wound horizontal tube furnace, used in purifying argon gas for the transpiration experiment. A Vycor tube 60 cms long and 17 mm in diameter was packed with steel wool and placed in the furnace. The temperature of this furnace was maintained at $700\,^\circ C$.

A Marshall "wire wound" furnace with 38 mm bore and 35 cms heated length was used for the solid electrolytic galvanic cell experiments. A vertical fused silica tube 28 mm I.D. and 91.5 cms long was used as the reaction chamber. A stainless steel baffle was used as the radiation shield. Fig. 5 shows a sketch of the apparatus used.

For MoO_2-SiO_2 chemical reaction experiments a silicon carbide resistance heated furnace capable of reaching $1600\,^\circ C$ was used. A vertical mullite tube 25 mm I.D. and 102 cms long was used as the reaction chamber. Fig. 6 schematically represents the apparatus used in this experiment.
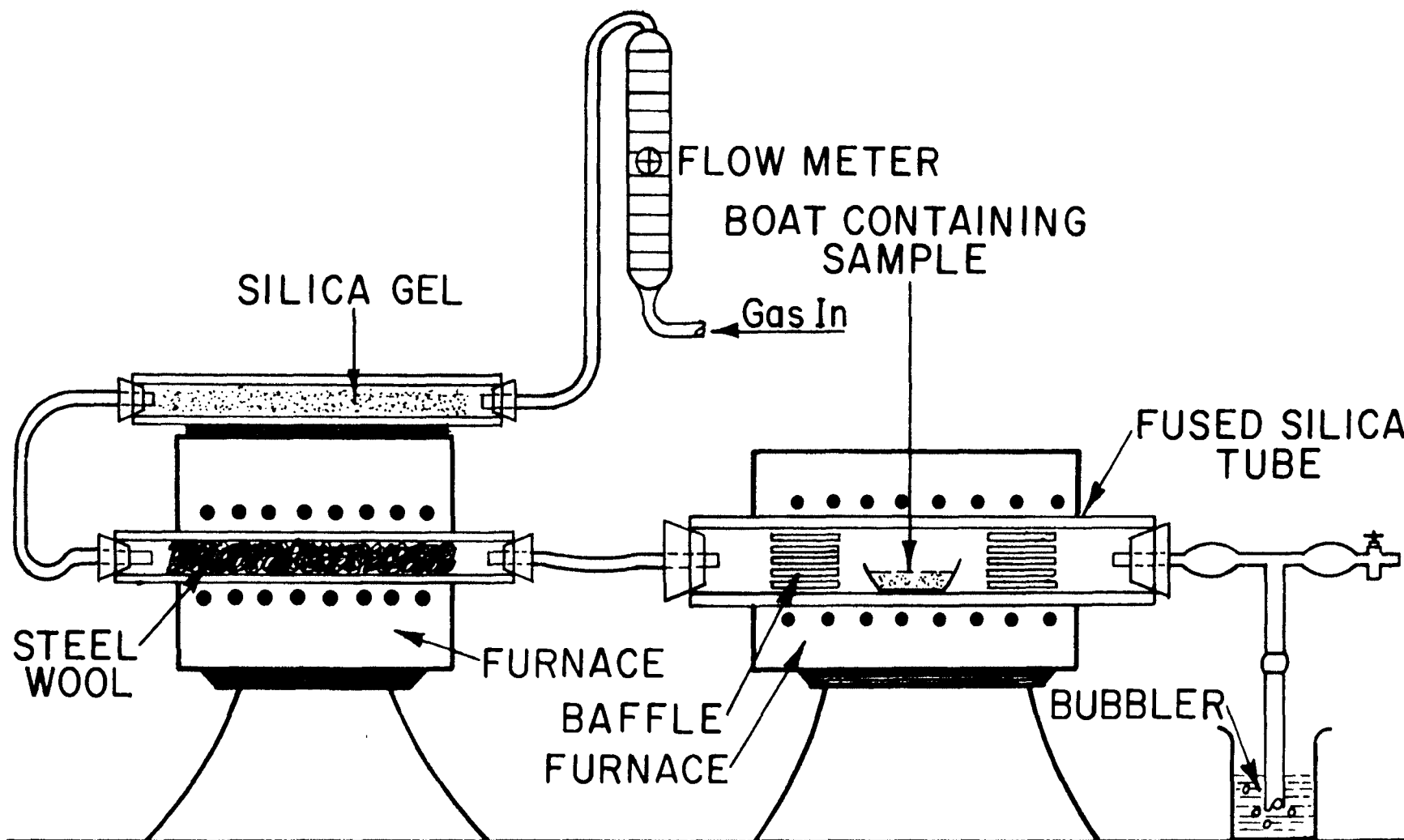
Figure 4. Schematic Diagram of the Apparatus for Transpiration Experiment.

REF. GAS

RUBBER CORK

VYCOR TUBE

RUBBER CORK

FUSED SILICA TUBE

MULLITE TUBE

C. S. Z. TUBE

PLATINUM DISC

ALUMINA DISC

RUBBER CORK

Rh THERMO-COUPLE

+ve

−ve Pt LEADS TO POTENTIOMETER

CONTROLLING PLATINEL THERMO-COUPLE

FURNACE

FIBRE FRAX

SILICA CRUCIBLE

SAMPLE

BAFFLE

ALUMINA PEDESTAL

ARGON GAS
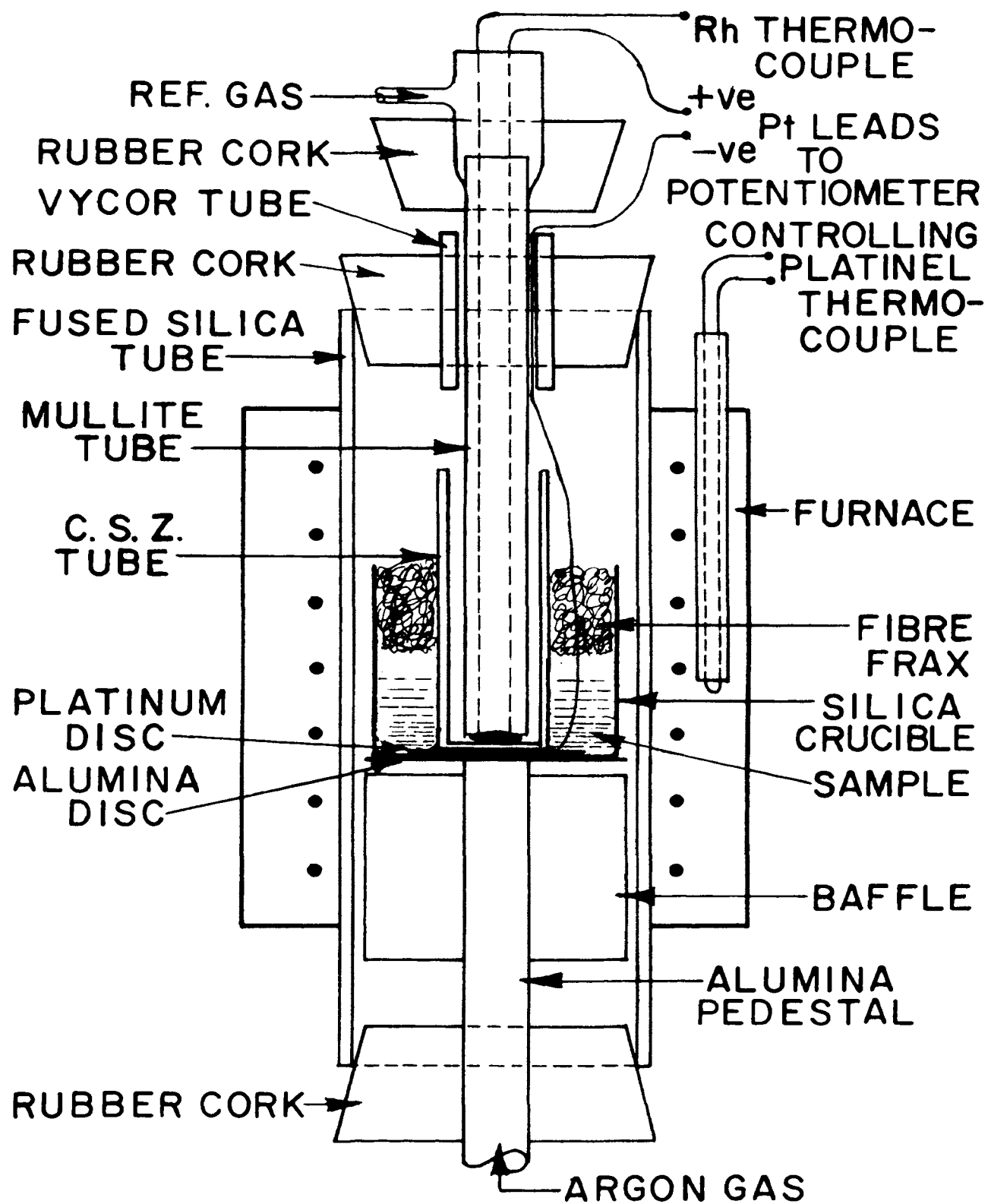
Figure 5. Apparatus for Solid Electrolytic Galvanic Cell Experiments.
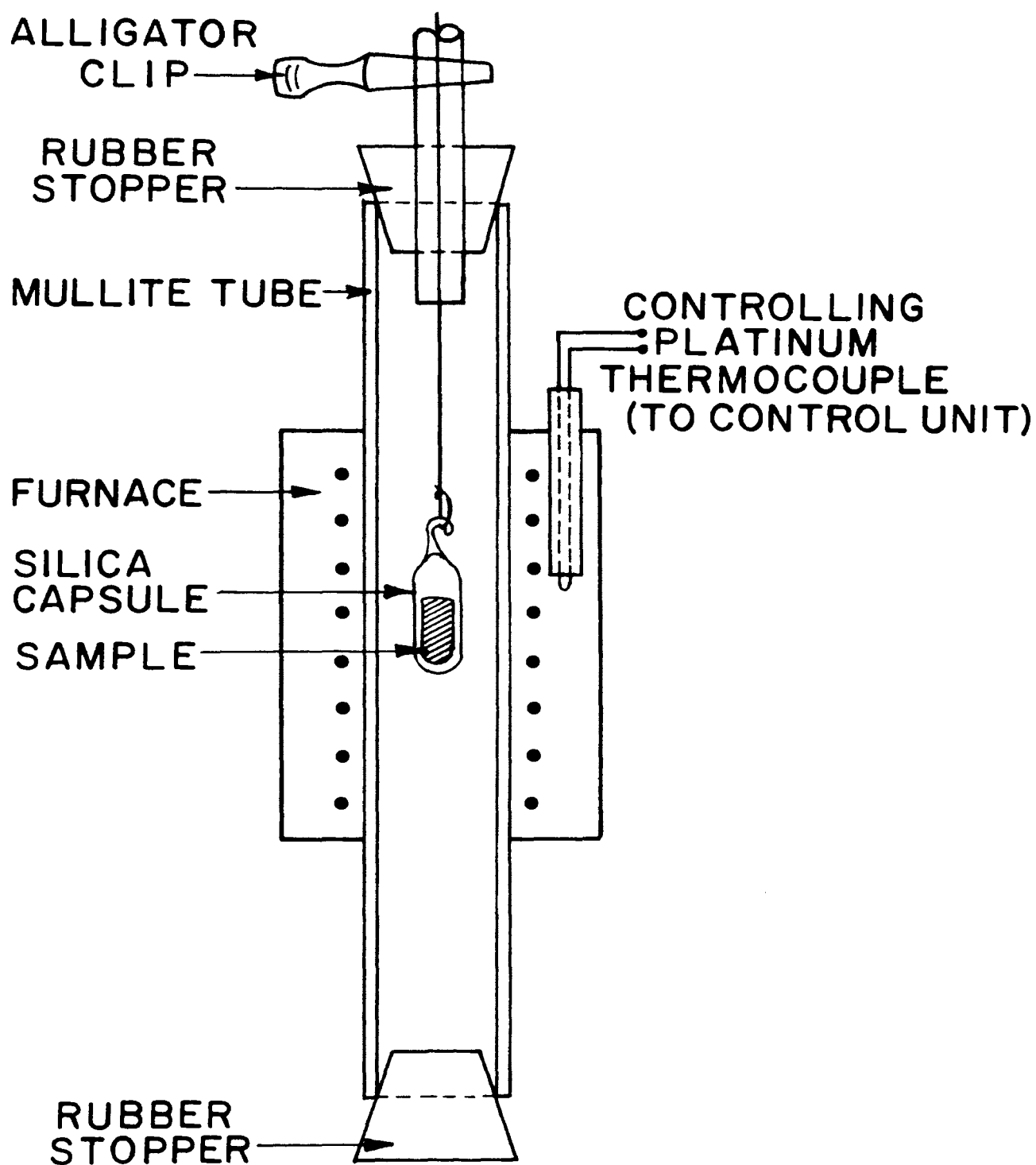
Figure 6.   Schematic Diagram of the Apparatus for
            Open and Closed Capsule Experiments.

The determination of the phase boundary between
solid MoO_2 and liquid molybdenum oxide was carried out
in the same furnace that was used for the solid electro-
lytic galvanic cell.

The temperature of the "wire wound" furnaces was con-
trolled by a Barber Colman 272P Capacitrol temperature
control unit with a Platinel thermocouple which regulated
the temperature to $\pm 2°C$. The temperature of the silicon
carbide furnace was controlled by a Barber Colman 472
Capacitrol controller with the aid of a Pt/Pt-13% Rh
thermocouple, which also regulated the temperature to $\pm 2°C$.

B.   Temperature Measurements

A Platinel II thermocouple was used for the tempera-
ture measurement of the "wire wound" furnaces. A similar
Platinel thermocouple, standardized by the National Bureau
of Standards at 900°, 1000° and 1100°C was used to cali-
brate the working thermocouple. The furnace temperature
was set using the controller setting and checked by the
working thermocouple. The working thermocouple was used
for temperature measurements before each run. Periodic
checks of the furnace temperature were made with the stand-
ardized thermocouple. The length of the hot zone where
temperature did not vary by more than $\pm 5°C$ was 5 cms.

A Pt/Pt-10% Rh thermocouple was used for temperature
measurements of the silicon-carbide furnace. The thermo-
couple was compared to a standard thermocouple of the
same composition calibrated by the National Bureau of
Standards. The length of the hot zone where temperature
did not vary by more than $\pm 5°C$ was 5 cms. A Leeds and
Northrup potentiometer model #8690 was used for the e.m.f.
measurements of the thermocouples.

C. Atmosphere Control

In transpiration experiments, argon gas was used as the carrier gas for molybdenum oxide vapors. Prepurified grade argon gas as supplied by Matheson was passed through a tube packed with silica gel to remove moisture, and then over hot ($700\,^\circ C$) steel wool which served as a getter for oxygen. After a couple of runs, any iron oxide on the steel wool was reduced with hydrogen gas.

In the solid electrolytic galvanic cell experiments, nitrogen or argon was used as the inert medium to sweep out the 1% O_2 + argon reference gas.

In order to generate a wide range of desired oxygen partial pressures during the equilibration of mixtures of MoO_2 and SiO_2, CO_2 and CO were mixed in desired proportions. Flow meter tubes in a gas proportioner were used for the mixing of CO_2 and CO and for maintaining the proper flow rates of argon gas in transpiration and solid electrolytic galvanic cell experiments. All the experiments to determine the phase boundary between solid MoO_2 and liquid molybdenum oxide were done in evacuated sealed silica tubes.

D. Preparation of Starting Materials

MoO_2 was prepared by reduction of MoO_3 with a calculated quantity of Mo metal at $900\,^\circ C$ in a sealed and evacuated silica capsule. The stoichiometry of MoO_2 and MoO_3 was determined by a gravimetric method. The details of preparation and stoichiometry experiments are presented in Appendix I.

The sample for the transpiration experiment was prepared by melting together MoO_2 and MoO_3. A calculated amount of MoO_3 and MoO_2 were weighed out in a porcelain

mortar using an analytical balance which was accurate to about 0.1 mg. The sample was mixed well in a mortar with the help of few drops of acetone. This mixture was dried and enclosed in an evacuated silica crucible. It was heated to 950°C in a Globar furnace for 2 hours, before cooling it rapidly in air. The same procedure of weighing and mixing of the sample was followed for other experiments.

For the galvanic cell, a mixture of 80% MoO_3 and 20% MoO_2 powders by weight were used at 900° and 950°C. A 75% MoO_3, 25% MoO_2 mixture was used at 1000°C.

The samples for MoO_2-SiO_2 chemical reaction experiments were prepared by mixing -200 mesh MoO_2 and SiO_2 in ratios 20 : 80, 40 : 60, 50 : 50, 60 : 40, 70: 30 and 80 : 20 by weight. 2% molybdenum metal was added to react with any excess oxygen in the MoO_2. The method of preparing SiO_2 from silicic acid is described in Appendix I.

E. Transpiration Experiment

A weighed premelted sample was placed in a platinum or silica boat. The boat with baffles on either side was pushed into the cold zone of the silica furnace tube. Purified argon was then passed over the boat for 10 min. into the tube to sweep away all the air inside the tube. Once completely free from air, the tube was pushed into the furnace so as to place the boat in the center of the hot zone. The boat reached the equilibrium temperature of 950 $\pm$ 5°C in about 10 minutes, during which about 5 cc/min of argon was passed to maintain a slight positive pressure in the tube. The argon flow was then increased to the desired rate and was maintained constant for one hour, the duration of each run. After a measured

volume of the gas had been passed, the sample was cooled
by withdrawing the tube from the furnace to cool the boat
while a very small flow rate of argon was passed. The
cooled boat was taken out of the furnace and the loss in
weight was noted. Sample was added in the boat to compen-
sate for this loss for the next run.

The loss in weight of the sample during the heating
and cooling period was determined by a separate exper-
iment. This loss was subtracted from the total loss to
determine the actual weight of the molybdenum oxides trans-
ported at 950°C. The condensed molybdenum oxide was cleaned
from the silica tube with a concentrated warm solution of
NaOH, which dissolved the oxides to a large extent. The
silica boat cracked after two or three runs, whereas the
platinum boat lasted for several runs.

The transpiration method involved some complication
in order to obtain the "plateau" region. Some preliminary
experiments were done with a bigger diameter reaction tube,
using nitrogen as carrier gas. A well defined plateau
could not be obtained. This could have been due to the
presence of a comparatively large "dead volume" above the
sample. This space between the sample and the reaction
tube made it difficult to obtain saturation of the carrier
gas stream over any range of carrier gas flows.

F. Preliminary Experiments for the Galvanic Cell

In order to have very good contact between the elec-
trodes and the calcia stabilized zirconia (CSZ) electro-
lyte tube, the inside and outside of the CSZ tube was
coated with a platinum paste. The tube was then heated
slowly to 600°C for ½ an hour to platinize the tube.

Before measurements were made on the molybdenum oxide

system, the solid electrolytic galvanic cell and circuit was tested at 950°C by using pure oxygen and a premixed 1% oxygen-argon mixture to create a difference in the potential on either side of the electrolyte. The e.m.f. in millivolts was noted with respect to different flow rates of gases used. The polarity of the cell was changed by changing the direction of gas flow and the e.m.f. was again noted with the same flow rates previously used. The e.m.f. obtained is shown in Table VI in Appendix IV, and was compared to the calculated e.m.f. by the equation:

$$\mathscr{E} = 4.97 \times 10^{-5} \, (1223) \, \log \frac{p''O_2}{p'O_2}.$$

The e.m.f. in millivolts was found to be 0, when pure oxygen was used on both sides of the cell.

G. Cell Assembly and Operation

Approximately 7-8 gms of sample was placed in a cylindrical silica crucible about 1" OD and 2" in length. This combination of sample weight and crucible size permitted an adequate sample volume to cover the electrodes and allowed enough space for the sample to expand without breaking the CSZ tube. A platinum disc was placed on the surface of the sample to minimize the direct contact between the molybdenum oxides and electrolyte. Another Pt disc was placed in contact with this Pt disc with a Pt wire spot welded to it. The platinized CSZ tube with a Pt/Pt-10% Rh thermocouple inside was placed firmly on this Pt disc. The Pt leg of the thermocouple acted as the lead from the inside (reference) electrode. The annular space between the CSZ tube and crucible was filled with Fibre Frax, to minimize the oxidation of MoO_2 by the reference gas and loss of vapors of molybdenum oxides.

The cell was lowered in the silica furnace tube at

room temperature and was supported by an alumina pedestal.
An axial compressive load was applied to the CSZ tube by
a weight which is not shown in Fig. 5. The load served
to assure good contacts between the platinum leads and the
CSZ electrolyte. The power was then supplied to the fur-
nace, and argon gas was passed through the cell and fur-
nace tube at 80-90 cc/min. As soon as the control thermo-
couple stabilized the furnace temperature, the cell tem-
perature was measured by the thermocouple. The e.m.f. in
millivolts was noted with varying flow rates of argon and
reference gas.

Since the expected MoO_2/liquid molybdenum oxide vs.
1% O_2-argon mixture reference gas e.m.f. was higher than
the e.m.f. that could be measured by the Leeds and Northrup
potentiometer model #8686, a bucking voltage of 200 milli-
volts was put in the circuit as shown in Fig. 7.

CIRCUIT DIAGRAM

Figure 7. Sketch of Circuit for E.M.F. Measurements
Using Solid Galvanic Cell.

The experiments were separately performed at $900°$, $950°$ and $1000°C$ with both $1\% \ O_2$ argon mixture and $Cu-Cu_2O$ as reference electrodes.

Two different sizes of CSZ tubes were obtained from ZIRCOA Co. The CSZ tubes were of ¼" and ½" OD and 6" in length.

H. Determination of Phase Boundary Between Solid MoO_2 and Liquid Molybdenum Oxide

About a gm of MoO_3 and MoO_2 sample was transferred to a 3 mm ID and 2 cms long platinum capsule, which was then fused shut. The sealed Pt capsule was placed in a silica capsule which was evacuated with a vacuum pump and sealed in a torch. The capsule and sample were lowered in the hot zone of the furnace at the desired temperatures (950-1100°C). The sample was allowed to remain in the furnace for approximately 12-16 hours. It was then rapidly removed from the furnace and quenched in water. Microscopic examination of the quenched sample was made as shown in Appendix II.

I. Chemical Reaction Between MoO_2 and SiO_2

1. Sealed Capsule Technique

A mixture of MoO_2 and SiO_2 was placed in a molybdenum foil envelope. The sample was then placed in a 6 mm ID and 3-4 cms long silica capsule which was sealed after evacuating. The silica capsule was then lowered into the hot zone of the Globar furnace at the desired temperatures (1300-1550°C). The sample was allowed to remain in the hot zone for approximately 24 hours. It was then quickly removed and cooled in air. Examination of the quenched sample was made by x-ray diffraction as shown in Appendix III.

2. CO_2/CO Atmospheres

Mixtures of MoO_2 and SiO_2 were placed in a silica capsule and lowered in a controlled CO_2/CO atmosphere in the wire wound or Globar Vertical furnace. The sample was in the hot zone for approximately 6 hours. It was then pulled up and was cooled in the cold zone of the furnace. The visual appearance of the sample served to determine if any melting has taken place.

V. EXPERIMENTAL RESULTS

The experimental results are presented in two forms, a tabular form in Appendix IV and in the form of summary tables and graphs in this section.

The results of transpiration and solid electrolytic galvanic cell measurements are presented in tables in Appendix IV. Fig. 8 summarizes the transpiration data as a graph of vapor density vs. flow rate of argon gas. The vapor density was calculated on the assumption that $(MoO_3)_{3(g)}$ was the only significant gaseous species at 950°C. In the plateau region BC, the vapor density is independent of the flow rate. The plateau region in the present study was found to be small due to the high vapor pressures of molybdenum oxides. At low flow rates of argon gas (curve AB), the vapor density is too high, while at high flow rates (curve CD) the vapor density is too low. Table II summarizes the transpiration results.

Table II Weight Loss and Vapor Density of
Molybdenum Oxide Transpired at
950°C. All Volumes at STP.

Run Number	Argon Flow Rate cc/min	Weight Loss in Gms/Hr	Vapor Density in Milli- moles per 100 cc Argon	Avg. Vapor Density in Millimoles per 100 cc Argon	pO_2 at Plateau in Atm.
1a	25	1.1841	0.183		
1b	25	1.1941	0.184		
2	32.5	1.39	0.165	0.1675	$10^{-7.20}$
3	41.0	1.805	0.1700		
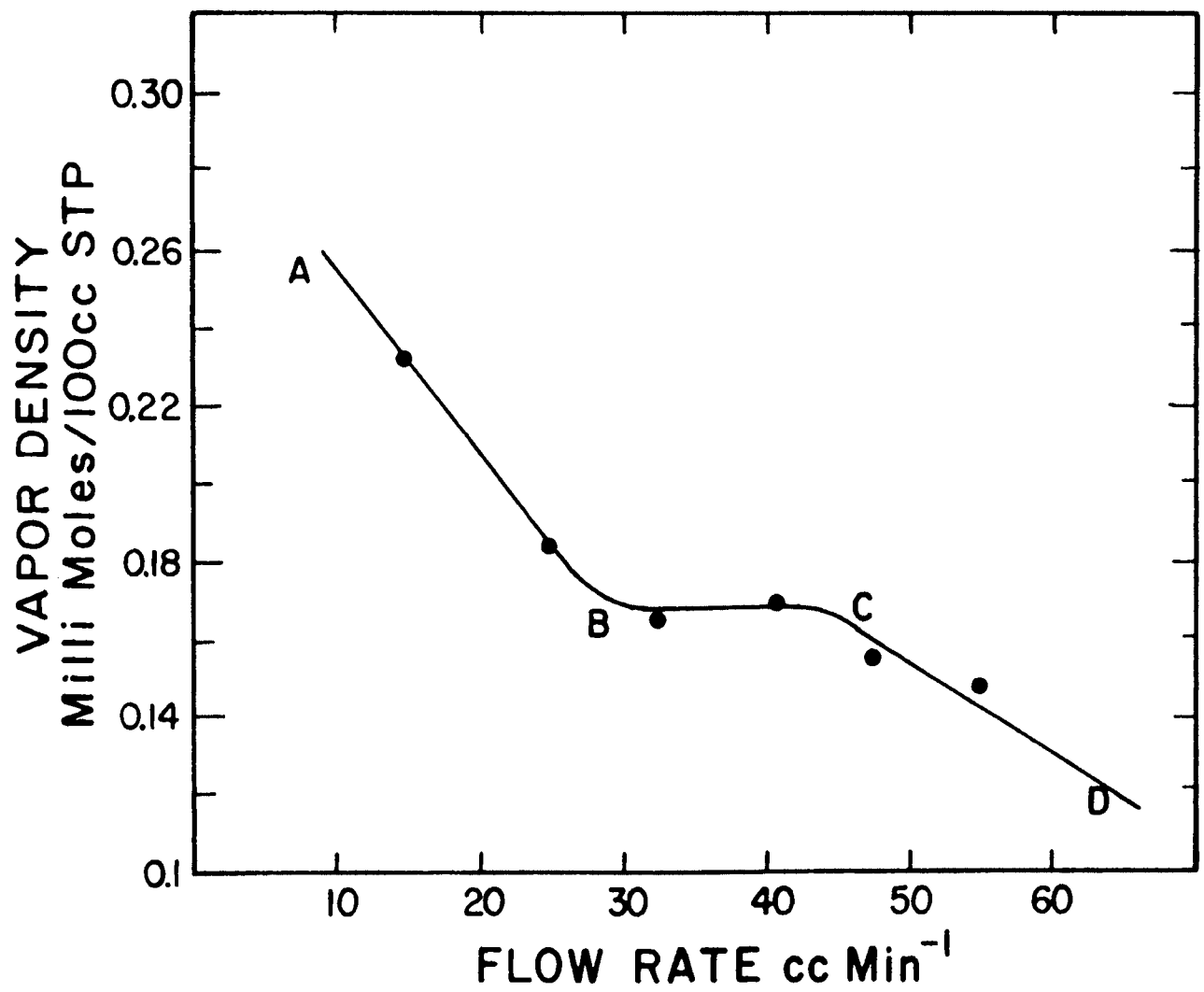
Figure 8. Variation of Vapor Density with Argon Flow.

The reproducibility of weight loss measurements was satisfactory as shown by run la and lb in the table. The pO_2 calculated from the average vapor density at the plateau (runs 2 and 3) was $10^{-7.2\pm.04}$ atm., based on $(MoO_3)_3$ as the only significant gaseous species. This calculation is shown in Appendix V.

Tables III and IV summarize the results of solid electrolytic galvanic cell measurements using $Cu-Cu_2O$ and gas as reference electrodes.

Table III pO_2 (in Atm) Obtained by Using Cell with $Cu-Cu_2O$ as Reference Electrode, Compared to Calculated pO_2 in Equilibrium with Solid MoO_2 and Pure $MoO_3(\ell)$, [21] and $a_{MoO_3(\ell)} < 1$ [1,21]

Temperature °C	pO_2 Obtained from the Galvanic Cell	Fictive Calculated pO_2 in Equilibrium with $MoO_2(s)$ and Pure $MoO_3(\ell)$	Calculated pO_2 in Equilibrium with $MoO_2(s)$ and Liquid Oxide where $a_{MoO_3(\ell)} < 1$
900	$10^{-7.60}$	$10^{-7.216}$	$10^{-7.33}$
950	$10^{-7.02}$	$10^{-6.86}$	$10^{-7.05}$
1000	$10^{-6.43}$	$10^{-6.53}$	$10^{-6.75}$

The pO_2 in the last column in Table III was calculated by assuming that liquid oxide in equilibrium with solid MoO_2 obeys Raoult's law. The liquid was assumed to be a solution of MoO_2 and MoO_3. The atomic percent of oxygen at the phase boundary given by Phillips and Chang[1] was about 74% at 900°C, 73.7% at 950°C and 73.3% at 1000°C. The pO_2 obtained by the solid electrolytic galvanic cell using $Cu-Cu_2O$ as a reference electrode, and the pO_2 calculated as above in the last column of Table III, were in good

agreement at 950°C but not as good at 900° and 1000°C.

Table IV Summary of the Galvanic Cell Results Using 1% O_2-Ar and Air as Reference Electrode, vs. MoO_2/Liquid Oxide. Flows at STP.

Temperature °C	Flushing Gas Flow (Argon or Nitrogen) in cc/min	Ref. Electrode Flow (1% O_2-Ar or Air) in cc/min	e.m.f. in mv	pO_2 in Atm Obtained from the Average e.m.f. of all Flow Rates
900	85	62	288.73	$10^{-6.87}$
900	85	43*	361.5	$10^{-6.86}$
950	85	48	281.94	$10^{-6.62}$
1000	90	30	287	$10^{-6.53}$

* Air used as a reference electrode.

The pO_2 obtained by using a gas reference electrode is higher at 900° and 950°C than those using a Cu-Cu_2O reference electrode. This is discussed more fully in the next section.

The flow rate of the flushing gas affected the e.m.f. of the cell. When using Cu-Cu_2O as a reference electrode, at 900°C the e.m.f. of the cell changed by only ± 0.5 mv with a flow of range of 0-100 cc/min. At 950°C, the e.m.f. decreased sharply at a high flow rate of about 180 cc/min. At 1000°C in a cell using 1% O_2-Ar gas mixture as a reference electrode, the e.m.f. dropped by more than 1 mv with the onset of the flow of flushing gas, but remained nearly constant at various high flow rates. Etsell and Flengas[34] have discussed more fully the effect of gas flow rate on the e.m.f. of a CSZ cell. The present experiments were

carried out before the above paper was published, so that we were unaware of the exact flow rate--e.m.f. dependency. The effect of flow rate on e.m.f. is discussed in the next section in light of the findings of Etsell and Flengas.[34]

In Fig. 9, log $P_{(MoO_3)_3(g)}$ vs. log pO_2 is plotted at 900°, 950° and 1000°C. The dashed dot line represents the 900°C data for pO_2 in equilibrium with solid MoO_2 and liquid molybdenum oxide. The solid lines represent the 950°C data, and the dash-cross lines represent the 1000°C data. The pressure of monomer trioxide was calculated to be less than 10^{-7} atm. at all temperatures, so is not shown on the diagram.

In MoO_2-SiO_2 chemical reaction experiments, no solid solution or compound formation was detected by x-ray diffraction of quenched samples. A shift of a few minutes in the lines for MoO_2 was noticed especially at $2\theta = 37°$, which could be expected due to a change in stoichiometry of MoO_2 by reaction with the molybdenum metal added to the sample. No evidence of melting occurred in any of the sample.

Some volatilization of MoO_2 was noticed at high temperatures (1550°C) in a CO_2:CO atmosphere of pO_2 equal to $10^{-4.6}$ atm.

The results of the liquidus phase boundary experiments between 950-1100°C are given in Table IX of the Appendix IV. These experiments were intended mainly to look for any large discrepancy between the actual MoO_2/liquid oxide phase boundary, and the published phase boundary,[1] and not to actually establish the boundary itself. Since the few experiments conducted gave results close to the phase boundary of Phillips and Chang,[1] no further experiments were carried out.
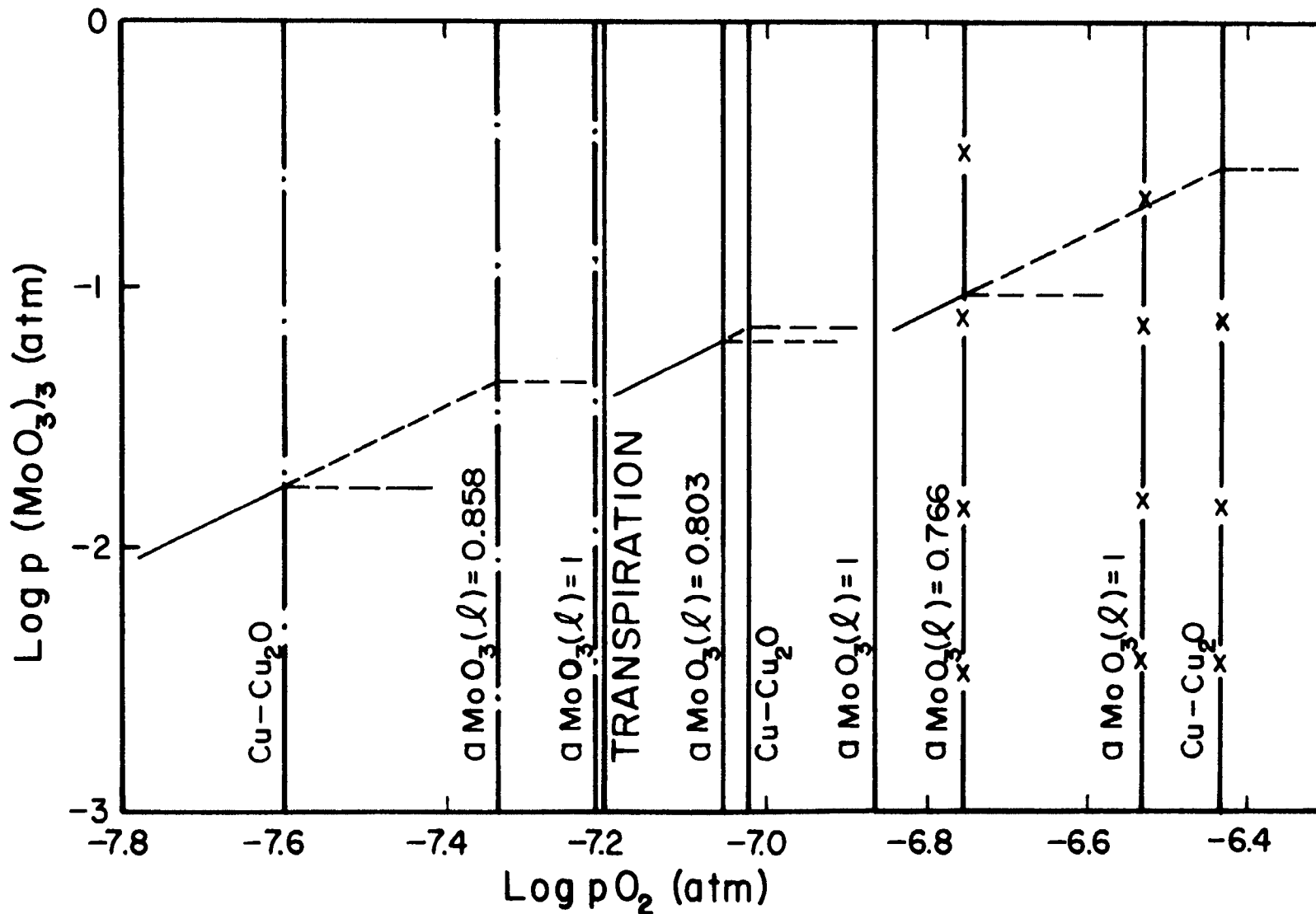
Figure 9. Summary of Experimental and Thermochemical Data for pO_2 at the MoO_2/Liquid Oxide Boundary. Dashed-dot Line Represents the Data at 900°, Solid Lines Represent the Data at 950° and Dashed-cross Line Represents the Data at 1000°C.

VI.   DISCUSSION OF RESULTS

The partial pressure of oxygen obtained at the $MoO_2/$ liquid oxide phase boundary by the transpiration experiments was $10^{-7.20} \pm 0.04$. This is in good agreement with the pO_2 of $10^{-7.02} \pm 0.20$ obtained by the e.m.f. method using Cu/Cu_2O as a reference electrode and $10^{-7.05}$ as obtained by thermodynamic calculations.[1,21] Such agreement confirms the assumption that $(MoO_3)_3$ is the only significant gas specie at $950°C$ in equilibrium with solid MoO_2 and liquid oxide. If significant amounts of transpired oxide were other than the trimer, the calculated pO_2 would be lower than $10^{-7.2}$ and thus would be in greater disagreement with the pO_2 obtained by the other measurements.

For purposes of discussion, all of the experimental results and thermodynamic calculations for pO_2 at the $MoO_2/$ liquid oxide phase boundary are plotted in Fig. 10. The line labeled $a_{MoO_3(\ell)} = 1$ gives the fictive pO_2 based on calculations from Gulbransen's data,[21] for the pseudo-equilibrium between pure $MoO_3(\ell)$ and MoO_2. The line labeled $a_{MoO_3(\ell)} = N_{MoO_3(\ell)}$ is the calculated pO_2 at the phase boundary between $MoO_2(s)$ and liquid molybdenum oxide of composition as inferred from the phase diagram.[1] As mentioned earlier, the pO_2 at the actual phase boundary was calculated as shown in Appendix V, and is based on an ideal MoO_2-MoO_3 solution. The line labeled 1% O_2-Ar is based on the pO_2 obtained by the galvanic cell measurements, using 1% O_2-Ar as a reference electrode. The line labeled Cu-Cu_2O is based on the pO_2 obtained by the galvanic cell measurements using Cu-Cu_2O as reference electrode.

The error bands on Fig. 10 represent estimates of the uncertainty in the experimental results. The error band on
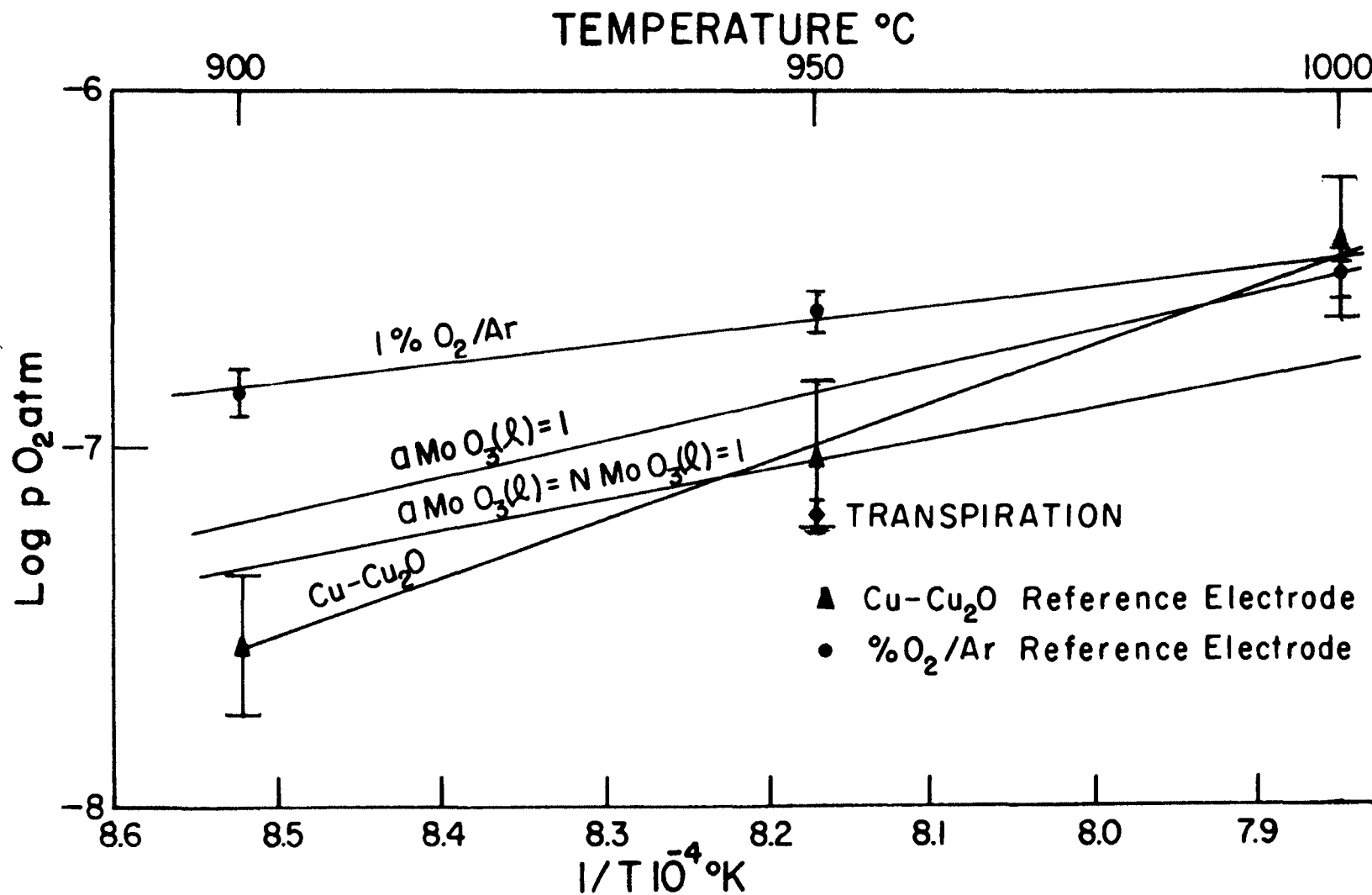
Figure 10. Log pO_2 as a Function of $1/T$ for All Experimental and Calculated pO_2 at MoO_2/Liquid Oxide Boundary.

the Cu-Cu$_2$O line is drawn taking in account about ± 500 calories/mol O$_2$ in the free energy of formation of Cu$_2$O as given by Rizzo et al.,[35] plus the fluctuations in e.m.f. of the cell. The error band on pO$_2$ obtained by the transpiration method is estimated from the scatter of data around the plateau. The error band on the 1% O$_2$-Ar line is a measure of the fluctuations in e.m.f. of the cell which were caused by changes in gas flow rate. Since there is no way of assessing the uncertainty in Gulbransen's thermochemical data,[21] and the phase boundary given by Phillips and Chang,[1] the uncertainty of the pure MoO$_3$(ℓ) line and the $a_{MoO_3(\ell)} = N_{MoO_3(\ell)}$ line are unknown.

There is reason to believe that the pO$_2$ obtained with Cu-Cu$_2$O as the reference is the most reliable pO$_2$ for equilibrium with solid MoO$_2$ and liquid molybdenum oxide. Cu-Cu$_2$O gave a slightly higher oxygen potential than MoO$_2$/ liquid oxide, which is in accord with certain earlier experiments that were not mentioned previously. A piece of copper wire was sealed in a capsule above a mixture of MoO$_2$(s) and liquid molybdenum oxide, and equilibrated at 950° and 1000°C for 6 hours. The Cu wire did not show any oxidation. Another check on the reliability of the e.m.f. data was the reproducibility of the e.m.f. at 950°C after the cell had been used at 1000°C. The e.m.f. obtained was compared with the e.m.f. obtained at 950°C in an independent experiment, and was found to be the same.

The discrepancies in partial pressure of oxygen obtained by using Cu-Cu$_2$O vs. gas as a reference electrode in the galvanic cell measurements at 900° and 950°C can not be explained without reference to the effect on e.m.f. of the flow rate of gases in and around the cell. The e.m.f. was found to be affected by the rate of flow of the gas

used as reference electrode and by the inert flushing gas. These flow rate effects were more marked as the temperature increased. A likely explanation is given by Etsell and Flengas[34] who discuss the effect of flow rate on e.m.f. of a CSZ cell at great length. They found that the effect is greater at high temperatures, and the e.m.f. is too low at inadequate flow rates.

Etsell and Flengas[34] also mention that a small amount of electronic conductivity and perhaps porosity in the electrolyte may exist. Both of these features lead to an unavoidable transfer of oxygen; in the present case, from the inner reference electrode to the outer electrode. Since the difference in oxygen potential between $Cu-Cu_2O$ and molybdenum oxide electrodes was very small, the electronic potential was eliminated to a greater extent than in the case of using gas as a reference electrode. Although investigators have shown that $Zr_{0.85}Ca_{0.15}O_{1.85}$ could be used at oxygen pressure as low as 10^{-15} atm, the observations of Peters and Moebius,[36] later confirmed by Schmalzried[37] indicate that an electronic component of zirconia based electrolytes could become significant at low oxygen chemical potential <u>and high differences in pO_2</u> at the two electrodes.

A drop in e.m.f. with time was noticed after operating the cell for a certain length of time. Rapp[33] stated that the drop could be due to the formation of a thin blocking layer of MoO_2 at the electrode/electrolyte interface. A thin layer of some sort was found on the CSZ tube in the present work which appeared to be MoO_2. If some unknown chemical reactions between the electrolyte and $MoO_2(s)$ or liquid oxide took place, some small e.m.f. could have been generated.

The data presented in Fig. 10 appears at first glance to be difficult to interpret. For example, the data at 900°C for Cu/Cu_2O reference electrode and that calculated from thermodynamic data and the phase diagram ($a_{MoO_3(\ell)}$ = $N_{MoO_3(\ell)}$) are in good agreement, as the same data plus transpiration data are at 950°C. The 1% O_2-Ar reference electrode data at 900° and 950°C stand by themselves; however, at 1000°C all experimental data are in good agreement, but the calculated pO_2 is significantly lower. Gulbransen's [21] data has no stated limits of uncertainty, nor does data from the JANAF table, [22] for the high temperature free energy data for $MoO_2(s)$ and $MoO_3(\ell)$. Therefore, an analysis of the uncertainty in the fictive and actual pO_2 calculated for MoO_2/liquid oxide equilibrium can not be made.

From the JANAF tables, $\Delta H°$ for the reaction:

$$MoO_2 + \frac{1}{2} O_2 \rightarrow MoO_3(\ell)$$
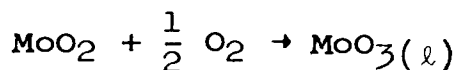
is -47,200 cal/mol O_2 at 1300°K, and is -46,800 cal/mol O_2 from Gulbransen's[21] data. For the equilibrium reaction between MoO_2, O_2 and the liquid oxide of equilibrium composition, ΔH is -42,800 cal/mol of O_2. These values compare with -74,000 cal/mol for the e.m.f. data using $Cu-Cu_2O$ as a reference electrode and -24,000 using a gas reference electrode. No explanation can be offered between these large differences in ΔH of reaction.

Since no chemical reactions were found between MoO_2 and SiO_2 up to 1550°C, it was felt justified to use silica capsules and crucibles to prepare MoO_2 and equilibrate the samples for the transpiration experiments. Bartlett et al. [38] in their work on oxidation of molybdenum silicides found separate phases of Mo, MoO_2 and MoO_3 and SiO_2, depending on oxygen pressure. They found no reports of any

mixed oxide compound of molybdenum and silicon in their
literature review.

The experiments performed to check the phase boundary
line between solid MoO_2 and liquid molybdenum oxide from
950°-1100°C were not sufficient to accurately establish the
phase boundary. The data obtained were in relatively close
agreement with the dashed line drawn on the diagram of
Phillips and Chang.[1]

The study of the Mo-O system should be continued.
Based on the results of this study and other published work,
the following areas seem to be the most important for
further research:

1. It would be desirable to find the exact proportions of
polymeric gaseous species in equilibrium with solid MoO_2
and liquid molybdenum oxide of specified composition, by
the use of a mass spectrometer or other refined technique
to resolve the reported discrepancies in the literature.

2. A vapor pressure study of liquid molybdenum oxide
should be made under different fixed pO_2 of the gas by the
transpiration method to determine the extent of change in
the vapor pressure of liquid molybdenum oxide with compo-
sition.

3. Due to the limitations of the furnace, reactions in the
MoO_2-SiO_2 system could not be studied above about 1550°C.
A study of this system to and above the melting point of
MoO_2 and SiO_2 would determine the extent of liquid forma-
tion between these oxides. This would help in understand-
ing the high temperature oxidation resistance of $MoSi_2$.

4. A new cell should be designed in which only oxide va-
pors (in equilibrium with condensed oxide phases) would be
allowed to come in contact with the CSZ tube. This would

eliminate any reactions between the CSZ tube and liquid or solid molybdenum oxides. The CSZ tube could be placed in a cell above the sample with any gas mixture or metal oxide as a reference electrode.

5.   Further work should be conducted with gas reference electrodes, in which the flow rate of gas is much more carefully controlled as discussed by Etsell and Flengas.[34]

VII. SUMMARY AND CONCLUSIONS

The object of this study was to determine the oxygen partial pressure in equilibrium with solid MoO_2 and liquid molybdenum oxide at $900°$, $950°$, and $1000°C$. The pO_2 is a primary factor in establishing thermodynamic equilibrium between solid and liquid molybdenum oxide.

At $950°C$ the pO_2 obtained by the e.m.f. method using $Cu-Cu_2O$ as a reference electrode was found to be in good agreement with the pO_2 obtained by the transpiration method and pO_2 calculated at the phase boundary between $MoO_{2(s)}$ and liquid molybdenum oxide of composition as inferred from the phase diagram drawn by Phillips and Chang.[1] Such an agreement confirmed the assumption that the trimer is the only significant gaseous specie at $950°C$.

X-ray studies of equilibrated MoO_2 and SiO_2 mixtures, quenched from temperatures as high as $1550°C$, confirmed that there is no compound or solid solution formation between the two oxides, at pO_2 ranging from that in equilibrium with Mo metal, up to about 10^{-4} atm. The phase boundary between $MoO_{2(s)}$ and liquid molybdenum oxide was found to be close to that inferred by Phillips and Chang.[1]

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VITA

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He is a student member of the American Society of Metals and the Metallurgical Society of AIME.

APPENDIX I

PREPARATION OF THE STARTING MATERIALS

Reagent grade molybdic oxide anhydride and molybdenum metal powder were obtained from Fisher Scientific Company. The molybdic oxide had the following chemical analysis

Assay (as MoO_3) - - - - - - - - - - - - - - - -	100.2%
Insoluble in dilute NH_4OH - - - - - - - - - -	0.001%
Chloride (Cl) - - - - - - - - - - - - - - - -	0.001%
Nitrate (NO_3) limit about 0.003%- - - - - - -	P.T.
Sulphate (SO_4)- - - - - - - - - - - - - - - -	0.020%
Heavy metals (as Pb)- - - - - - - - - - - - -	0.002%
Ammonium (NH_4)- - - - - - - - - - - - - - - -	0.001%
Arsenate, Phosphate and Sulphate (as SiO_2)- -	0.0003%

Molybdic oxide anhydride was heated in a porcelain crucible at 550°C in air for two hours to obtain MoO_3 powder free from any moisture and volatile impurities.

The molybdenum metal was of 99.8% purity.

A.   Preparation of Molybdenum Dioxide

Molybdenum dioxide was prepared by heating a 100 gm mixture of MoO_3 and Mo metal, weighed out in a ratio of two moles of oxide to one mole of metal. The mixture was heated slowly in an evacuated and sealed vycor or quartz capsule and held for 24 hours. A uniform dark brown powder was obtained, which gave an x-ray diffraction pattern of molybdenum dioxide. The MoO_2 was ground to pass a 100 mesh screen.

B.   Stoichiometry of MoO_2 and MoO_3

The O/Mo ratio in the prepared molybdenum dioxide and the reagent grade trioxide was determined by weight loss on hydrogen reduction to metallic Mo. MoO_2 or MoO_3 were placed in a nickel boat in a tube furnace, similar

to the transpiration experiment set up shown in Fig. 4.
The furnace was slowly heated while a steady flow of
H_2 was passed over the oxide. The sample was held at
700°C for 10-12 hours until the reduction of both oxides
to Mo metal was complete, according to the following over-
all chemical reactions:

$$MoO_2 + 2H_2 \rightarrow Mo + 2H_2O.$$

$$MoO_3 + 3H_2 \rightarrow Mo + 3H_2O.$$
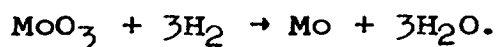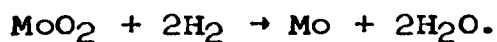
The molar ratio of O/Mo was found to be 2.02 and 2.99
for MoO_2 and MoO_3 respectively.

The SiO_2 for MoO_2-SiO_2 chemical reaction experiments
was prepared by heating silicic acid in a platinum cruci-
ble at 1300°C in air for 12 hours. The SiO_2 was ground to
pass 200 mesh screen.

APPENDIX II

MICROSCOPIC EXAMINATION OF QUENCHED SAMPLE

The capsules containing quenched molybdenum oxide samples were cut open with an abrasive wheel. The opened capsule was then mounted in a liquid epoxy resin which permeated the pores and cracks of the specimens before hardening, and greatly facilitated polishing. A standard metallographic technique was used for grinding and polishing of the sample. The final polish was carried out with "Linde C" abrasive, suspended in reagent grade alcohol. The phases present (solid MoO_2 and quenched liquid molybdenum oxide) before quenching were inferred from the appearance of the polished sample under the metallograph, using bright field, sensitive tint and polarized light.

The same technique was used before and after certain transpiration runs to determine that the two condensed phases, solid MoO_2 and liquid molybdenum oxide, were both present throughout the experiment.

APPENDIX III

EXAMINATION OF MoO_2-SiO_2 QUENCHED SAMPLE

BY X-RAY DIFFRACTION

The MoO_2-SiO_2 quenched sample was ground to a fine
powder and was spread over a glass slide uniformly with
the help of collodion. The glass slide was placed in a
Norelco x-ray diffractometer. Copper Kα radiation was
generated at 17 ma and 35 kilovolts. A chart speed of
1"/min and a scanning speed of 1° 2θ/min was used. The
base line adjustment was maintained approximately the
same for every diffraction pattern. The sample was scanned
from 0-90° 2θ.

The diffraction pattern was examined for new lines
or a shift in existing lines to detect any compound
formation or solid solution between MoO_2 and SiO_2. Char-
acteristic lines for MoO_2 were at the following 2θ angles:
triplet peaks near 53° and 37°, and the strongest peak at
25.9°. Characteristic lines for SiO_2 obtained were at low
angles of 2θ. The strongest peak was at 21.9° and two
small peaks were at 28.4° and 31.4° respectively. Silica
existed predominantly in the α cristobalite polymorphic
form. Characteristic lines obtained for MoO_2 and SiO_2 were
compared with A.S.T.M. cards.

APPENDIX IV

SUMMARY OF EXPERIMENTAL RESULTS

A. Transpiration Experiment

Weight loss in molybdenum oxides in handling, heating and cooling of the sample--0.1134 gms.

Table V Transpiration Experimental Data at 950°C

Run Number	Argon Flow Rate cc/min STP	Total Wt Loss in Gms	Actual Wt Loss in Gms during Timed Run	Wt Loss in mgm/ 100 cc of Ar	Vapor Density in Mil- limoles of MoO_3/ 100 cc STP	Vapor Pressure of $(MoO_3)_3(g)$ in atm.
1	15	1.0180	0.9046	100.4	0.232	4.94×10^{-2}
1a	25	1.2975	1.1841	79.0	0.183	3.94×10^{-2}
1b	25	1.3096	1.1962	79.6	0.1845	3.96×10^{-2}
2	32.5	1.5034	1.3900	71.4	0.165	3.57×10^{-2}*
3	41	1.9305	1.805	73.4	0.1700	3.67×10^{-2}*
4	47.5	1.0233	1.9100	67.2	0.155	3.35×10^{-2}
5	55	2.2422	2.1288	64.2	0.1492	3.23×10^{-2}

* Vapor pressure of $(MoO_3)_3(g)$ at plateau.

B.   Solid Electrolytic Galvanic Cell Experiment

Table VI   Testing of the Galvanic Cell

Pt Pure $O_2/Zr_{0.85}Ca_{0.15}O_{1.85}/1\% \; O_2$-Ar Pt at 950°C

Oxygen Flow Rate cc/min (STP)	1% O_2-Ar Mixture Flow Rate cc/min (STP)	e.m.f. in mv	Calculated e.m.f. in mv
30	9	122.2	
30	22.2	122.54	122.0
30	31	121.4	

Table VII   E.M.F. of $MoO_{2(s)}$/Liquid Molybdenum Oxide Mixture, vs. Cu/CuO_2 Reference Electrode, as Affected by Flow Rate of Inert Flushing Gas, cc/min STP.

Part A: 900°C, Nitrogen as Flushing Gas

Flow Rate	0	44	97	97	97	110
E.M.F. mv	13.88	13.28	13.6	13.1	13.05	13.16

Avg. e.m.f.   13.345

Part B: 950°C, Nitrogen as Flushing Gas

Flow Rate	0	42	42	98	187
E.M.F. mv	16.8	15.2	16.4	17	14.7

Avg. e.m.f.   16.02

Part C: 1000°C, Argon as Flushing Gas

Flow Rate	0	0	27	27	65	65
E.M.F. mv	14.4	14.5	14.7	14.36	14.92	15

Avg. e.m.f.   14.64

Table VIII E.M.F. of $MoO_{2(s)}$/Liquid Molybdenum Oxide Mixture vs. 1% O_2-Ar or Air Reference Electrode as Affected by Flow Rate of Inert Flushing and Reference Gas, cc/min STP.

Part A: 900°C

Argon Flow Rate	85	85		85	85	85
Ref. Gas Flow Rate; 1% O_2-Ar:	44	62	Air: 30	43	43	
E.M.F. in mv	288.15	288.73	361.5	361.4	361.04	
Avg. e.m.f.	288.44		361.31			

Part B: 950°C

Argon Flow Rate	37	85	85	85	85	85
1% O_2-Ar Flow Rate	48	22	48	48	62	84
E.M.F. in mv	281.06	282.4	281.4	281.94	283.34	281.42
Avg. e.m.f.	281.93					

Part C: 1000°C

Argon Flow Rate	0	27	60	88	90	95	122.5
1% O_2-Ar Flow Rate	40	70	70	40	30	70	70
E.M.F. in mv	288.8	286.4	287.0	287.5	287.0	286.4	286.4
Avg. e.m.f.	286.99						

Table IX Results of Runs to obtain Phase Boundary
between Solid MoO_2 and Liquid Molybdenum
Oxide

Temperature °C	$MoO_3:MoO_2$ by Weight Percent	Atomic Ratio O:Mo	Estimated Amount of MoO_2 Present	Remarks
950	50:50	71.20:28.20	One Third	
950	60:40	72.00:28.00	One Quarter	
950	80:20	73.80:26.15	≈ 10%	
950	85:15	73.92:26.08	≈ 5%	
950	87.5:12.5	74.10:25.90	≈ 2%	
950	90:10	74.31:25.69	≈ 1%	
950	95:5	74.60:25.40	Trace	Boundary Point
1000	50:50	71.18:28.82	One Quarter	
1000	70:30	72.78:27.22	≈ 10%	
1000	80:20	73.85:26.15	≈ 5%	
1000	92.5:7.5	74.46:25.54	Trace	
1050	87.5:12.5	74.10:25.90	≈ 1%	
1050	90:10	74.31:25.69	Trace	Boundary Point
1100	87.5:12.5	74.10:25.90	Trace	Boundary Point

APPENDIX V

SAMPLE CALCULATIONS

A. Calculation to find pO_2 on the Plateau Region in Vapor Density vs. Flow Rate Curve

$$MoO_2 + \frac{1}{2} O_2 \rightarrow \frac{1}{3} (MoO_3)_{3(g)} \qquad (1)$$
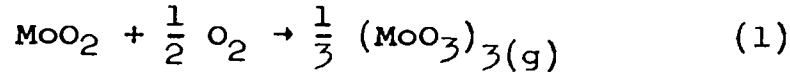
At 950°C (1223°K), 3.12 = log K.[21] Assuming $(MoO_3)_{3(g)}$ is the only gaseous specie, average vapor density on the plateau = 0.1675 millimoles per 100 cc of argon. Volume of $(MoO_3)_{3(g)}$ = 1.675 x 10^{-4} x 22.4 x 10^3 cc = 3.755 cc. Total volume = 100 + 3.755 = 103.755 cc.

$$p(MoO_3)_3 = \frac{3.755}{103.755} = 0.0362 \text{ atm. Hence,}$$

$$\log p(MoO_3)_3 = -1.4413;$$

substituting in the equation for the equilibrium constant:

$$\log K = 3.12 = \frac{1}{3} \log (p_{MoO_3})_3 - \frac{1}{2} \log pO_2 - \log a_{MoO_2}.$$

Since MoO_2 is present at unit activity, $\log pO_2$ = -7.20.

The fluctuation of data around the "plateau" indicates that the above $\log pO_2$ may be in error by ± .04, so that the $\log pO_2$ at MoO_2/liquid oxide equilibrium is -7.20 ± .04.

B. **Calculation of Partial Pressure of Oxygen at 950°C Using $Cu-Cu_2O$ as Reference Electrode in Solid Electrolytic Galvanic Cell**

Average e.m.f. obtained = 16.02 mv. Reaction taking place at cathode:

$$2Cu + \frac{1}{2} O_2 \rightarrow Cu_2O$$
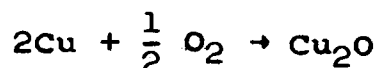
$\Delta G° = -40,200 + 17.37\ T$ (Rizzo et al.[35]).

Hence, $pO_2 = 10^{-6.76}$ atm. at cathode at 950°C.

$$\mathcal{E} = 4.97 \times 10^{-5}\ (1223)\ \log \frac{p''O_2}{p'O_2}.$$

$$\mathcal{E} = 4.97 \times 10^{-5}\ (1223)\ (\log p''O_2 - \log p'O_2).$$

Log $p''O_2 = -6.76$. Hence, $\log p'O_2 = -7.02$.

Taking into account about ± 500 calories/mol of O_2 in the free energy of formation of Cu_2O as given by Rizzo et al.[35] plus the fluctuations in e.m.f. of the cell, the above log pO_2 may be in error by ± 0.2, so that the log pO_2 at MoO_2/liquid oxide equilibrium is -7.02 ± 0.2.

C.   Sample Calculation for Finding pO_2 from the Data of Gulbransen as Modified by Activity of MoO_3 Inferred from the Phase Diagram of Phillips and Chang.[1]

At 950°C O/Mo at phase boundary = 0.737/0.263.
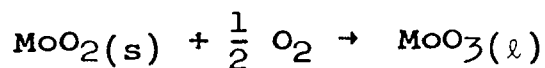
Let MoO_3 be x moles and MoO_2 be y moles.   Hence,

$3x + 2y = 0.737$

$x + y = 0.263$

Therefore, x = 0.211 moles and y = 0.052 moles.

Therefore, $N_{MoO_3} = \dfrac{0.211}{0.263} = 0.8035$

$a_{MoO_3} = N_{MoO_3}$ (Raoult's law)

$MoO_2(s) + \dfrac{1}{2} O_2 \rightarrow MoO_3(\ell)$

log $K_{reaction} = 3.43$ (Gulbransen[21] data)

Therefore, $3.43 = \log a_{MoO_3} - \dfrac{1}{2} \log pO_2.$

$3.43 = \log (0.803) - \dfrac{1}{2} \log pO_2.$

Log $pO_2 = -7.05$, therefore, $pO_2 = 10^{-7.05}$ atm.