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A STUDY ON THE ENHANCEMENT OF Ag EXTRACTION  
THROUGH COMPLEXATION IN THE VAPOR PHASE

by

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science - Metallurgical Engineering.

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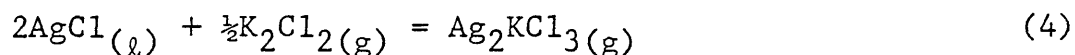
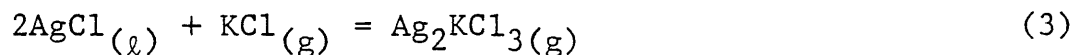
ABSTRACT

A classical transpiration apparatus was used to obtain fundamental vaporization data for the Ag-Cl and Ag-K-Cl Systems over the temperature range 1000-1150°C. For the reaction:



$$\Delta G_T^{\circ} = 47331 - 26.97 T (\pm 2561) \text{ cal} \cdot \text{mole}^{-1} \quad (2)$$

A second series of transpiration experiments was conducted in which potassium chloride was added to the system as well as silver chloride. This caused a significant enhancement in the apparent vapor pressure of silver chloride which was attributed to the formation of the gaseous complex molecule  $\text{Ag}_2\text{KCl}_3$ . The complexation reactions for the formation of this species from the potassium chloride monomer and dimer were assumed to be:



The standard Gibb's Free Energy of formation for each of these reactions was measured:

For Reaction 3:

$$\Delta G_T^{\circ} = -22567 + 21.95 T (\pm 10470) \text{ cal} \cdot \text{mole}^{-1} \quad (5)$$

For Reaction 4:

$$\Delta G^{\circ}T = -868 + 8.24 T (\pm 10470) \text{ cal} \cdot \text{mole}^{-1} \quad (6)$$

From these results, the extent of enhancement of the vapor pressure of silver chloride was calculated to be 900% and 300% at 727° and 827° respectively.

A bench scale rotary kiln reactor was then used to determine the optimum conditions for vapor phase silver extraction in both the Ag-Fe-Cl and Ag-K-Cl Systems.

For the Ag-Fe-Cl System, better than 90% silver extraction was achieved by mixing 2% hematite with a silver-silica synthetic ore and then roasting for 1 hour at 700°C. It was found that by using chlorine gas instead of hydrogen chloride, a higher vapor pressure of the complexing agent (FeCl<sub>3</sub>) was generated. This then resulted in an increase in the extent of complexation.

Problems were encountered during the extraction tests on the Ag-K-Cl System. When potassium chloride was added to the reactor as the complexing agent, the charge agglomerated and no silver was volatilized.

An industrial-scale silver extraction scheme utilizing the results obtained from the study of the Ag-Fe-Cl System is presented and commented upon.

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## 1. INTRODUCTION

### 1.1 The Current Need for New Methods of Extracting Precious Metals from Ores

As the price of noble metals such as gold and silver steadily increases, the type of ores being processed to obtain these metals is becoming more complex and lower in grade. Due to this, the most common method of extraction, cyanide leaching, is not always amenable or economical. Conditions such as high acidity in the ore, lack of sufficient water in some arid regions, and especially today's focus on waste disposal problems, all have created the need for alternate methods.

Generally, flotation is the most economical method of gold and silver concentration but is limited in that only sulfide ores are easily floated. One new method being studied in Peru on a pilot plant scale<sup>(1)</sup> is the segregation process. This method involves the deposition of a copper-silver alloy upon a carbonaceous material via a vapor transport reaction. The major drawback to this process is that only copper oxide ores which will segregate can be treated<sup>(2)</sup>. Another more widely accepted method is selective chloride volatilization. By passing chlorine gas over an ore

at high temperature, (700 - 1000°C) or heating the ore in the presence of a metal chloride salt, volatile metal chlorides may be formed which can be separated from the gangue material.

Pilot plant tests have been conducted to optimize this method<sup>(3,4,5)</sup> with good results. In at least one case<sup>(6)</sup> the results have been applied to the extraction of gold on a commercial basis. However, until now, very little emphasis has been placed upon silver extraction. For this reason, the thrust of this study will be on the development of fundamental silver vaporization data that can be used to devise new process schemes for the vapor phase extraction of silver from ores.

### 1.2 Previous Investigations Which Led to this Study

There are two ways silver can be transported in the vapor state. One way is as the simple chloride molecule AgCl. The second way, which is not as well known, is as a gaseous complex species which contains silver as well as another metal atom.

As early as the 1920's, evidence has been noted for the formation of complex silver vapors<sup>(7,8)</sup>. These early studies mention noticeable increases in silver losses from ores in the presence of chlorine, but make no attempt



to explain the phenomena other than through simple chloride volatilization. Only in the last fifteen years have attempts been made at predicting the molecularity and thermodynamics of formation of various silver complex species with any success<sup>(9,10,11,12)</sup>.

Recent studies at the Colorado School of Mines<sup>(11,12)</sup> have identified  $\text{CuCl}$ ,  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{KCl}$ , and  $\text{PbCl}_2$  as complexing salts which result in significant enhancement of the apparent vapor pressure of  $\text{AgCl}$  due to the formation of vapor complexes. For one of these systems, the Ag-Fe-Cl System, detailed thermodynamic data on the complexation reaction between  $\text{AgCl}_{(l)}$  and  $\text{FeCl}_3_{(g)}$  has been obtained<sup>(12)</sup>. Of the other systems studied, the Ag-K-Cl System showed the next largest increase in the apparent vapor pressure of  $\text{AgCl}$ . For this reason, it was chosen for further investigation in this study.

The thermodynamic data obtained by studying the various vaporization reactions can be used to make predictions concerning the rate at which silver can be extracted from an ore. For example, assuming equilibrium saturation of the gas phase, the concentration of silver in a given volume of gas can be calculated taking into account the presence of both  $\text{AgCl}_{(g)}$  and any Ag-Me-Cl gaseous complexes. Though these predictions have been made, to date no attempts

have been made to confirm them by conducting silver extraction tests in a bench scale reactor. Furthermore, no measurements have been made of the residence time required for the ore and the concentration of complexing agent that must be added.

### 1.3 Purpose and Summary of this Study

The purpose of this research effort was twofold:

1. To obtain fundamental thermodynamic vaporization data for the AgCl and Ag-K-Cl Systems.
2. To confirm the predicted rates of extraction based upon the thermodynamic data and to determine the optimum conditions for vapor phase silver extraction in both the Ag-Fe-Cl and Ag-K-Cl Systems.

During the first phase of the research, transpiration studies were made on pure silver chloride to document  $P_{\text{AgCl}}$  as a function of temperature. Once this was established and confirmed with previously published data, potassium chloride was added to the system and the partial pressure of the complex species, which was then formed, was calculated. In order to document the equilibrium constant and free energy of formation for the complex as a function of temperature, this experiment was repeated for several

different temperatures. From these results, initial conditions for silver extraction tests could be determined.

The second phase of this study, bench scale extraction, was accomplished by conducting tests on a synthetic silver ore. High-purity silica sand, coated with metallic silver, was placed in either a rotary kiln or a packed bed reactor and chlorinated to volatilize the silver. By conducting tests with and without a complexing agent, extraction curves were obtained which clearly showed the effects of complexation. In addition, minimum residence times and the amount of complexing agent required were determined for consistently high extraction rates. Further, the results were used to design a proposed flowsheet for the extraction of silver from pyrite cinder based on the formation of the  $\text{AgFeCl}_4(\text{g})$  complex.

## 2. LITERATURE SURVEY

### 2.1 Fundamental Vaporization Studies of Silver Complexation

An excellent review of most vapor complex species which have been experimentally observed was done by Annamalai<sup>(13)</sup> in 1972. Special note was given to species which were only proposed and those which have been positively identified by such techniques as mass spectrometry. It must be stated that much of the thermodynamic data is based upon some form of transpiration study. When this is the case, the data tends to be ambiguous due to assumptions about the molecularity of the species. Very often, an observed relative change in vapor pressure is attributed to a single vapor complex species of a proposed molecularity when, in fact, the total observed pressure may be the sum of several different species all contributing their individual partial pressures. Therefore, in this review, the same format will be used and any species which have not been positively identified will be noted as such.

In 1925, Maier<sup>(7)</sup> proposed the first silver vapor complex species. By combining equal molar parts of silver and sodium chloride and fusing them under nitrogen, he was able to measure a relative increase in the apparent AgCl

vapor pressure over the temperature range  $972^{\circ}$  -  $1195^{\circ}\text{C}$ . How he arrived at the molecularity is not stated, but it is safe to say that the species proposed,  $\text{AgNaCl}_2$ , was only a guess.

Sorokina and Reznik<sup>(9)</sup> proposed the formation of the complex species  $\text{AgCaCl}_2$ . They generalized the stoichiometry of the reaction to be  $\text{Me} + \text{CaCl}_2 \longrightarrow \text{MeCl}_2\text{Ca}$  where Me corresponds to several metals including silver. The calculations were performed using isobar potentials for the formation of compounds and thermodynamic data taken from manuals which had been published in recent years.

James<sup>(11)</sup>, Rupert<sup>(12)</sup>, and Schafer<sup>(14)</sup> made use of the transpiration technique to observe that  $\text{AgCl}$  transport was significantly enhanced by adding  $\text{AlCl}_3$ ,  $\text{KCl}$ ,  $\text{FeCl}_3$ ,  $\text{PbCl}_2$ , or  $\text{CuCl}$  to the system. James<sup>(11)</sup> speculated that since silver and gold were both group IB elements, their complexing characteristics would be similar and the species  $\text{AgCu}_2\text{Cl}_3$  was proposed based on his previous observance of  $\text{AuCu}_2\text{Cl}_3$ . For the  $\text{Ag-Fe-Cl}$  System, James<sup>(11)</sup> proposed the species  $\text{AgFeCl}_4$ , again using similarities between this and other systems. Rupert<sup>(12)</sup> documented the thermodynamics of the complexation reaction between  $\text{FeCl}_3$  and  $\text{AgCl}$  and proposed the  $\text{AgFeCl}_4$  molecule. A mass spectrometer fitted with a Knudsen Cell Inlet System was then used in attempts

to confirm this prediction. However, due to the vast difference in the vapor pressure of AgCl and FeCl<sub>3</sub>, the attempt was unsuccessful.

In an earlier study by Binneweis and Schafer<sup>(15)</sup>, mass spectrometry studies were made on a number of systems including the Ag-Th-Cl system. Confirmation of complexation was made and the species AgThCl<sub>5</sub> was identified.

In 1966, Svedburg<sup>(10)</sup> made extensive studies on the formation of vapor complexes between AgCl and the Alkali metals. After conducting eighty experiments on a mass spectrometer fitted with a conventional Knudsen Cell Inlet System, he states, "Ions of the form MAgCl<sup>+</sup>, M<sub>2</sub>AgCl<sub>2</sub><sup>+</sup>, and MAg<sub>2</sub>Cl<sub>2</sub><sup>+</sup>, where M represents the alkali metal atom, were identified over each of the alkali-silver chloride mixtures<sup>(10)</sup>". An analysis of his data indicated that the MAgCl<sup>+</sup> ion was a result of fragmentation only.

In an attempt to study the vapors above molten AgCl by mass spectrometry, Wagner and Grimley<sup>(16)</sup> observed the following ionic species: AgCuCl<sup>+</sup>, AgCu<sub>2</sub>Cl<sub>2</sub><sup>+</sup>, AgCu<sub>2</sub>Cl<sub>3</sub><sup>+</sup>, AgCu<sub>3</sub>Cl<sub>4</sub><sup>+</sup>, Ag<sub>2</sub>CuCl<sub>2</sub><sup>+</sup>, Ag<sub>2</sub>CuCl<sub>3</sub><sup>+</sup>, Ag<sub>2</sub>CuCl<sub>4</sub><sup>+</sup>, Ag<sub>3</sub>CuCl<sub>3</sub><sup>+</sup>, Ag<sub>3</sub>CuCl<sub>4</sub><sup>+</sup>. These species had not been expected since the copper in the system came from a reaction between the molten silver chloride and the sterling silver knudsen cell they had been using. Since this was considered

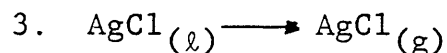
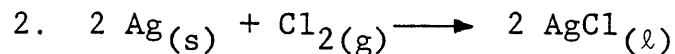
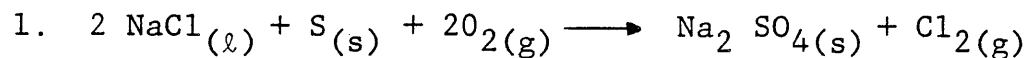
to be a problem in their original experimental setup, the sterling silver knudsen cell was discarded and no further effort was made at identifying the actual gaseous species.

In one of the most recent mass spectrometry studies by Schafer<sup>(17)</sup> in 1976, the complexation characteristics of  $\text{AlCl}_3$  were studied. Schafer<sup>(17)</sup> identified the complex species  $\text{AgAlCl}_4$  and presented an excellent summary of gaseous chloride complex formulas, structures and formation enthalpies.

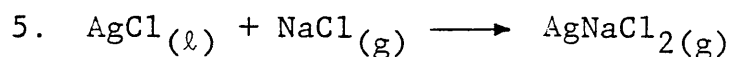
In reviewing the literature, it is clear that emphasis has been placed on both the identification of systems which exhibit vapor enhancement through complexation and the determination of the molecularity of the complex species. Very few studies, with the exception of Rupert<sup>(12)</sup>, have attempted to obtain quantitative data for predicting the partial pressures of the silver chloride complexes.

## 2.2 Silver Extraction Studies And the Complexation Phenomena

Around the turn of the century, tests were being conducted simultaneously by Stuart Croasdale and Edwin C. Pohle (from Varley<sup>(8)</sup>) on the volatilization of gold and silver. By adding salt, sulfur and oxygen to a silver/gold ore they were able to affect the volatilization of the precious metals by the stepwise reactions:



Optimum results were obtained by adding the stoichiometric amount of sulfur necessary to liberate the chlorine required for the second reaction. Further testing with excess sulfur produced a sharp decrease in the extraction rate. This was not satisfactorily explained at the time but some insight into these results is now offered. If two more reaction steps are added,



then the rate of reaction may be controlled by Step 4. With excess sulfur in the system, Step 1 may consume sufficient NaCl to prevent Step 4 and thus Step 5 from occurring. This could not have been hypothesized at the time of these experiments since the first proposal of a complex chloride vapor species was not made until 1925 by Maier<sup>(7)</sup>.

Chloridization tests by Varley<sup>(8)</sup>, on silver and gold in 1923 showed fairly good extraction of both metals, (in excess of 80%). Again, several different salts were



used as chloridizing agents and no mention was made of the possibility of forming complex vapor species.

Engel and Heinen, in several studies<sup>(3,5)</sup>, achieved high extractions of silver by roasting silver bearing ores under oxidizing conditions in the presence of several chloride salts. In these studies, as before by Varley<sup>(8)</sup>, the object of the tests was to determine which salt acted as the best chloridizing agent. Again, no mention was made of forming complex vapor species.

In summary, it may be safe to say that all of these preliminary tests were successful due at least partially to the formation of silver chloride vapor complex species which contributed to the overall vapor transport process. The fact that the salts were originally used as chlorinating agents prohibited the prospect of conducting extraction tests with and without their presence. With this in mind, the bench scale extraction tests conducted in this study were designed so that the chloridizing agent was fed separately to the system, independent of the complexing agent.

### 3. EXPERIMENTAL APPARATUS AND PROCEDURE

As discussed previously, there were two experimental phases in this study. Fundamental vaporization studies on the Ag-K-Cl system were conducted using a transpiration apparatus to obtain quantitative vapor pressure data, and silver extraction studies on a synthetic ore were conducted using both a rotary kiln reactor and a packed bed reactor. A thorough description of this equipment and the experimental procedure is now given.

#### 3.1 The Transpiration Apparatus

##### 3.1.1 Principles of Operation

The transpiration technique, also referred to as the entrainment or transportation technique, is the most widely used, non-absolute, method of measuring vapor pressure. A concise summary of its versatility is taken from Norman and Winchell<sup>(18)</sup>:

"Its applicability is wide, and its accuracy is often excellent. It can be used in making measurements of vapor pressures up to a few atmospheres, and its use is practically limited to pressures above  $10^{-6}$  atm. However, when radioactive tracers are used, this limit may sometimes be considerably exceeded. In the transpiration method, a carrier gas is employed. The gas may be inert, or partially or wholly composed of chemically reactive gases. The applicable temperature range is limited only by the experimental system and chemical kinetics."

When using the transpiration technique, vapor pressures are calculated from a mass balance of both the materials transported and the carrier gas. However, one must be sure this vapor pressure corresponds to an equilibrium saturation of the carrier gas. It has been found by Norman and Winchell<sup>(18)</sup> and Alcock and Hooper<sup>(19)</sup> that an equilibrium plateau region exists, as indicated in Figure 1, for a range of carrier gas flowrates. Within this range, the measured vapor pressure will be constant. As the flowrate is decreased below this plateau region, the rate at which volatiles are diffusing throughout the carrier gas becomes sufficient to disrupt the equilibrium condition. This will result in a sharp increase in the calculated vapor pressure due to the additional mass transport by the diffusion mechanism. Flowrates above the plateau region are characterized by a decrease in the measured vapor pressure. This is attributed to an insufficient rate of volatilization to saturate the carrier gas.

Assuming measurements are made within this region, the vapor pressure of a species,  $A_xCl_y$ , can be calculated using Formula 3.1.

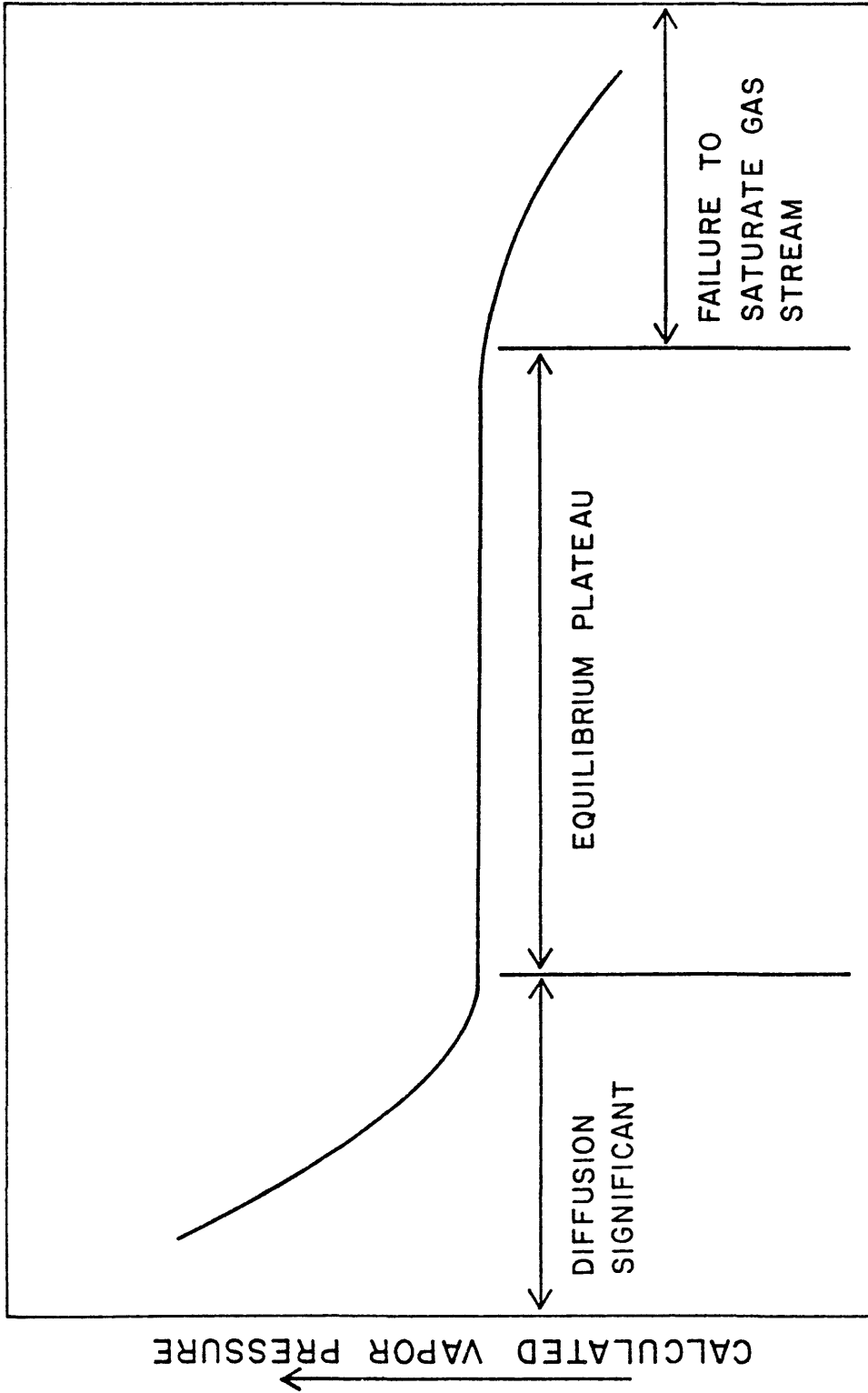


FIGURE I - VARIATION OF THE CALCULATED VAPOR PRESSURE WITH CARRIER GAS FLOWRATE

$$P_{A_xCl_y} = \frac{M_a}{(M_a + M_{cg})} \times P_T \quad (3.1)$$

Where:  $P_{A_xCl_y}$  = Equilibrium vapor pressure of  $A_xCl_y$

$M_a$  = Moles of  $A_xCl_y$  transported

$M_{cg}$  = Moles of carrier gas

$P_T$  = Total reactor pressure

The total reactor pressure was calculated by adding the pressure difference between the reactor and the barometric pressure, as measured by an oil manometer, to the barometric pressure.

$M_{cg}$  refers to the total moles of carrier gas which pass over the volatilizing sample, and can be calculated using Formula 3.2.

$$M_{cg} = \frac{F_{c.g.} \times t_r \times P_a}{R \times T_a} \quad (3.2)$$

Where:  $F_{c.g.}$  = Volumetric flowrate of carrier

$T_a$  = Ambient temperature

$R$  = Universal gas constant

$P_a$  = Ambient pressure

$t_r$  = Runtime

The disadvantage of the transpiration method, as mentioned in Section 2.2, becomes obvious when one attempts

to calculate the moles of  $A_xCl_y$ . After determining the total moles of metal A transported during the run, the value of X must be used to calculate the total moles of  $A_xCl_y$  transported. Unless it is already known, an assumption must be made as to the molecularity of the species being measured, i.e.: the value of X. Determination of the value of X through transpiration experiments, as described by Annamalai<sup>(13)</sup>, is quite tedious and susceptible to experimental error. Consequently, unless there is some other experimental evidence, such as from mass spectrometry, the molecularity of most proposed complex species is usually assumed.

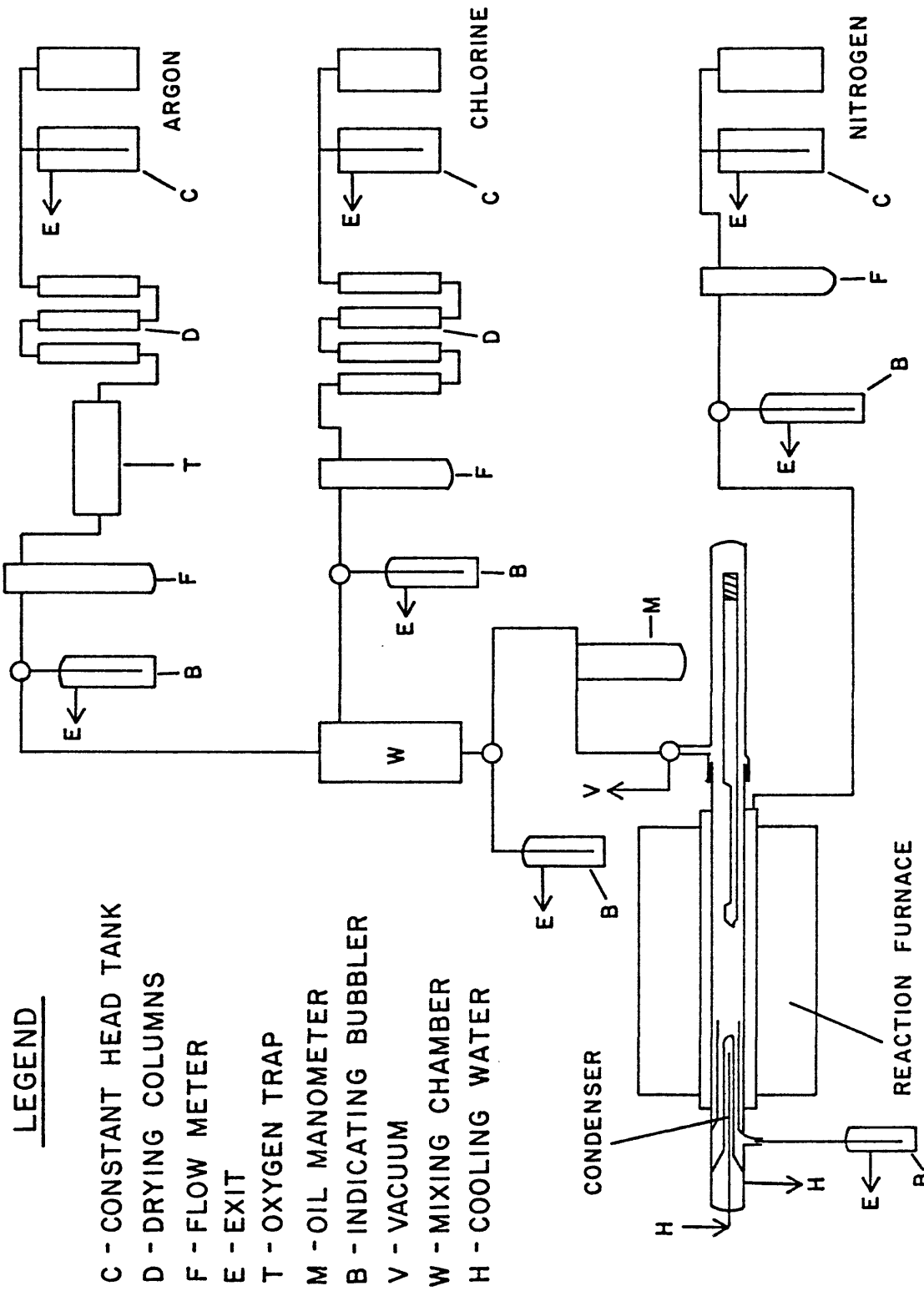
### 3.1.2 Description of Experimental Setup

An overall schematic of the transpiration apparatus in this study is shown in Figure 2 and a photograph is shown in Figure 3. For purposes of discussion, the system is divided into the following component parts:

- a. The carrier gas train
- b. The reactor
- c. The inlet system
- d. The condenser system

These individual parts will now be covered in detail.

The carrier gas purification and metering system is shown in Figure 4. Commercially supplied high-purity



LEGEND

- C - CONSTANT HEAD TANK
- D - DRYING COLUMNS
- F - FLOW METER
- E - EXIT
- T - OXYGEN TRAP
- M - OIL MANOMETER
- B - INDICATING BUBBLER
- V - VACUUM
- W - MIXING CHAMBER
- H - COOLING WATER

FIGURE 2 - OVERALL SCHEMATIC OF TRANSPIRATION SYSTEM

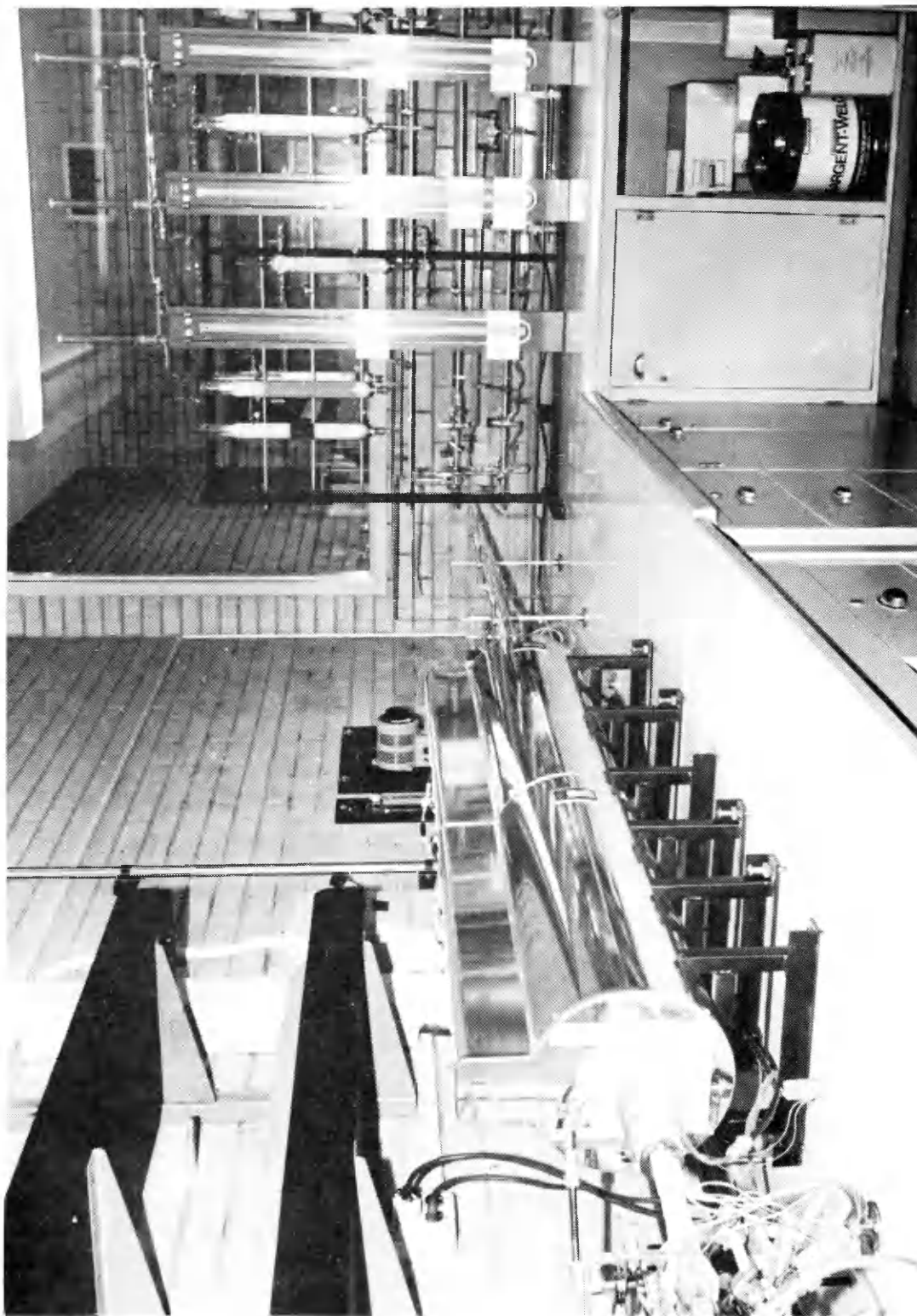


Figure 3 - Transpiration Apparatus: Overall View



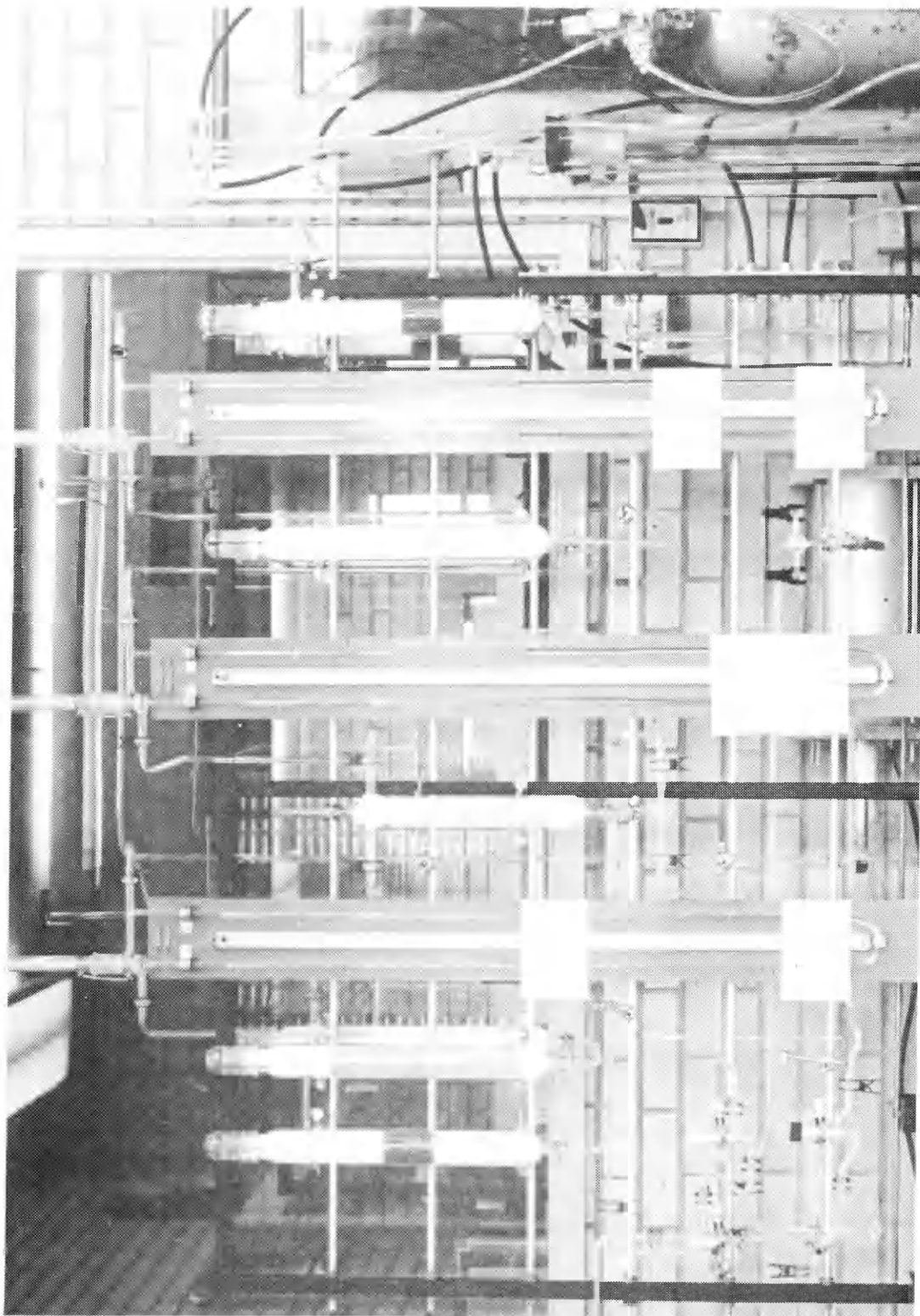


Figure 4 - Transpiration Apparatus: View of Carrier Gas Train

chlorine, argon and industrial grade nitrogen were introduced into three separate lines with the capability of mixing the argon and chlorine. The nitrogen line was used strictly as a gas source for flushing the space between the reaction tube and the protection tube of the reactor, and therefore will not be discussed at this time.

The argon and chlorine gases were dispensed from their respective tanks by using commercial regulators and shut-off valves. Fluctuations in delivery pressure were eliminated by using constant pressure head tanks for each flowmeter. The tanks consisted of a 5-ft. pyrex cylinder which was filled with mineral oil in the case of argon and carbon tetrachloride in the case of chlorine. A teflon plug, with a pyrex T and a vent line inserted through it, was used to cap the tanks. Two legs of the pyrex T were connected to the delivery line and the third leg was submerged in the tank oil. By adjusting the depth of the Pyrex T in the oil, providing the pressure in the line was sufficient to displace the oil from the T, the flowrate of the gas was controlled.

Moisture was removed from the gases by passing them through columns packed with a dessicant. For the argon line, three 2-in. by 14-in. columns of 6-16 mesh silica gel were used. Four of the same size columns packed with anhydrous magnesium perchlorate were used for the chlorine line. The

argon was also passed through a column packed with copper turnings held at 500°C. This removed any oxygen by reacting it with the copper turnings to form copper oxide (which remained on the turnings). Annamalai<sup>(13)</sup> states that after measuring the HCl content in the grade of chlorine used both for his study and this study, the amount of HCl found was negligible. Based upon his results, no attempt was made to remove HCl from the chlorine gas.

Capillary flowmeters were used to measure the volumetric flowrate of the gases. Since the pressure drop across the capillary is proportional to the rate at which the gas flows through the capillary (from Annamalai<sup>(13)</sup>), the volumetric flowrate was obtained from a previous calibration of flowrate versus pressure drop. Manometers, filled with dibutylphthalate for the argon line and Halocarbon\* oil for the chlorine line, were used to measure the pressure drop.

The entire gas train, including the lines to and from the reactor, were made of 3/8-in. pyrex tubing with ground glass joints for all connections. Halocarbon\* grease was used as a lubricant on all ground-glass joints.

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\*Halocarbon is a blend of completely halogenated chlorofluorocarbons and is inert to all acids, alkalis and oxidizing agents, wet or dry. Halocarbon oil (Series 13-21, 100 cs at 100°F) and Halocarbon grease were obtained from Halocarbon products, Hackensack, New Jersey.

The reactor consisted of two mullite tubes, one inside the other, placed inside a cylindrical furnace. The outer, or protection tube served to protect the furnace windings from the hot corrosive gases if the inner, or reaction tube broke during a run. The annular space between these tubes was flushed with nitrogen and vented to an exit bubbler which was connected to an exhaust system. Tapered ground-glass joints were fused to both ends of the reaction tube. This allowed the gas-tight connection of both the sample inlet system and the off-gas condenser system to the reaction tube.

A single Marshall resistance-heating furnace was used in this study for both saturating the carrier gas with  $\text{KCl}_{(g)}$  and for reacting the potassium chloride vapors with the molten silver chloride. Previous investigations<sup>(11,12)</sup> have used a double furnace arrangement to accomplish this. However, if the temperatures of the reaction and saturation furnaces are the same, a 25° to 50°C drop in temperature can be expected at the junction of the two furnaces. This will result in a somewhat lower partial pressure of the complexing agent due to condensation, as it encounters a decreasing temperature gradient on its way to the reaction zone. The saturation temperature necessary to produce sufficient potassium chloride vapor in this study posed just

this problem. Though the partial pressure of potassium chloride was needed for calculations, it could be obtained from a mass balance of the condensate. Therefore, it was decided that only the temperature across the reaction zone need be constant and well documented. This constant temperature zone, in which the silver chloride samples were located, was obtained by shunting current from sections of the furnace windings and dissipating the power through external resistors. The potassium chloride could then be placed at any position upstream from the reaction zone where it would only "see" an increasing temperature gradient. A schematic of the furnace temperature gradient and sample boat position is shown in Figure 5. The furnace temperature was controlled by a Research Incorporated (thermac Series 6000) temperature controller. A photograph of the controller and shunt resistors is shown in Figure 6.

The inlet system was designed to provide for both a way to introduce the carrier gas to the reactor and a method of moving the samples in and out of the reaction zone. It consisted of a sample carrier tube, a guide tube and T adaptor. The sample carrier tube was made of  $\frac{1}{2}$ -in. O.D. fused silica. A ceramic magnet was sealed inside one end of the tube and the other end was notched so as to hold the sample boats. By coupling the sealed magnet with another

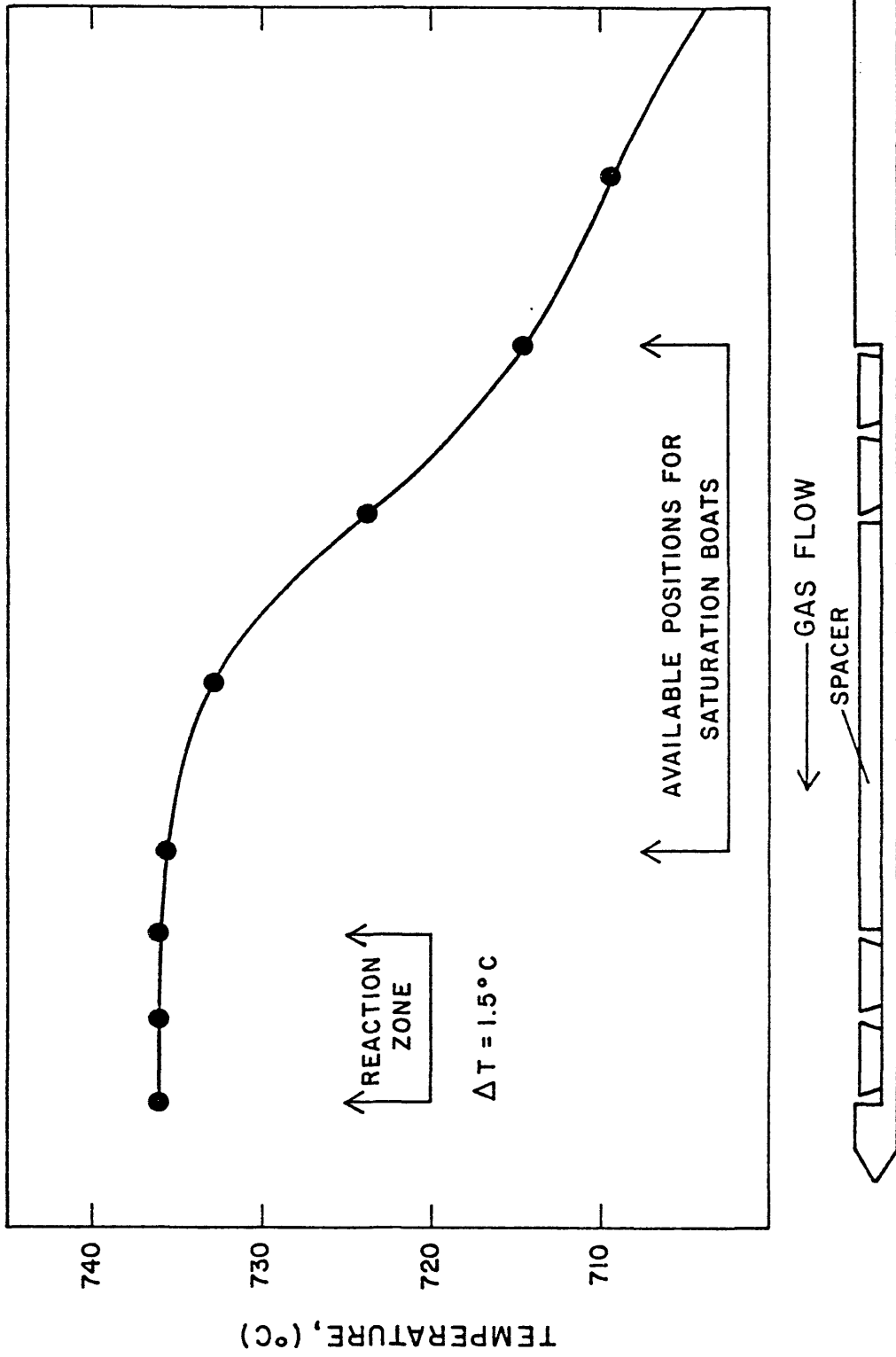


FIGURE 5 - EXAMPLE OF FURNACE TEMPERATURE PROFILE SHOWING THE POSITION OF THE AgCl AND KCl SAMPLE BOATS



Figure 6 - Transpiration Apparatus: View of Temperature Controllers and the External Shunt Resistors

more powerful magnet held outside the guide tube, the sample carrier tube could be moved. The notch in the carrier tube ran from 1-in. to 19-in. from the end of the tube. This allowed the complexing agent samples to be placed at various positions in the furnace. Cylindrical spacers were placed in the notch on either side of the sample boats to minimize the reaction zone area and obtain plug flow of the carrier gas. The guide tube was made of 1-in. O.D. pyrex with one end closed off and a tapered ground-glass joint at the open end. With the guide tube in place, the sample carrier tube could be moved out of the furnace and into the guide tube without opening the system. The T adaptor fit between the guide tube and the reaction tube and served as an entry port for the carrier gas. A photograph of the inlet system with sample boats in place is shown in Figure 7.

The temperature in the reaction zone was measured with a chromel-alumel (Type K) thermocouple which had been previously calibrated against the melting points of pure lead and pure aluminum. A second thermocouple, external to the reaction zone, was placed in the space between the inner and outer reaction tubes at a position just below the sample boats. By taking measurements with both thermocouples at various temperatures, the plot shown in Figure 8 was constructed. This plot was then used during a run to



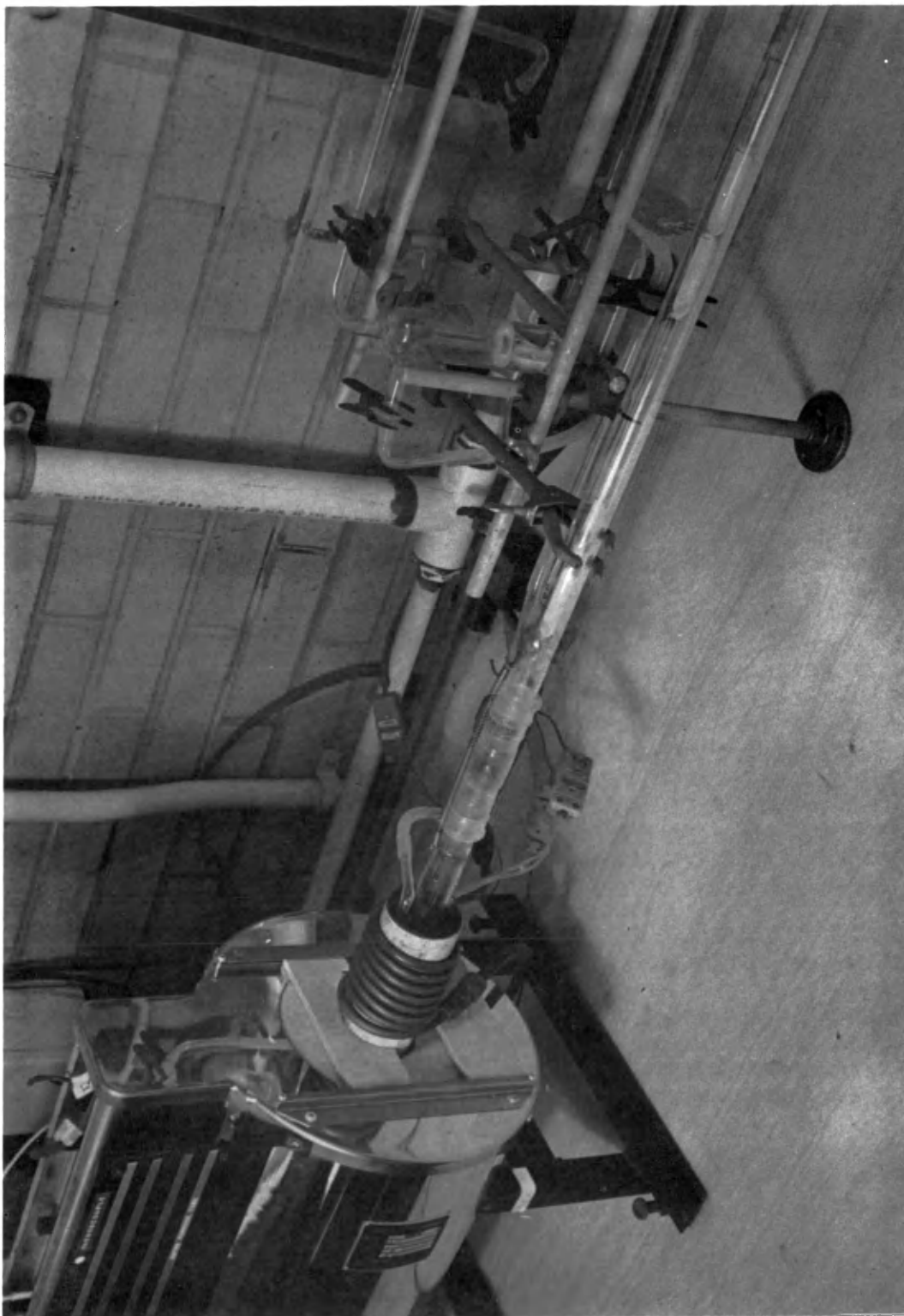


Figure 7 - Transpiration Apparatus: View of Inlet System Showing the Sample Boats Positioned on the Carrier Tube

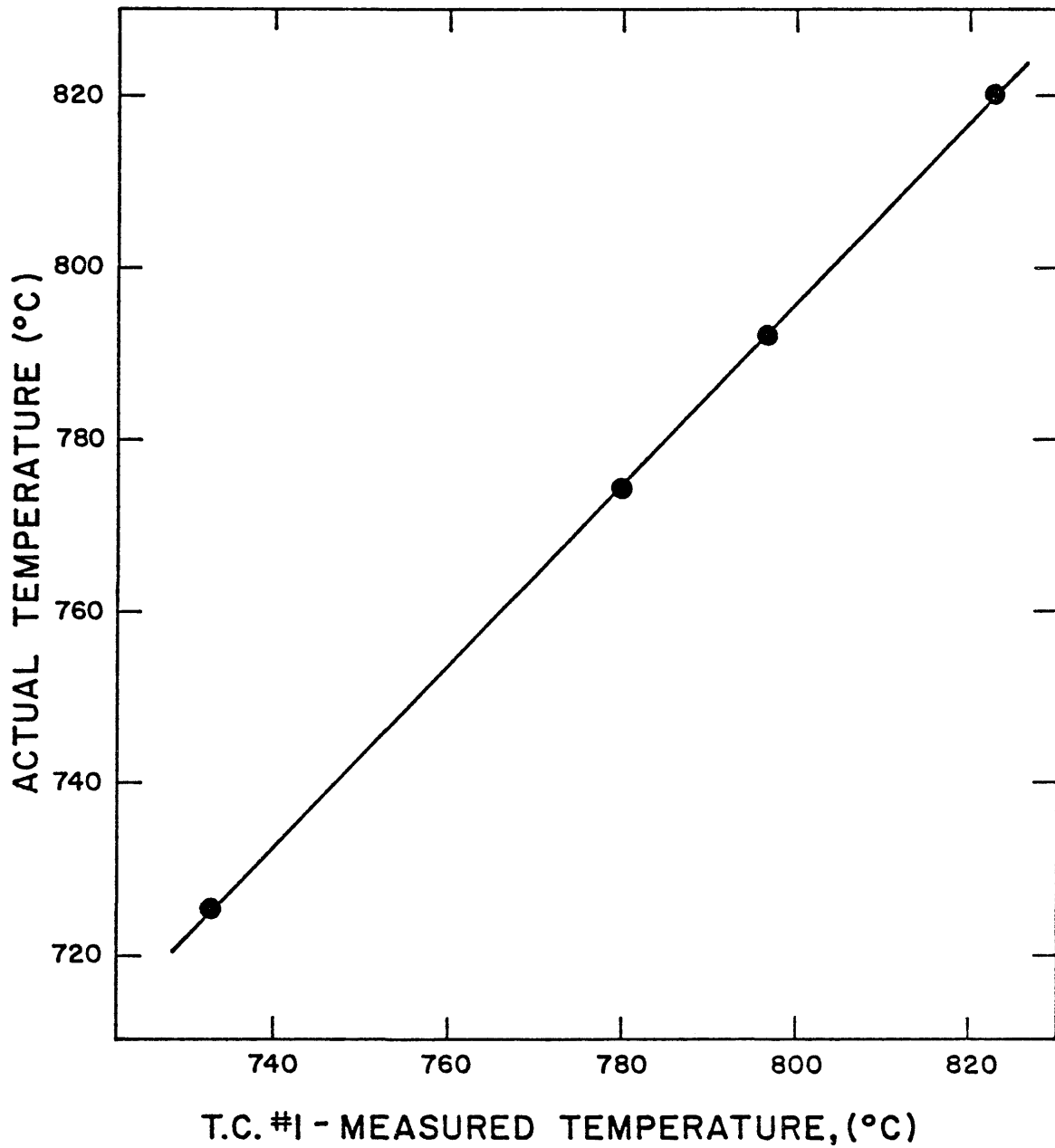


FIGURE 8 - THERMOCOUPLE CORRELATION PLOT FOR  
EXTERNAL T.C.#1 VERSUS ACTUAL  
REACTION ZONE TEMPERATURE

determine the actual reaction zone temperature from a reading made with the external thermocouple.

The off-gas condenser system consisted of a water-cooled "cold-finger" condenser, a mullite condenser sleeve, and a secondary water-cooled condenser located in the exhaust line. A photograph of the disassembled condenser system is shown in Figure 9. The cold-finger condenser was inserted into the condenser sleeve and sealed to it with a tapered ground-glass joint. By sealing the condenser sleeve inside the reactor tube, the carrier gas was forced to flow through the sleeve and around the water-cooled condenser. The sleeve and condenser could then be removed from the reactor, as a unit, for analysis of the condensate. An overall view of the assembly, in position, is shown in Figure 10.

### 3.1.3 Experimental Procedure

The guide tube, with the sample carrier tube inside it, was connected to the evacuation port of the nitrogen filled dry box. After evacuating the system with a mechanical vacuum pump and backfilling with dry nitrogen, the inner door on the dry box could be opened and the carrier tube moved inside. The sample material was then placed in high-purity alumina boats and the boats were positioned on

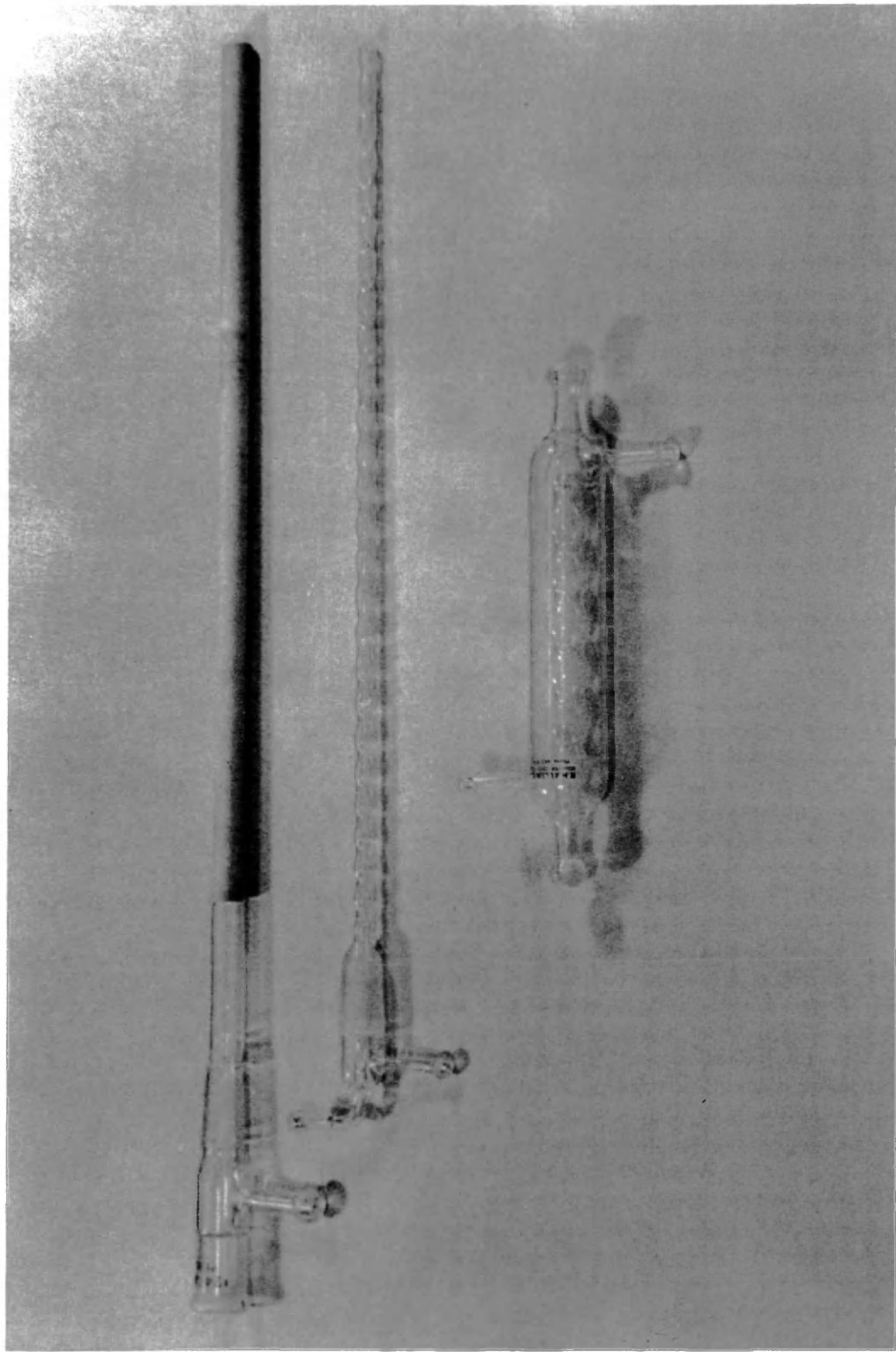


Figure 9 - Transpiration Apparatus: View of Disassembled Off-gas Condenser System

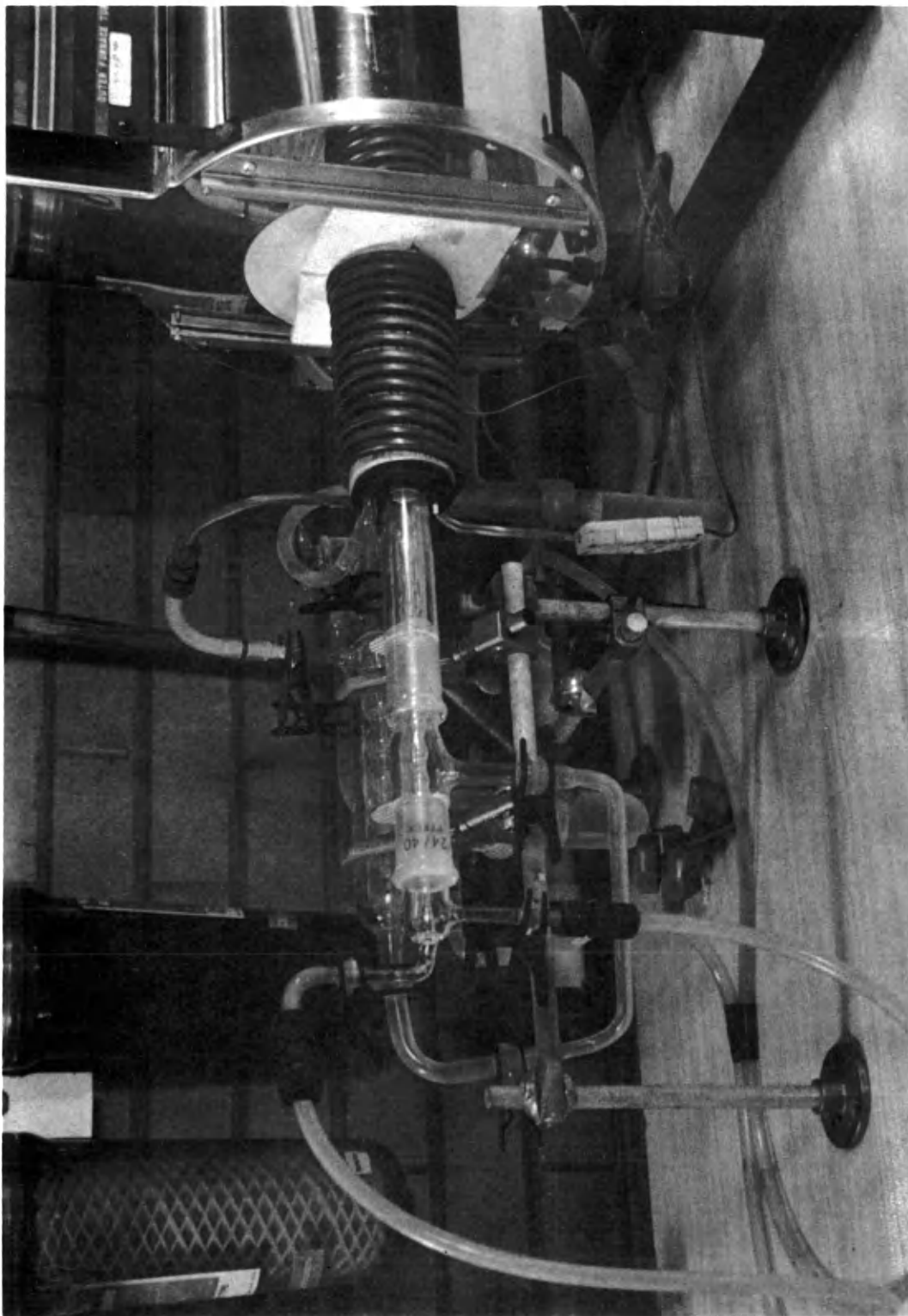


Figure 10 - Transpiration Apparatus: View of Condenser System in Position

the carrier tube as shown in Figure 6. The carrier tube was then moved back into the guide tube and the guide tube was removed from the dry box and connected to the reactor. The reactor and guide tube were then evacuated by a mechanical vacuum pump and backfilled with the carrier gas to be used for that run. To start a run, the sample boats were moved into the reactor by coupling an external magnet to the magnet sealed within the carrier tube. At the completion of a run, the samples were removed from the reactor, and the carrier gas was switched to provide a pure argon flush gas. After flushing the system for twenty minutes to remove all volatiles from the reaction zone, the condenser assembly was removed and the condensate was leached and analyzed according to the procedure outlined in Appendix D.

Runtime was measured from the time the sample was in position until the time it was removed from the hot zone. The runtime, along with the A-A results, total pressure, reactor temperature, room temperature and carrier gas flowrate were fed into a computer which calculated the partial pressure of the species volatilized. An example of these calculations is given in Appendix A, and the program used to reduce the data is listed in Appendix B.

#### 3.1.4 Experimental Error

The variables measured during a transpiration run are:

- a. Reactor temperature
- b. Room temperature
- c. Reactor pressure
- d. Carrier gas flowrate
- e. Runtime
- f. Weight of material transported

An estimate of the error in measuring each of these variables will now be presented.

As stated previously, the reactor temperature was measured with a chromel-alumel thermocouple which had been previously calibrated against the melting points of several pure metals. It was found to be in error by less than  $1^{\circ}\text{K}$ . In addition to this, the temperature profile across the reaction zone varied by  $\pm 1.5^{\circ}\text{K}$ . Therefore, a liberal estimate of the total error in measuring the reactor temperature was assumed to  $\pm 3^{\circ}\text{K}$ .

Ambient temperature was measured by a centigrade thermometer which was calibrated at  $0.5^{\circ}$  intervals. Assuming the thermometer to be correct, the temperatures

could be read to within  $\pm 0.25^{\circ}\text{C}$ .

Reactor pressure was calculated as the sum of the barometric pressure and the reactor manometer pressure. For this, an error of  $\pm 0.5$  mmHg was assumed.

Annamalai<sup>(13)</sup> states that an error of  $\pm 2$  ml/min can be expected in the measurement of carrier gas flowrates when using a capillary-type flowmeter. In this study, the same error was assumed.

After studying the temperature profile in the furnace and estimating that the samples could be moved into the furnace at about 4-in. per minutes, it was found that the samples may heat to reactor temperature as much as 1 minute before the carrier tube was in position. In addition, the samples may stay at reactor temperature for about 2 minutes after the carrier tube was moved from the reaction zone. This means that an error of  $\pm 3$  minutes in measuring the runtime is possible.

The weight of material transported was determined by leaching the condensate from the condenser and then quantitatively analyzing the leach liquor by atomic absorption spectrophotometry. This procedure was subject to error in leach recovery, dilution, standard preparation and random fluctuations in the A-A readings. The error in leach



recovery was found to be no more than 0.5%. This was determined by releaching the condenser in several different solvents and then comparing the additional material obtained with that obtained from the initial leaching process. Dilution errors were minimized by diluting samples for analysis in triplicate and then averaging the results. However, since it was found that the samples would sometimes differ by about 1%, an error of 0.5% was assumed possible after averaging. To determine the error in the standards, solutions were prepared from 1000 ppm commercial standard solutions purchased from four different vendors. The difference in absorbance readings obtained from comparing the standards was negligible and, therefore, no error was assigned to this. The most significant error arose in obtaining consistent absorbance readings from the A-A unit. By repeatedly analyzing a silver condensate leach liquor over a several day period, it was found that a 3 to 4% error could be expected for no apparent reason. From these tests, it was decided to assign a conservative 4% error to the determination of materials transported.

The chance that all of these measurements were in error at the same time was quite small. Therefore, rather than assign an error to the results from these

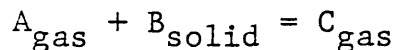
assumptions, a statistical analysis was performed on the raw data.

It should be noted that although the reactor temperature measurement and the atomic absorption analysis are the most crucial parameters, the error in measuring the carrier gas flowrate becomes significantly larger as the runtime is increased.

## 3.2 The Rotary Kiln Reactor

### 3.2.1 Principles of Operation

A rotary kiln reactor is most applicable to heterogeneous reactions involving a solid and a gas. According to Levinspiel<sup>(20)</sup>, when a solid phase reacts with a gas phase:



The reaction occurs in three steps:

- Step 1: Diffusion of reactant A from the main body of gas through a gas film to the surface of the solid.
- Step 2: Reaction at the surface between reactant A and the solid B.
- Step 3: Diffusion of reaction products from the surface of the solid through the gas film back into the main body of gas.

If the rate of diffusion is the controlling step, the

overall rate of reaction can be increased by making the gas film at the solid surface as thin as possible. The rotary kiln accomplishes this by tumbling the charge. This causes turbulence in the gas film at the surface of the solid, which sweeps away the product layer and leaves the surface exposed to the reactive gas at its bulk chemical potential. Another advantage to tumbling the charge is the increase in solid surface area available for reaction. With some static reactors, the major portion of the charge is buried and essentially unavailable for reaction. The fact that rabble arms are used in many types of reactors is evidence to support this.

A major advantage of a rotary kiln reactor is its versatility. The apparatus used in this study was capable of operation up to 1000°C for sustained periods of time. The carrier gas flowrates were only limited by the dusting problems which occurred from using finely ground ores. Reactor pressures are practically limited between 0.01 atm and 1.5 atm. However, when toxic gases are being used, it is not advisable to exceed ambient pressure. By using two different size reactors, experiments could be conducted on charges ranging up to 500 grams. (This weight is based on a sample density of 2.5). Lastly, it should be noted that unlike many types of reactors which require a specific

feed particle size, the rotary kiln can operate with good results using material of mixed particle size or lumps which may disintegrate during the process.

### 3.2.2 Description of Experimental Setup

The rotary kiln reactor used in this study was purchased from Hazen Research Inc. of Golden, Colorado. The component parts which came with the unit included:

1. Split-shell cylindrical furnace
2. Temperature controller
3. Fused quartz reactor
4. Rotary drive mechanism

In addition to this, a carrier gas source and an off-gas condenser system were constructed. A schematic of the system is shown in Figure 11 and a photograph of the apparatus is shown in Figure 12.

The carrier gas source consisted of a chlorine line and a nitrogen line, each equipped with a rotameter type flowmeter. The gases were dispensed from commercially supplied high-pressure bottles by standard regulators and shut-off valves. Purification and drying of the gases was not necessary for this type of experiment so no attempt was made to do so. From the flowmeters, the gas lines were connected to a mixing column packed with Rashig rings. Flexible tubing made of ethylene vinyl acetate was then

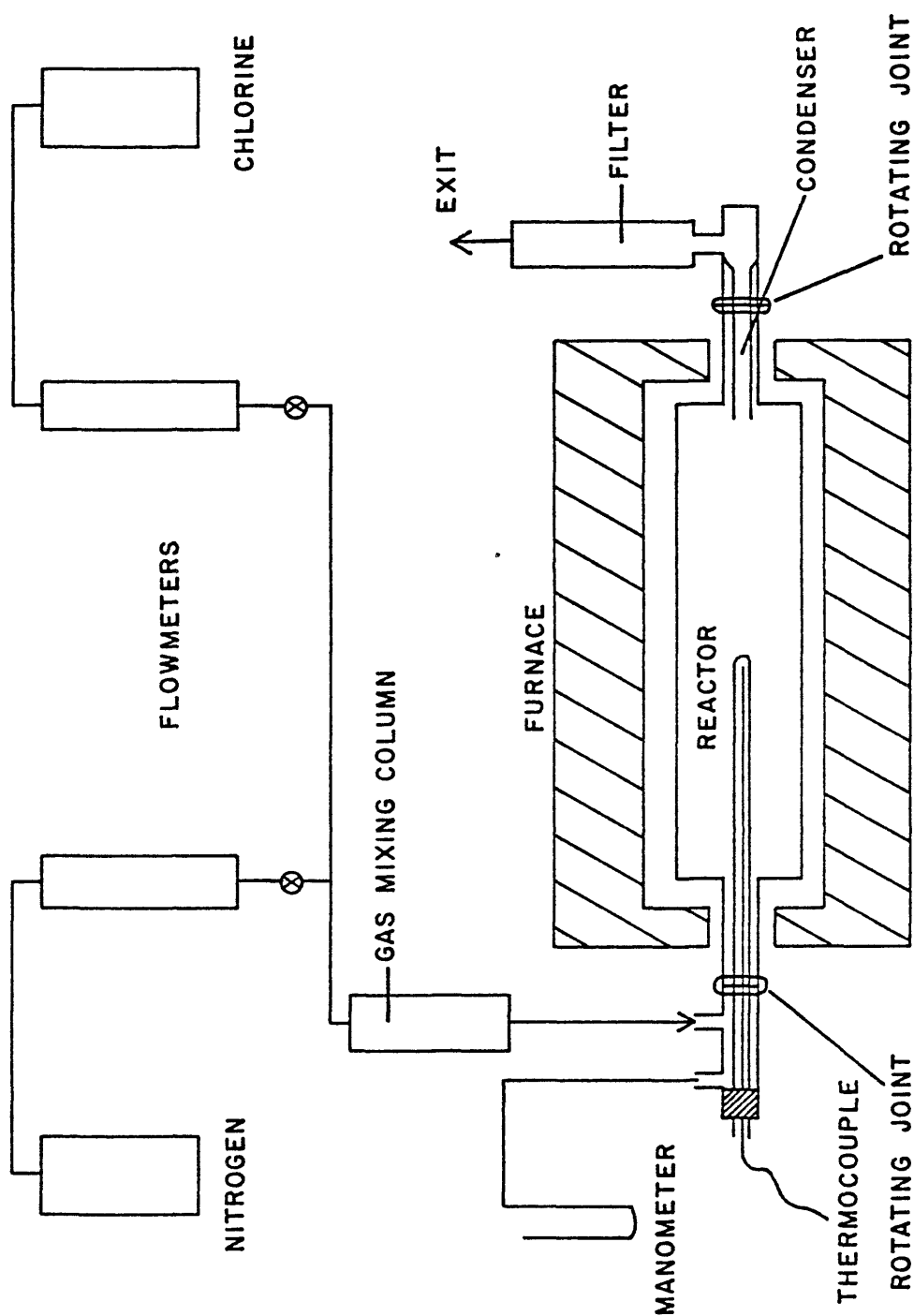


FIGURE II - SCHEMATIC FOR ROTARY KILN REACTOR

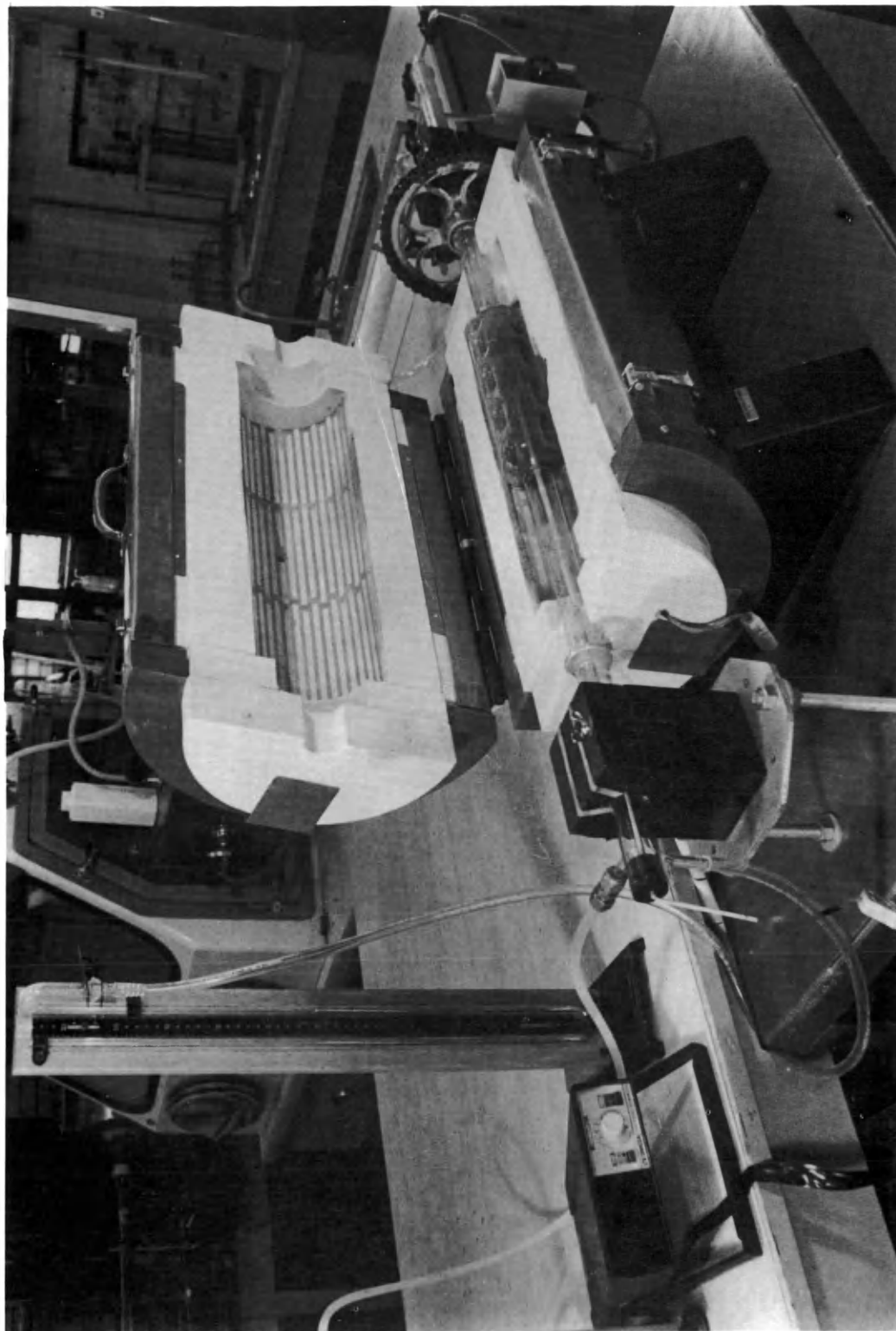


Figure 12 - Rotary Kiln Reactor: Overall View Showing the Reactor in Position

used to connect the gas system to the reactor. The flowmeters and the inlet system are shown in Figure 13.

A split-shell cylindrical furnace (Applied Test Systems, Inc., Series 3210) and temperature controller (Applied Test Systems, Inc., Series 230) were mounted on a steel table equipped with dolly-wheels. Wooden bearing blocks, fastened to the table on each end of the furnace, held the pyrex furnace supports. At the inlet end of the reactor the furnace support was equipped with two sidearms. One was fastened to the carrier gas source line and the other to a mercury manometer used to measure the reactor pressure. The end of the furnace support tube was fitted with a rubber stopper which held a thin vycor tube. By positioning the sealed end of the tube at the center of the furnace, a chromel-alumel thermocouple could be placed inside the tube and used to measure the reaction zone temperature.

One of two fused silica reactors were used, depending on the size of the charge. A photograph of the two reactors is shown in Figure 14. The smaller reactor had a total reaction zone volume of 650 ml. and could handle charges of up to 175 grams. The larger reactor with a 1500 ml. total volume was capable of holding samples of up to 500 grams. Both reactors were dimpled so as to lift the charge as they rotated. At each end ground-glass joints were used to

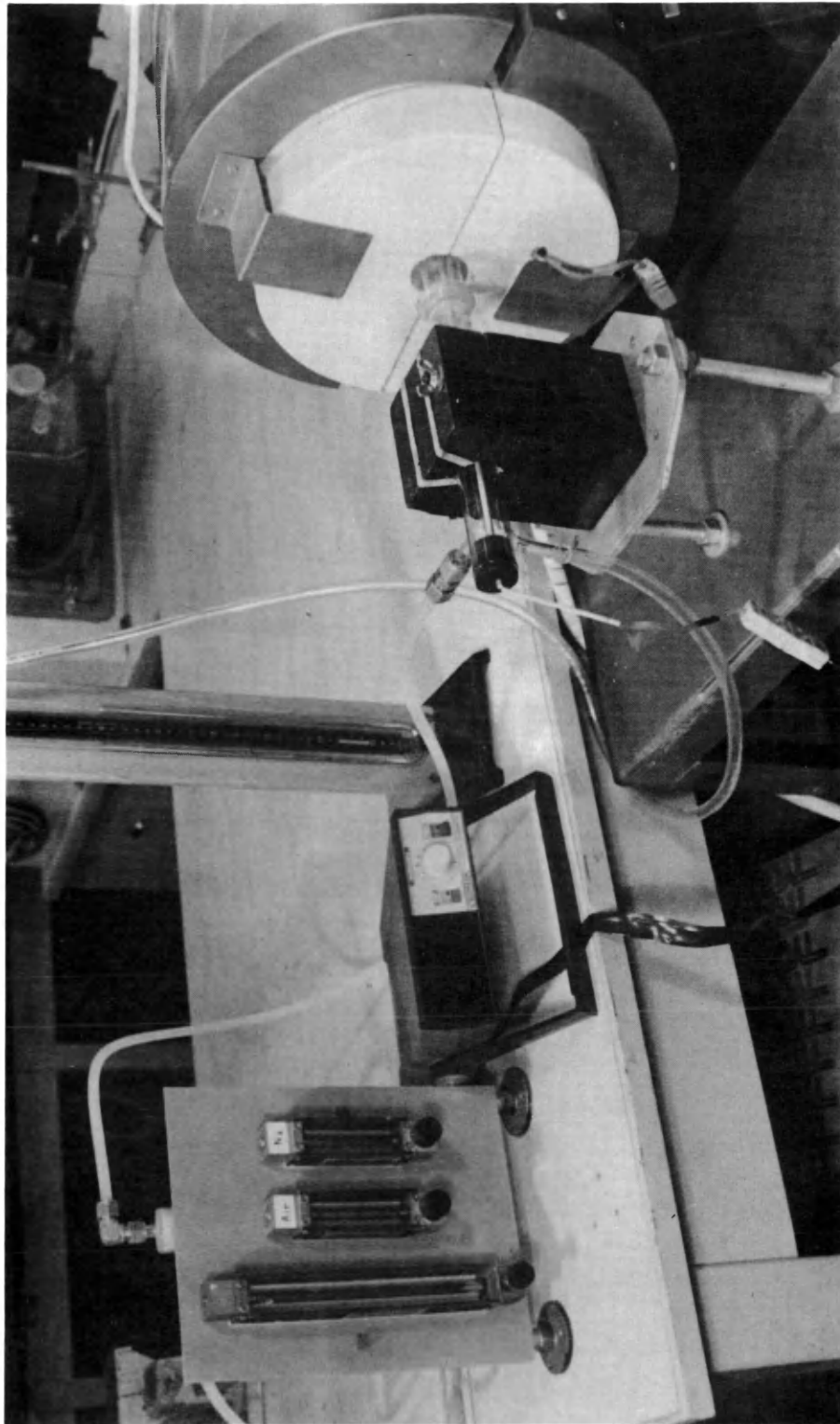


Figure 13 - Rotary Kiln Reactor: View of the Inlet System Showing the Carrier Gas Flowmeters, Reactor Manometer, and Digital Thermometer with Thermocouple



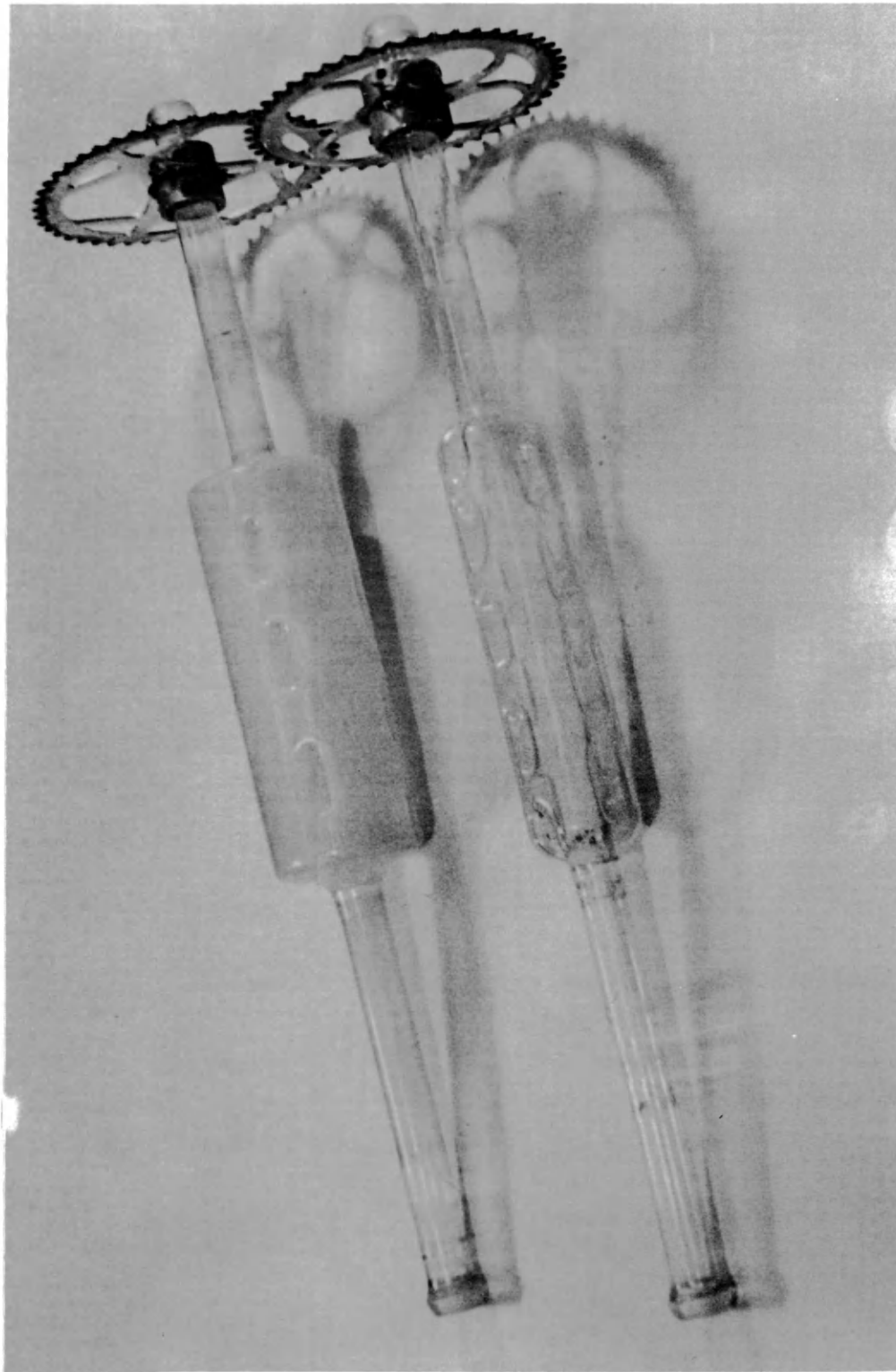


Figure 14 - Rotary Kiln Reactor: View of the two Fused Silica Reactors with the Drive Sprockets Attached

seal the reactor to the reactor supports and provide a greased surface on which the reactor could rotate. A 7-in. sprocket was fastened to one end of the reactor with asbestos tape and set screws. This sprocket was connected by a #42 machine chain to a drive sprocket mounted on a Model 2Z800 Dayton gearmotor.

At the exit end of the reactor support tube, a tapered ground-glass joint was used to seal the condenser system to the reactor. The same type of condenser system as used on the transpiration apparatus was used for the rotary kiln. However, instead of the secondary condenser, a column packed tightly with glass wool was used to trap any volatiles which escaped the water-cooled condenser. A photograph of the condenser system in place on the reactor is shown in Figure 15.

### 3.2.3 Experimental Procedure

From preliminary testing, it was found that sufficient ore should be charged to the kiln to provide approximately 50 mg. of silver available for extraction. At approximately 9.8 troy ounces (T.O.) Ag/ton of synthetic ore (from bulk assays of the ore), this meant charging 160 grams of ore to the kiln. Since this was still within the upper limit of the small reactor, it was used for this study. Again, from preliminary testing, it was found that the synthetic ore was most easily

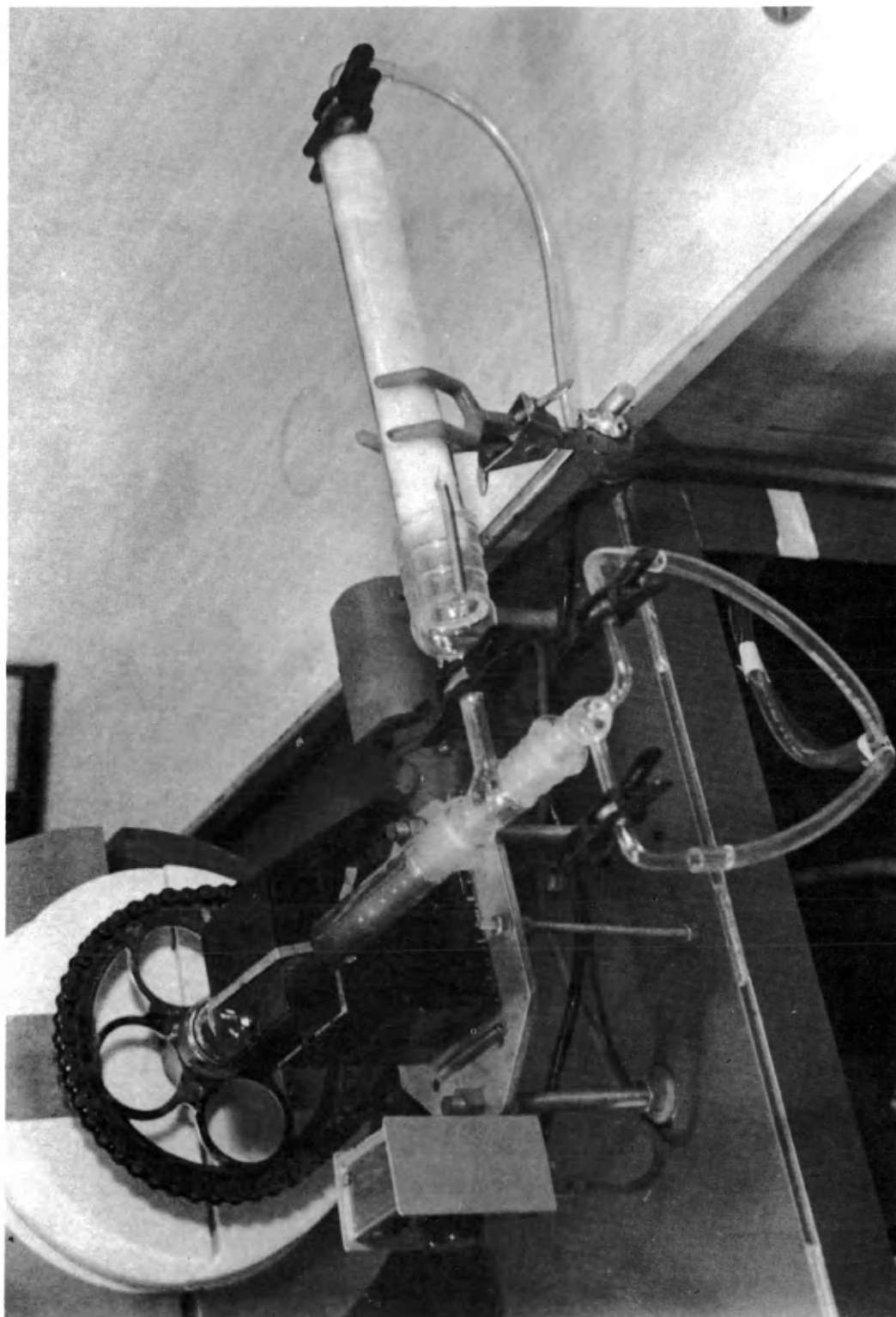


Figure 15 - Rotary Kiln Reactor: View of the Off-Gas Condenser System

chlorinated when pure chlorine, flowing at 750 ml./min. was used as a carrier gas.

After charging the ore to the kiln, the furnace was closed and brought up to run temperature with the kiln rotating. A pure nitrogen flush gas was used during the warm-up period to carry any moisture and oxygen from the system. The run was started by shutting off the nitrogen and turning on the chlorine. Experiments were conducted for 30, 45, and 60 minutes so that not only the percent extraction but also the rate of extraction could be determined. At the end of a run, the furnace and chlorine flow were shut off and the system was purged with nitrogen. The furnace was then cracked open to cool for fifteen minutes before it was fully opened.

Once the chlorine had been purged from the system, the off-gas condenser and filter were removed and leached according to the procedure outlined in Appendix D. When the reactor had cooled down sufficiently, it was removed from the furnace and the ore was dumped into a beaker. After thoroughly mixing the ore, two 30 gram tail samples were obtained using a standard laboratory sample splitter, and analyzed according to the procedure outlined in Appendix D.

Initial runs were made with no complexing agent to

provide a baseline from which the success of a complexing experiment could be measured. Once this was established, the complexing agent was added and thoroughly mixed with the ore before charging it to the reactor. The initial experiments were then repeated to determine the effect of the complexation reaction on the percent silver extracted.

To determine the minimum amount of complexing agent required to maintain high extraction rates, tests were conducted holding the runtime and temperature constant. The weight percent of complexing agent added to the charge was then decreased until a sharp drop in extraction was obtained.

#### 3.2.4 Experimental Errors

Since the extraction tests conducted in this study were of a qualitative nature, an error analysis of the results would be of questionable value.

### 3.3 Packed Bed Reactor

#### 3.3.1 Application to this Study

During the extraction studies on the AgCl-KCl system, problems were encountered in using the rotary kiln reactor. When KCl was added to the synthetic ore as the complexing agent, the ore became sticky at 400 to 450°C. This caused the ore to accumulate on the walls of the reactor long

before the actual run temperature was reached. Since the rotary kiln was not effective on this type of ore, several tests were conducted using a packed bed reactor. It was hoped that the combination of low flowrates, i.e.: long solids residence times, and a static charge would provide conditions which were unaffected by agglomeration of the ore.

### 3.3.2 Experimental Setup

The reactor consisted of a permeable fused silica frit centered in a 36-in. by 2-in. O.D. fused silica tube. The frit acted to distribute the carrier gas over the base of the bed and also provided a surface on which the ore could rest. Reactor endcaps were made by fusing one-half of a ground-glass tapered joint to each end of the tube. The other halves of the joints were then closed off to form caps. Two ports were provided in each cap on which flexible tubing could be attached. By connecting one port from each cap to either leg of a manometer filled with halocarbon oil, the pressure drop across the bed could be measured during a run. The second port in each cap was then used to introduce and exhaust the carrier gas from the reactor.

The reactor was held vertically inside a 26-in. long cylindrical furnace with each end sealed by a firebrick to prevent excessive heat loss. A small hole was drilled in

the firebrick at the top of the furnace to allow a thermocouple to be positioned alongside the packed bed.

The carrier gases were obtained by attaching the packed bed reactor to the transpiration apparatus gas train.

### 3.3.3 Experimental Procedure

A preliminary run was made to determine the reaction time necessary to achieve 30% extraction of the silver in a non-complexing run. It was felt that this would provide a good baseline from which to measure the effects of complexation. At 750°C, this runtime was found to be twelve hours.

To start a run, the reactor was brought up to temperature with argon purging the system. Once the temperature had stabilized, the ore charge was dumped in the top of the reactor and the cap was replaced. If the run was to show the effects of complexation, the complexing agent was mixed with the ore before it was charged to the reactor.

At the end of a run, the furnace and chlorine gas were shut off and the system was purged with argon until all the chlorine had been removed. When the reactor had cooled down, it was removed from the furnace and the ore charge was mixed and split for assaying in the same manner as was used for the rotary kiln experiments.

### 3.4 Sample Preparation and Handling

#### 3.4.1 Transpiration Studies

Due to the hygroscopic nature of the chlorides used in this study, the sample material was completely dried before being used in the transpiration apparatus. This was accomplished with the packed bed sample drying system shown in Figure 16. To prevent recontamination after drying, storage and any handling of the material was done inside a nitrogen filled dry box. A photograph of the dry box, showing the sample carrier guide tube attached, is shown in Figure 17. Samples were dried by packing 25 to 30 grams into a fused silica drying tube while inside the dry box. This tube was then stoppered and transferred to the drying furnace. The sample material, in this case silver chloride or potassium chloride, was then "dried" by baking at  $420^{\circ}\text{C}$  under a slow chlorine purge. After six to eight hours, the furnace was shut off and the gas was switched to argon. When the chlorine had been completely flushed from the system and the reactor had cooled enough to handle, the drying tube was again stoppered and transferred to the dry box. Once under dry nitrogen, the sample material was removed from the tube and stored in screw-cap bottles for future use.



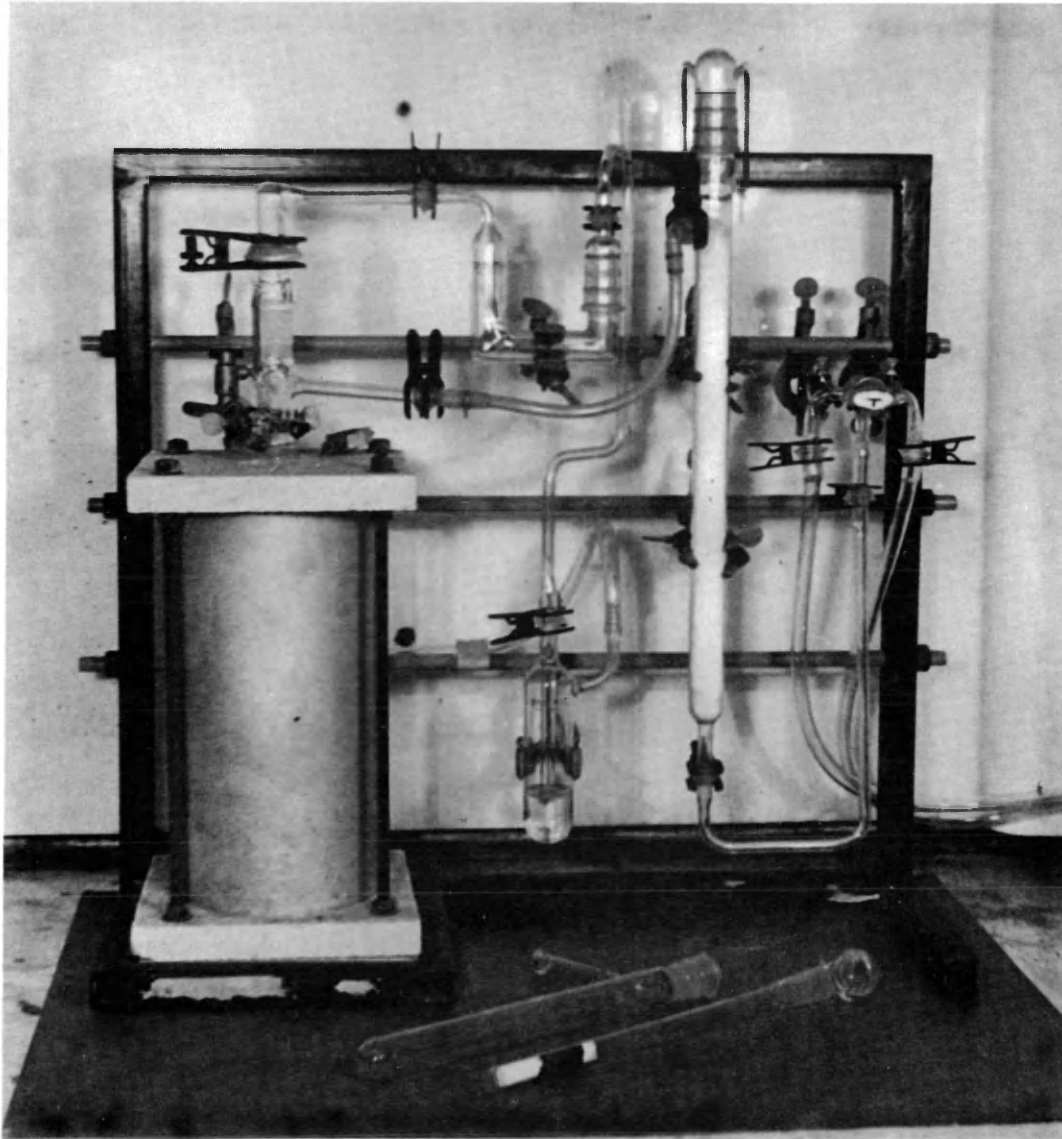


Figure 16 - Overall View of the Sample Drying Apparatus  
Showing the Inner and Outer Sample Drying  
Tubes in the Foreground

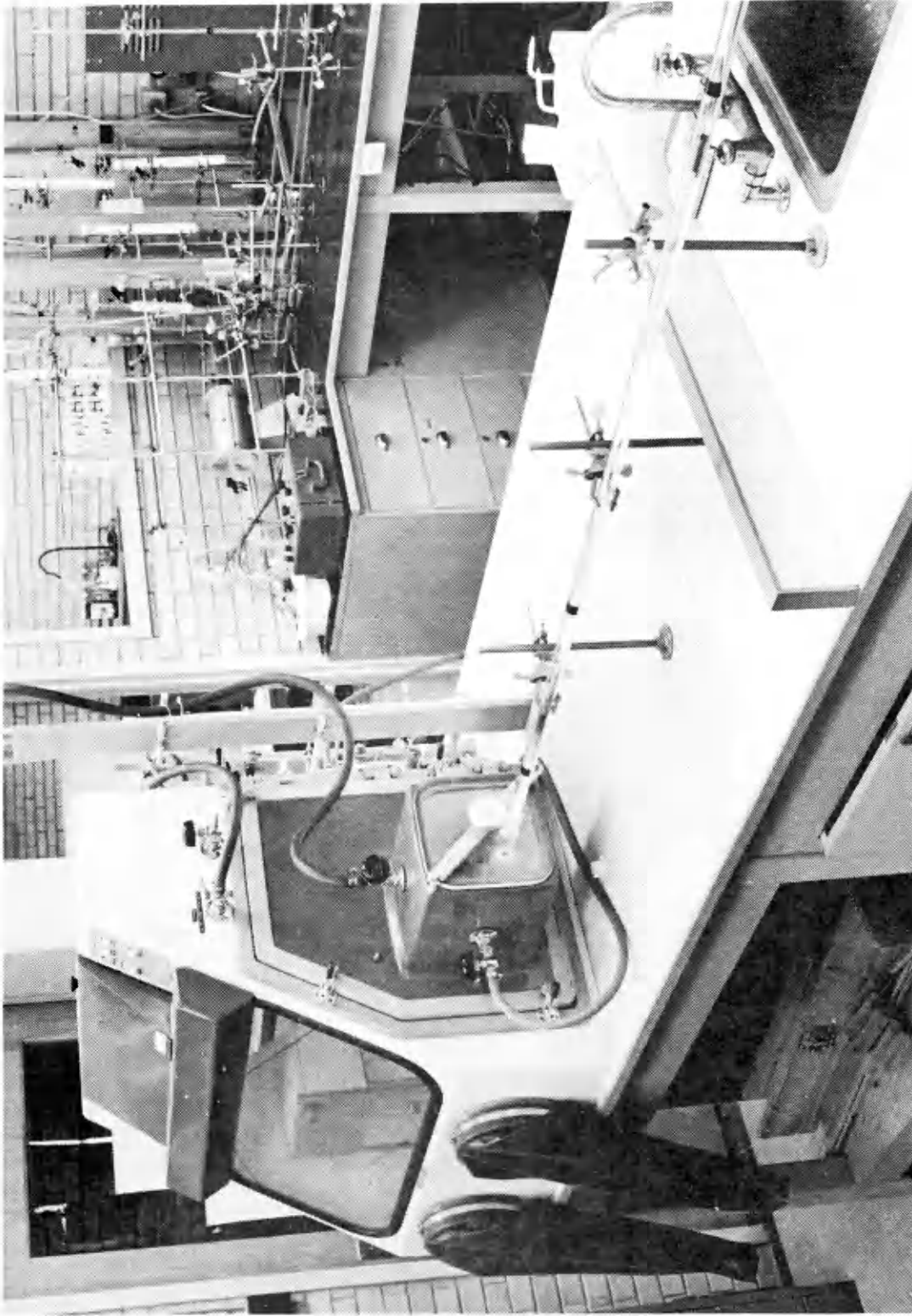


Figure 17 - View of the Nitrogen-filled Dry Box with the Sample Carrier Guide Tube Attached

### 3.4.2 Silver Extraction Studies

Since as-received reagent-grade chemicals were used for the complexing agents, the only material preparation required for this phase of the study involved making the synthetic silver ore. Several attempts were made at producing the grade of ore required for these experiments. From this, the following procedure was derived.

Foundry silica sand was wet screened until twelve pounds of a -100 mesh, +200 mesh size fraction were obtained. Several 30 gram samples of the sand were then assayed for iron. Results of these tests showed more than 15 milligrams of Fe per 100 grams of sand. Therefore, to remove all metallic and acid-soluble impurities, the remaining sand was leached in aqua regia, (3 parts hydrochloric acid to 1 part nitric acid) for twenty-four hours. After decanting the acid, the sand was washed in tap water and rinsed with deionized water until no trace of  $\text{Cl}^-$  ions was found in the rinse water\*. The leached sand was then spread out on plastic trays to dry.

Next, a 15 gram per liter silver nitrate solution was vacuum filtered over 200 gram batches of the dry sand.

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\* $\text{Cl}^-$  ion determination: To a test tube of the rinse water, add concentrated silver nitrate solution drop-wise. A milky-white precipitate of silver chloride indicates the presence of  $\text{Cl}^-$ .

The filter cakes were then spread out to dry on plastic trays. Once dried, each batch was roasted in the rotary kiln reactor for two hours at 550°C to affect the decomposition of the silver nitrate to metallic silver.

When all the synthetic ore had been roasted, it was combined and thoroughly mixed. Six head samples were then split out and assayed according to the procedure outlined in Appendix D.

## 4. RESULTS

### 4.1 Thermodynamic Studies

#### 4.1.1 The Silver-Chlorine System

A series of transpiration experiments were conducted to determine the vapor pressure of silver chloride over the temperature range 727°-877°C. The results of these experiments were then used as a basis for determining the increase in the apparent vapor pressure of silver chloride due to complexation with potassium chloride.

Before any transpiration calculations could be performed, it was necessary to determine the molecularity of the predominant vapor species in the system. From mass spectrometry studies of the silver-chlorine system, Svedburg<sup>(12)</sup> established the two predominant species to be the silver chloride monomer and trimer. He then developed the following functional relationship for the monomer/trimer vapor pressure ratio:

$$\text{Log} = \frac{P_{\text{AgCl}}}{P_{\text{Ag}_3\text{Cl}_3}} = \frac{-0.142}{T} + 2.323 \quad (4.1)$$

Where: T = °KELVIN

For the temperature range of this study, this ratio is approximately 210 to 1. Therefore, only the species AgCl was considered in the transpiration calculations.

The logarithm of the vapor pressure of silver chloride, calculated from the experimental data, is plotted as a function of temperature in Figure 18. To place the best-fitting line on the plot, a standard least squares regression was used to obtain the following equation:

$$\text{Log } P_{\text{AgCl}} \text{ (atm)} = \frac{-10226}{T} + 5.7786 \quad (4.2)$$

Where:  $T = \text{°KELVIN}$

The results from several other recent studies are plotted for comparison. It should be noted that only Rupert's data was generated over the temperature range of this study. To plot the data of Bloom, et.al.,<sup>(21)</sup>, a least squares regression, performed by Bloom himself, was used to extrapolate the data from 1028°C to this temperature range.

In addition to measuring  $P_{\text{AgCl}}$  as a function of temperature, it was necessary to prove that the measurements were made within the constant vapor pressure plateau as described in Section 3.1.1. This was accomplished by conducting several experiments at different carrier gas flowrates. The results of these experiments are plotted in Figure 19.

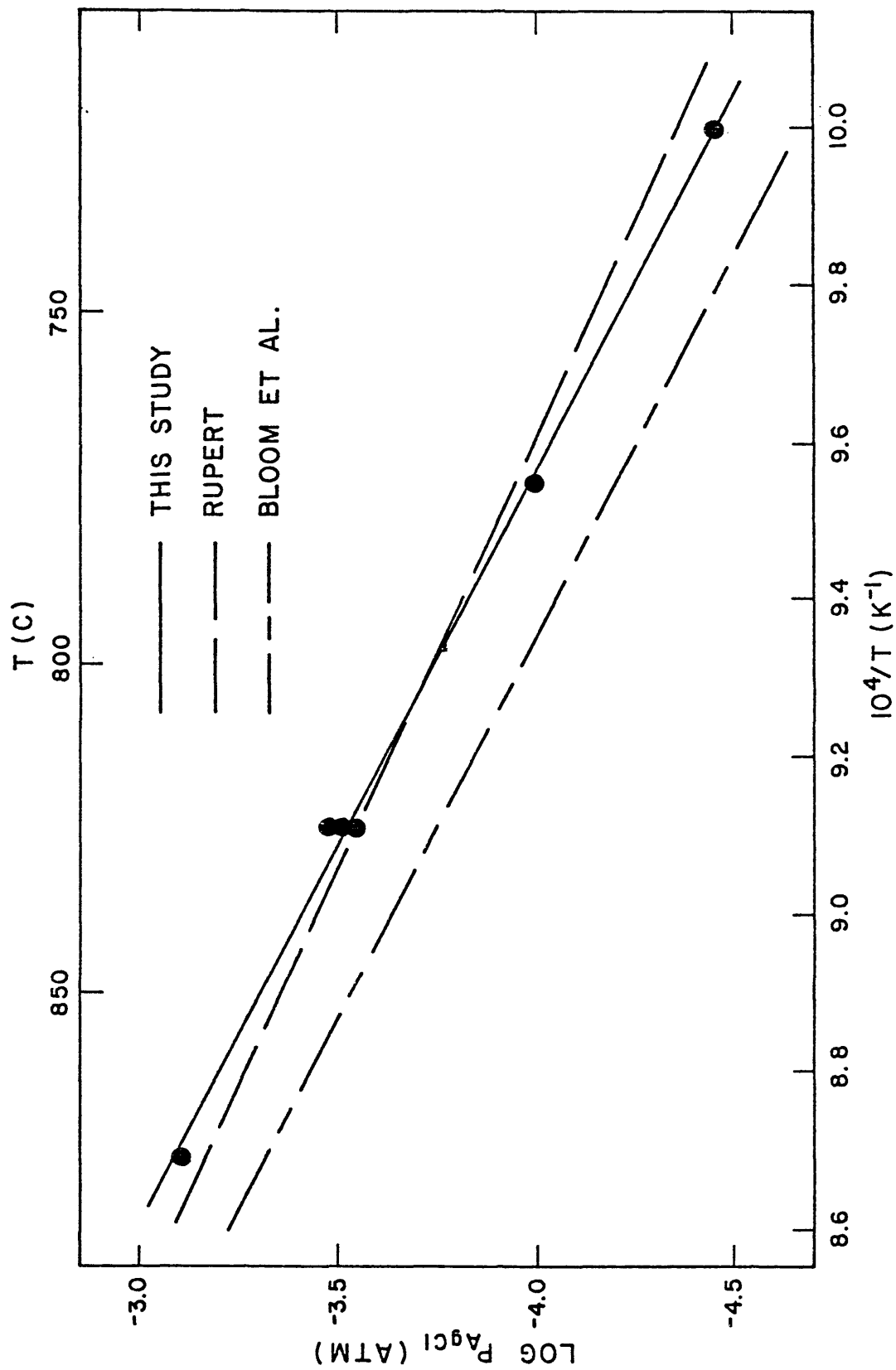


FIGURE 18 - VAPOR PRESSURE AS A FUNCTION OF TEMPERATURE FOR THE REACTION:  
 $\text{AgCl}_{(l)} = \text{AgCl}_{(g)}$

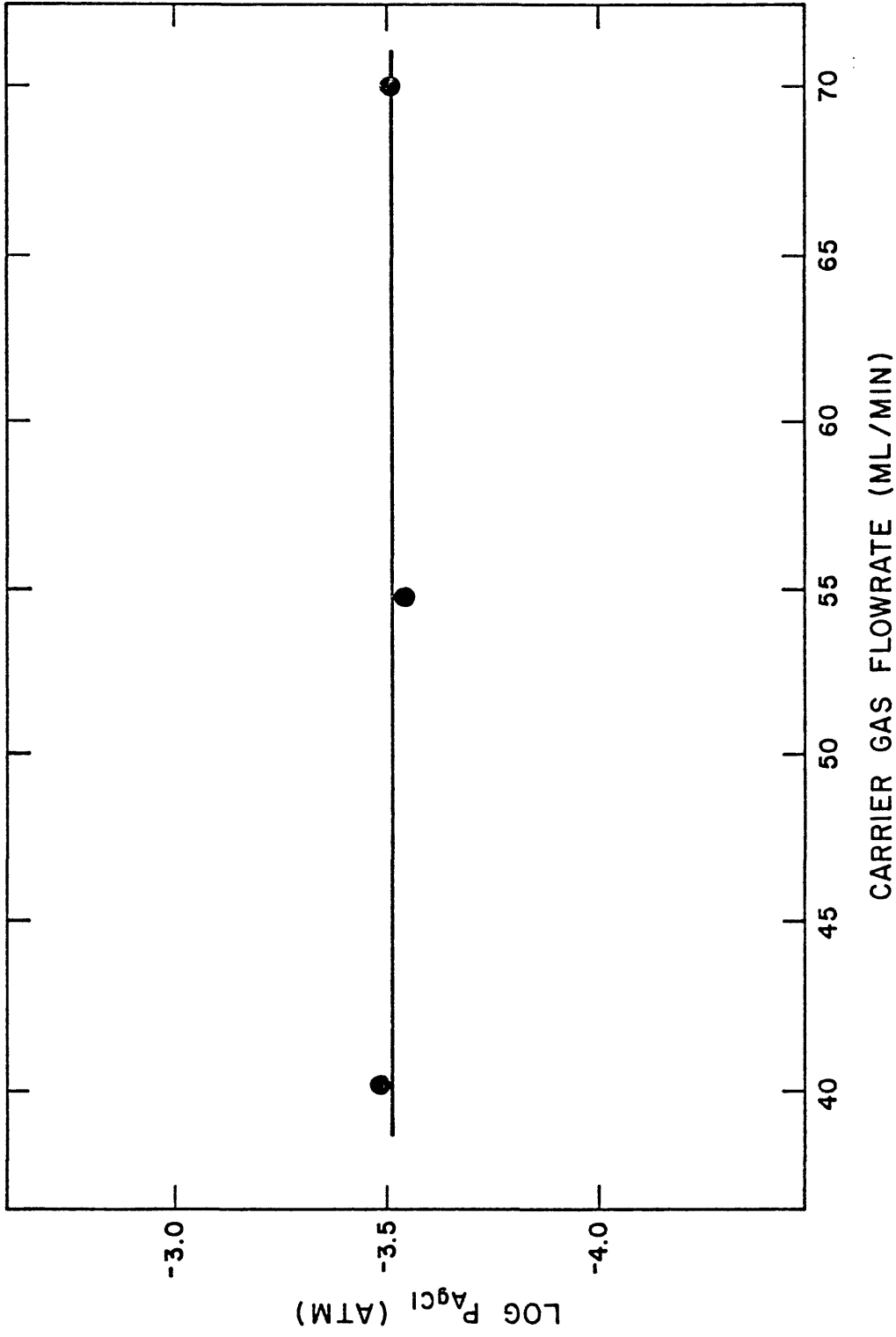
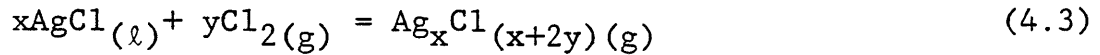


FIGURE 19 - RESULTS OF TESTS CONDUCTED TO DETERMINE THE INDEPENDENCE OF CARRIER GAS FLOWRATE FOR THE REACTION:  $\text{AgCl}_{(l)} = \text{AgCl}_{(g)}$  AT 825°C



Finally, it was necessary to determine if the chlorine gas in the system acted as an inert carrier or as an additional reactant. By proposing the reaction:



the following equilibrium constant could be written:

$$K_1 = \frac{P_{\text{Ag}_x\text{Cl}_{(x+2y)}}}{a_{\text{AgCl}}^x * P_{\text{Cl}_2}^y} \quad (4.4)$$

By taking the logarithm of this expression:

$$\text{Log } P_{\text{Ag}_x\text{Cl}_{(x+2y)}} = y \text{ Log } P_{\text{Cl}_2} + \text{Log } K_1 \quad (4.5)$$

a linear relationship is obtained between the chlorine potential and the calculated partial pressure of AgCl. Note that since high-purity AgCl was used, the activity of the molten samples equals 1 and the activity term drops out of the logarithmic expression. Several experiments were conducted at 825°C in which the chlorine potential of the carrier gas was varied. The vapor pressure of silver chloride calculated from these runs was then plotted using this equation in Figure 20. It can be seen that the slope of this plot, which represents the value of y, is indeed zero and, therefore, the chlorine did act only as an inert carrier gas.

A summary of the experimental conditions and the results

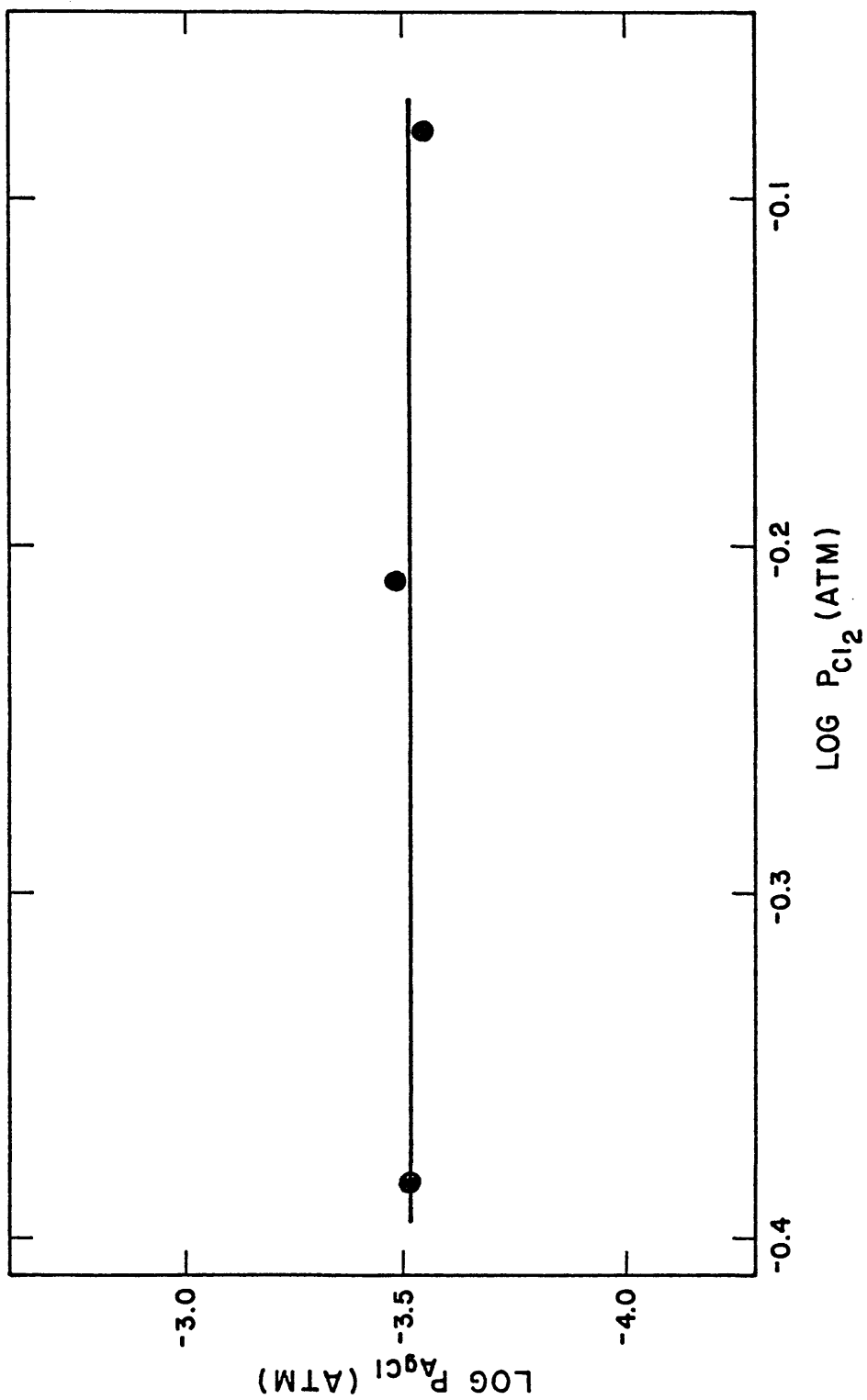


FIGURE 20 - DETERMINATION OF Y IN THE REACTION:  
 $X \text{ AgCl}_{(l)} + Y \text{ Cl}_{2(g)} = \text{Ag}_X \text{ Cl}_{(X+2Y)(g)}$  AT 825° C

obtained for the silver-chlorine system are presented in Table 1.

#### 4.1.2 The Silver-Potassium-Chlorine System

Once  $P_{\text{AgCl}}$  was established as a function of temperature, a new series of experiments were conducted in which the previous run conditions were duplicated. However, in this series, high purity potassium chloride was placed in the saturation boats, (See Figure 5) and the condensate was analyzed for potassium as well as silver.

Again, a knowledge of the molecularity of all transported species was necessary before the vapor pressure of the complex species could be calculated. Since the species  $\text{AgCl}$  was previously determined, it was necessary to identify only the complex species and the predominant potassium chloride species.

As stated previously in Section 2.1, Svedburg<sup>(10)</sup> observed the species  $\text{AgKCl}^+$ ,  $\text{Ag}_2\text{KCl}_2^+$ , and  $\text{AgK}_2\text{Cl}_2^+$  using a mass spectrometer. He then concluded that the  $\text{AgKCl}^+$  species was probably the result of fragmentation only. No further comment was made as to either the origin of the other species or which species was most predominant. If it is assumed that all of these species are the result of fragmentation, i.e.: the loss of one chlorine atom,

TABLE 1  
SUMMARY OF RUN CONDITIONS AND RESULTS FOR AgCl TRANSPIRATION RUNS

Run No.	Run Temp(°C)	Carrier Gas Flowrate(ml/min)	Mg Silver Transported	Reactor Pressure(mm.Hg)	Runtime (min)	Carrier Gas Composition	Log P <sub>AgCl</sub>
AgCl-1	727	55.8	1.64	620.2	185	100%Cl <sub>2</sub>	-4.448
AgCl-2	775	56.3	4.81	622.0	182	100%Cl <sub>2</sub>	-3.977
AgCl-3	825	54.6	8.28	621.5	120	100%Cl <sub>2</sub>	-3.546
AgCl-4	877	55.7	25.50	626.0	132	100%Cl <sub>2</sub>	-3.108
AgCl-5	825	70.1	11.53	628.9	120	50%Cl <sub>2</sub> -50%Ar	-3.512
AgCl-6	825	40.1	10.65	628.3	182	75%Cl <sub>2</sub> -25%Ar	-3.483

then the original parent molecules were  $\text{AgKCl}_2$ ,  $\text{Ag}_2\text{KCl}_3$ , and  $\text{AgK}_2\text{Cl}_3$ . In an attempt to simplify the transpiration calculations,  $\text{AgKCl}_2$  was assumed to be the predominant species and the vapor pressure contribution from the other species was assumed insignificant.

Svedburg<sup>(10)</sup> also studied the potassium-chlorine system with a mass spectrometer and found both the monomer,  $\text{KCl}$ , and the dimer,  $\text{K}_2\text{Cl}_2$ , to be the predominant gaseous species. This meant that neither species could be neglected in the transpiration calculations.

To evaluate the equilibrium constants for the complexation reactions between  $\text{AgCl}_{(l)}$  and both  $\text{KCl}_{(g)}$  and  $\text{K}_2\text{Cl}_{2(g)}$ , it was necessary to calculate their vapor pressures at the reactor temperature. This was accomplished by solving the following equations simultaneously.

$$M_K = M_{\text{KCl}} + 2 M_{\text{K}_2\text{Cl}_2} \quad (4.6)$$

where:

$M_K$  = Moles of potassium transported

$M_{\text{KCl}}$  = Moles of  $\text{KCl}$  at equilibrium with the complex

$M_{\text{K}_2\text{Cl}_2}$  = Moles of  $\text{K}_2\text{Cl}_2$  at equilibrium with the complex

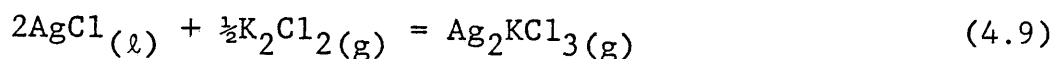
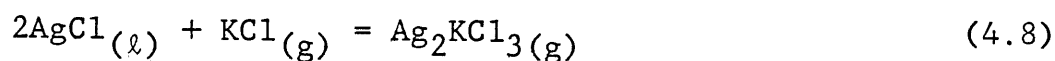
$$K_{\text{eq}} = \frac{P_{\text{K}_2\text{Cl}_2}^{\frac{1}{2}}}{P_{\text{KCl}}} \quad (4.7)$$

where:  $K_{\text{eq}}$  represents the equilibrium constant for the reaction between  $\text{KCl}_{(g)}$  and  $\text{K}_2\text{Cl}_{2(g)}$ .

The value of the equilibrium constant,  $K_{eq}$ , was obtained for several temperatures over the range of interest from the JANAF Thermochemical Tables<sup>(22)</sup>. This data was then regressed as a function of temperature for use in Equation 4.7. For given values of  $M_K$  and  $K_{eq}$ , the two equations were combined and the resulting equation in one unknown was then solved by an interval halving routine.

The transpiration data obtained from the complexing runs was fed into a microprocessor which calculated the mole balances and partial pressures of all species in the gaseous state. A thorough description of the calculations performed is given in Appendix A. A listing of the computer program as well as a sample printout are presented in Appendix B.

The results obtained from the first few experiments clearly showed that the initial assumption about the molecularity of the complex ( $AgKCl_2$ ) was wrong. Assuming this species, insufficient potassium had been transported to account for the increase in silver transported. This problem was resolved by assuming  $Ag_2KCl_3$  was the most predominant species. No further mass balance problems were encountered after this assumption. The formation reactions for the new species were proposed as follows:



From these reactions, the equilibrium constants can be written.

$$K_2 = \frac{P_{\text{Ag}_2\text{KCl}_3}}{a_{\text{AgCl}}^2 \times P_{\text{KCl}}} \quad (4.10)$$

$$K_3 = \frac{P_{\text{Ag}_2\text{KCl}_3}}{a_{\text{AgCl}}^2 \times P_{\text{K}_2\text{Cl}_2}^{\frac{1}{2}}} \quad (4.11)$$

The run conditions for this series of experiments are listed in Table 2. The results from these experiments, including the calculated values of Log  $K_2$  and Log  $K_3$  are listed in Table 3.

The van't Hoff Equation was used to express the functional dependence of the data upon temperature. In terms of the common logarithm, the van't Hoff Equation may be written:

$$\frac{d \text{Log}K}{d (1/T)} = \frac{-\Delta H^{\circ}}{(2.303)R} \quad (4.12)$$

Where: T = absolute temperature

R = gas constant

$\Delta H^{\circ}$  = standard enthalpy change of the reaction

TABLE 2  
 RUN CONDITIONS FOR AgCl-KCl COMPLEXATION RUNS

Run No.	Reaction Temp(°C)	Carrier Gas Flowrate(ml/min)	Reactor Pressure(mm.Hg)	Runtime (min)	Carrier Gas Composition	Comments
AgKCl-1	725	59.0	622.2	240	100%Cl <sub>2</sub>	
AgKCl-2	725	60.0	624.6	240	100%Cl <sub>2</sub>	
AgKCl-3	774	58.2	621.0	240	100%Cl <sub>2</sub>	
AgKCl-4	774	59.4	615.2	240	100%Cl <sub>2</sub>	
AgKCl-5	792	56.8	618.2	247	100%Cl <sub>2</sub>	
AgKCl-6	794	61.4	618.7	243	100%Cl <sub>2</sub>	
AgKCl-7	820	69.1	617.1	240	100%Cl <sub>2</sub>	
AgKCl-8	820	59.8	617.4	240	49%Cl <sub>2</sub> -51%Ar	
AgKCl-9	820	59.7	618.9	240	51%Cl <sub>2</sub> -49%Ar	
AgKCl-10	850	49.0	625.2	180	100%Cl <sub>2</sub>	spilled sample- not used
AgKCl-11	850	49.3	624.1	180	100%Cl <sub>2</sub>	
AgKCl-12	850	59.0	624.0	180	100%Cl <sub>2</sub>	
AgKCl-13	880	50.8	626.9	120	100%Cl <sub>2</sub>	run scratched- poor data
AgKCl-14	880	59.6	627.1	120	100%Cl <sub>2</sub>	
AgKCl-15	749	49.6	624.7	435	100%Cl <sub>2</sub>	
AgKCl-16	749	59.2	624.4	360	100%Cl <sub>2</sub>	
AgKCl-17	749	46.7	624.4	420	100%Cl <sub>2</sub>	
AgKCl-18	734	54.4	625.5	344	100%Cl <sub>2</sub>	
AgKCl-19	734	67.3	626.4	426	100%Cl <sub>2</sub>	spilled sample- not used
AgKCl-20	839	57.3	620.7	120	100%Cl <sub>2</sub>	
AgKCl-21	839	56.3	621.8	120	100%Cl <sub>2</sub>	
AgKCl-22	842	58.2	624.1	120	100%Cl <sub>2</sub>	



TABLE 3  
EXPERIMENTAL DATA FROM AgCl-KCl COMPLEXATION RUNS

Run No.	Total Moles Carrier Gas	Moles Ag Total	Moles K Total	Moles AgCl	Moles KCl	Moles K <sub>2</sub> Cl <sub>2</sub>	Moles Ag <sub>2</sub> KCl <sub>3</sub>
AgCl-1	0.4777	3.42x10 <sup>-5</sup>	1.25x10 <sup>-5</sup>	1.99x10 <sup>-5</sup>	5.07x10 <sup>-6</sup>	1.45x10 <sup>-7</sup>	7.17x10 <sup>-6</sup>
AgCl-2	0.4869	3.22x10 <sup>-5</sup>	9.98x10 <sup>-6</sup>	2.02x10 <sup>-5</sup>	3.81x10 <sup>-6</sup>	8.06x10 <sup>-8</sup>	6.00x10 <sup>-6</sup>
AgCl-3	0.4639	7.58x10 <sup>-5</sup>	3.27x10 <sup>-5</sup>	5.83x10 <sup>-5</sup>	2.20x10 <sup>-5</sup>	9.98x10 <sup>-7</sup>	8.76x10 <sup>-6</sup>
AgCl-4	0.4738	8.46x10 <sup>-5</sup>	2.71x10 <sup>-5</sup>	6.01x10 <sup>-5</sup>	1.41x10 <sup>-5</sup>	3.96x10 <sup>-7</sup>	1.23x10 <sup>-5</sup>
AgCl-5	0.4686	1.13x10 <sup>-4</sup>	3.32x10 <sup>-5</sup>	8.65x10 <sup>-5</sup>	1.89x10 <sup>-5</sup>	5.12x10 <sup>-7</sup>	1.33x10 <sup>-5</sup>
AgCl-6	0.5004	1.22x10 <sup>-4</sup>	4.42x10 <sup>-5</sup>	9.62x10 <sup>-5</sup>	2.90x10 <sup>-5</sup>	1.08x10 <sup>-6</sup>	1.31x10 <sup>-5</sup>
AgCl-7	0.5538	2.24x10 <sup>-4</sup>	9.16x10 <sup>-5</sup>	1.81x10 <sup>-4</sup>	6.38x10 <sup>-5</sup>	2.90x10 <sup>-6</sup>	2.19x10 <sup>-5</sup>
AgCl-8	0.4766	2.00x10 <sup>-4</sup>	6.85x10 <sup>-5</sup>	1.55x10 <sup>-4</sup>	4.31x10 <sup>-5</sup>	1.54x10 <sup>-6</sup>	2.24x10 <sup>-5</sup>
AgCl-9	0.4767	2.09x10 <sup>-4</sup>	1.06x10 <sup>-4</sup>	1.55x10 <sup>-4</sup>	7.03x10 <sup>-5</sup>	4.11x10 <sup>-6</sup>	2.71x10 <sup>-5</sup>
AgCl-11	0.2943	2.01x10 <sup>-4</sup>	1.06x10 <sup>-4</sup>	1.69x10 <sup>-4</sup>	7.94x10 <sup>-5</sup>	4.99x10 <sup>-6</sup>	1.62x10 <sup>-5</sup>
AgCl-12	0.3521	2.84x10 <sup>-4</sup>	1.62x10 <sup>-4</sup>	2.02x10 <sup>-4</sup>	1.06x10 <sup>-4</sup>	7.51x10 <sup>-6</sup>	4.09x10 <sup>-5</sup>
AgCl-14	0.2399	2.73x10 <sup>-4</sup>	6.73x10 <sup>-5</sup>	2.36x10 <sup>-4</sup>	4.62x10 <sup>-5</sup>	1.25x10 <sup>-6</sup>	1.86x10 <sup>-5</sup>
AgCl-15	0.7216	7.18x10 <sup>-5</sup>	1.61x10 <sup>-5</sup>	5.20x10 <sup>-5</sup>	6.04x10 <sup>-6</sup>	8.13x10 <sup>-8</sup>	9.91x10 <sup>-6</sup>
AgCl-16	0.7047	6.70x10 <sup>-5</sup>	1.92x10 <sup>-5</sup>	5.09x10 <sup>-5</sup>	1.06x10 <sup>-5</sup>	2.56x10 <sup>-7</sup>	8.08x10 <sup>-6</sup>
AgCl-17	0.6502	6.40x10 <sup>-5</sup>	1.82x10 <sup>-5</sup>	4.69x10 <sup>-5</sup>	9.21x10 <sup>-6</sup>	2.10x10 <sup>-7</sup>	8.53x10 <sup>-6</sup>
AgCl-18	0.6193	4.94x10 <sup>-5</sup>	1.46x10 <sup>-5</sup>	3.17x10 <sup>-5</sup>	5.48x10 <sup>-6</sup>	1.08x10 <sup>-7</sup>	8.88x10 <sup>-6</sup>
AgCl-20	0.2262	1.33x10 <sup>-4</sup>	3.50x10 <sup>-5</sup>	1.06x10 <sup>-4</sup>	2.07x10 <sup>-5</sup>	5.32x10 <sup>-7</sup>	1.33x10 <sup>-5</sup>
AgCl-21	0.2217	1.33x10 <sup>-4</sup>	3.27x10 <sup>-5</sup>	1.04x10 <sup>-4</sup>	1.73x10 <sup>-5</sup>	3.80x10 <sup>-7</sup>	1.47x10 <sup>-5</sup>
AgCl-22	0.2339	1.39x10 <sup>-4</sup>	4.42x10 <sup>-5</sup>	1.15x10 <sup>-4</sup>	3.05x10 <sup>-5</sup>	1.07x10 <sup>-6</sup>	1.16x10 <sup>-5</sup>

TABLE 3 (Continued)  
 EXPERIMENTAL DATA FROM AgCl-KCl COMPLEXATION RUNS

Run No.	$P_{AgCl}$	$P_{KCl}$	$P_{K_2Cl_2}$	$P_{Ag_2KCl_3}$	Log K2 (Monomer)	Log K3 (Dimer)
AgCl-1	$3.40 \times 10^{-5}$	$8.69 \times 10^{-6}$	$2.48 \times 10^{-7}$	$1.23 \times 10^{-5}$	0.1502	-1.6075
AgCl-2	$3.40 \times 10^{-5}$	$6.44 \times 10^{-6}$	$1.36 \times 10^{-7}$	$1.01 \times 10^{-5}$	0.1966	-1.5612
AgCl-3	$1.03 \times 10^{-4}$	$3.87 \times 10^{-5}$	$1.76 \times 10^{-6}$	$1.54 \times 10^{-5}$	-0.3997	-1.9341
AgCl-4	$1.03 \times 10^{-4}$	$2.40 \times 10^{-5}$	$6.77 \times 10^{-7}$	$2.09 \times 10^{-5}$	-0.0595	-1.5939
AgCl-5	$1.50 \times 10^{-4}$	$3.29 \times 10^{-5}$	$8.90 \times 10^{-7}$	$2.31 \times 10^{-5}$	-0.1539	-1.6114
AgCl-6	$1.57 \times 10^{-4}$	$4.72 \times 10^{-5}$	$1.76 \times 10^{-6}$	$2.13 \times 10^{-5}$	-0.3464	-1.7955
AgCl-7	$2.65 \times 10^{-4}$	$9.36 \times 10^{-5}$	$4.25 \times 10^{-6}$	$3.21 \times 10^{-5}$	-0.4643	-1.8072
AgCl-8	$2.65 \times 10^{-4}$	$7.34 \times 10^{-5}$	$2.62 \times 10^{-6}$	$3.82 \times 10^{-5}$	-0.2842	-1.6271
AgCl-9	$2.65 \times 10^{-4}$	$1.20 \times 10^{-4}$	$7.01 \times 10^{-6}$	$4.62 \times 10^{-5}$	-0.4147	-1.7576
AgCl-11	$4.71 \times 10^{-4}$	$2.21 \times 10^{-4}$	$1.39 \times 10^{-5}$	$4.53 \times 10^{-5}$	-0.6888	-1.9153
AgCl-12	$4.71 \times 10^{-4}$	$2.48 \times 10^{-4}$	$1.75 \times 10^{-5}$	$9.55 \times 10^{-5}$	-0.4149	-1.6414
AgCl-14	$8.12 \times 10^{-4}$	$1.59 \times 10^{-4}$	$4.30 \times 10^{-6}$	$6.39 \times 10^{-5}$	-0.3950	-1.5111
AgCl-15	$5.93 \times 10^{-5}$	$6.88 \times 10^{-6}$	$9.26 \times 10^{-8}$	$1.13 \times 10^{-5}$	0.2154	-1.4302
AgCl-16	$5.93 \times 10^{-5}$	$1.23 \times 10^{-5}$	$2.98 \times 10^{-7}$	$9.42 \times 10^{-6}$	-0.1170	-1.7627
AgCl-17	$5.93 \times 10^{-5}$	$1.16 \times 10^{-5}$	$2.65 \times 10^{-7}$	$1.08 \times 10^{-5}$	-0.0336	-1.6792
AgCl-18	$4.20 \times 10^{-5}$	$7.28 \times 10^{-6}$	$1.43 \times 10^{-7}$	$1.18 \times 10^{-5}$	0.2094	-1.5057
AgCl-20	$3.82 \times 10^{-4}$	$7.46 \times 10^{-5}$	$1.92 \times 10^{-6}$	$4.80 \times 10^{-5}$	-0.1916	-1.4600
AgCl-21	$3.82 \times 10^{-4}$	$6.38 \times 10^{-5}$	$1.40 \times 10^{-6}$	$5.41 \times 10^{-5}$	-0.0713	-1.3397
AgCl-22	$4.05 \times 10^{-4}$	$1.07 \times 10^{-4}$	$3.74 \times 10^{-6}$	$4.09 \times 10^{-5}$	-0.4179	-1.6749

Plotting the logarithm of the equilibrium constant versus  $1/T$  should yield a straight line with a slope equal to  $-\Delta H^{\circ}/(2.303)R$ . The results of this study are plotted in Figures 21 and 22 using this equation.

To place the best-fitting lines through the data in these figures, an absolute-value regression routine was used. (It was felt that the least squares criteria for regression places too much emphasis on widely scattered and possibly spurious data points.) From these regressions, the following equations expressing the equilibrium constants as a function of temperature were obtained:

$$\text{Log } K_2 = \frac{4931.5}{T} - 4.7961 \quad (4.13)$$

$$\text{Log } K_3 = \frac{189.6}{T} - 1.8006 \quad (4.14)$$

where:  $T = ^{\circ}\text{KELVIN}$

After regressing the data, the linear model was tested to determine whether it fit within the limits of experimental error. The ratio of the variance of the model to the variance of the data was compared to an F-statistic based upon the degrees of freedom of the data. This test proved that both regressions were well within these limits. Finally, a 95% confidence interval was generated on either side of the regressed line. This interval, based again

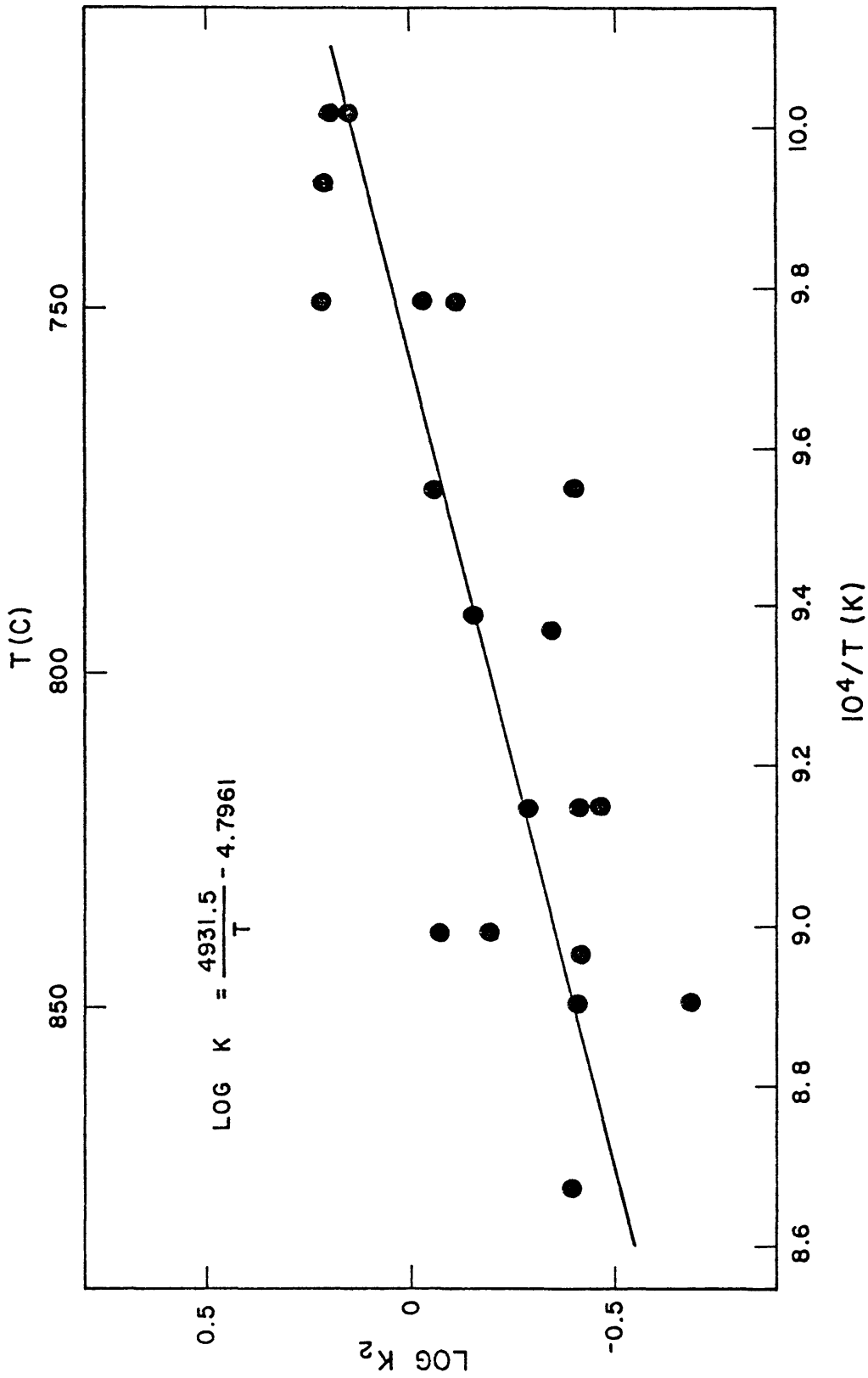


FIGURE 21 - VARIATION OF LOG K<sub>2</sub> WITH TEMPERATURE FOR THE REACTION:  
 $2AgCl_{(l)} + KCl_{(g)} \rightleftharpoons Ag_2KCl_3(g)$

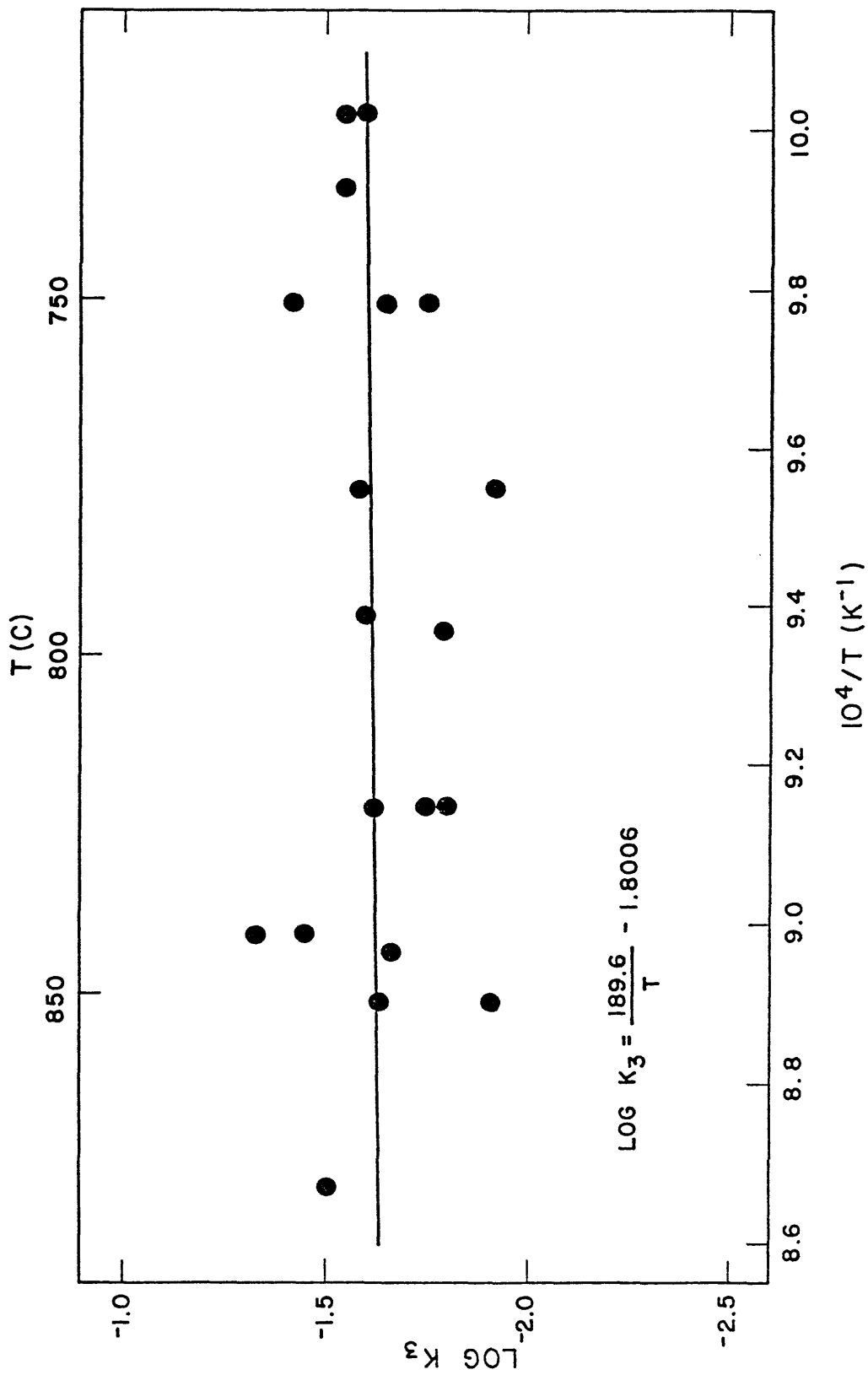
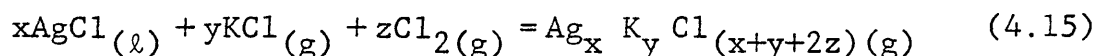


FIGURE 22 - VARIATION OF LOG K<sub>3</sub> WITH TEMPERATURE FOR THE REACTION:  
 $2\text{AgCl}_{(l)} + 1/2\text{K}_2\text{Cl}_{2(g)} = \text{Ag}_2\text{KCl}_3(g)$

upon the F-statistic, means that the chance that the true line may lie outside of the interval is less than 5%. A thorough discussion of the absolute value regression and the statistics applied to the model are given in Appendix C.

As in the silver-chlorine experiments, it was necessary to prove that these measurements were independent of the carrier gas flowrate. Three tests at 820°C and two at 749°C were conducted in which all parameters were held constant while the flowrate was varied. The results, presented in Figures 23 and 24, show that the flowrates from 45 to 70 ml/min are indeed within the equilibrium plateau described by Norman and Winchell<sup>(18)</sup> and Alcock and Hooper<sup>(19)</sup>.

To determine if the chlorine gas was taking part in the complexing reaction, the following equation was proposed:



After taking the logarithm of the equilibrium expression for this reaction, the resulting equation may be written:

$$\text{Log } K = -z \text{Log } P_{\text{Cl}_2} + (\text{Log } P_{\text{Ag}_x \text{K}_y \text{Cl}_{(x+y+2z)}} - Y \text{Log } P_{\text{KCl}}) \quad (4.16)$$

If all parameters are held constant except the chlorine potential and the log of the equilibrium constant is plotted versus the log of the partial pressure of chlorine, the slope of the line generated will represent the coefficient z. Several tests were conducted to determine this and the

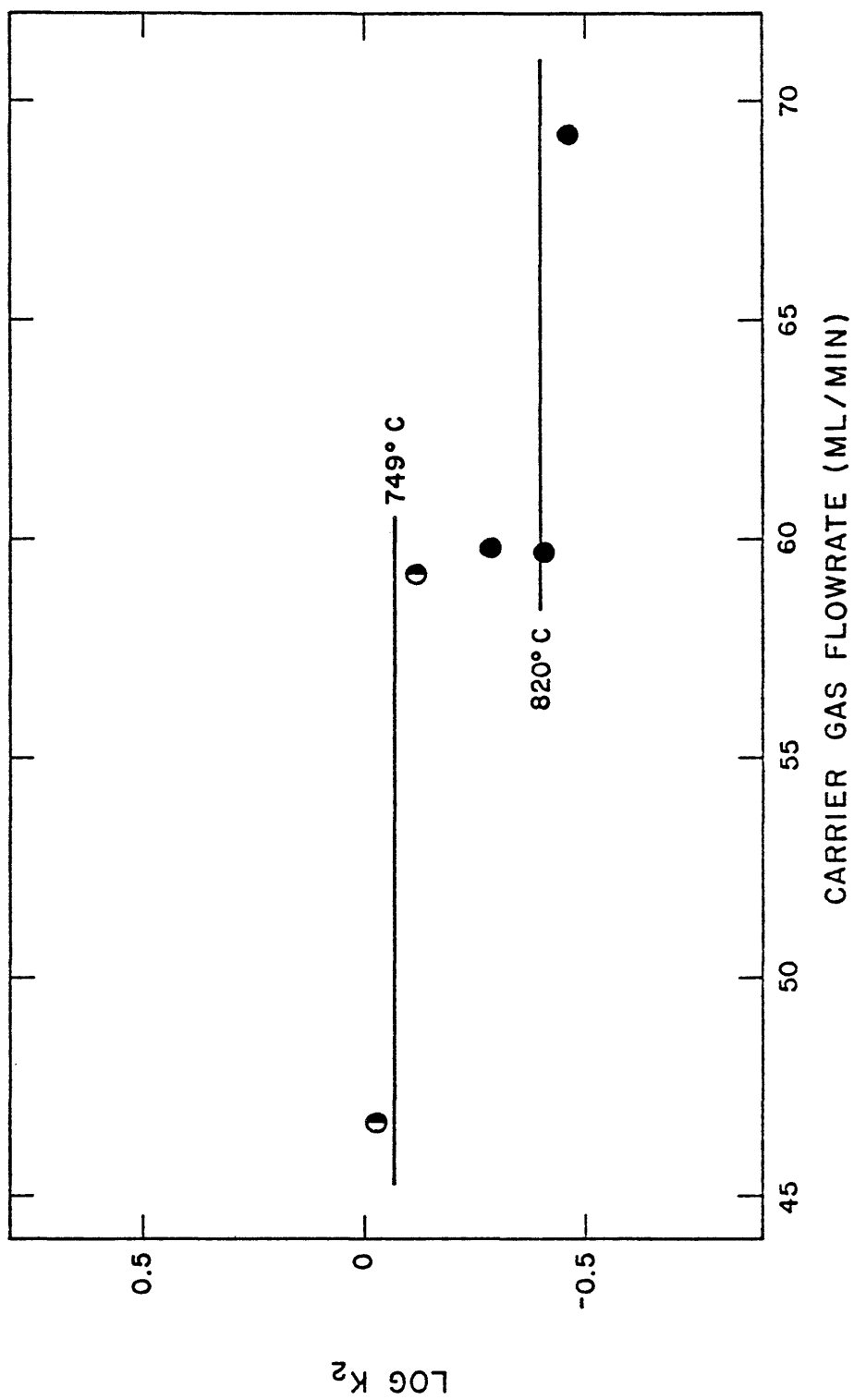


FIGURE 23- DETERMINATION OF CARRIER GAS FLOWRATE INDEPENDENCE  
FOR THE REACTION:  $2\text{AgCl}_{(l)} + \text{KCl}_{(g)} = \text{Ag}_2\text{KCl}_3(g)$

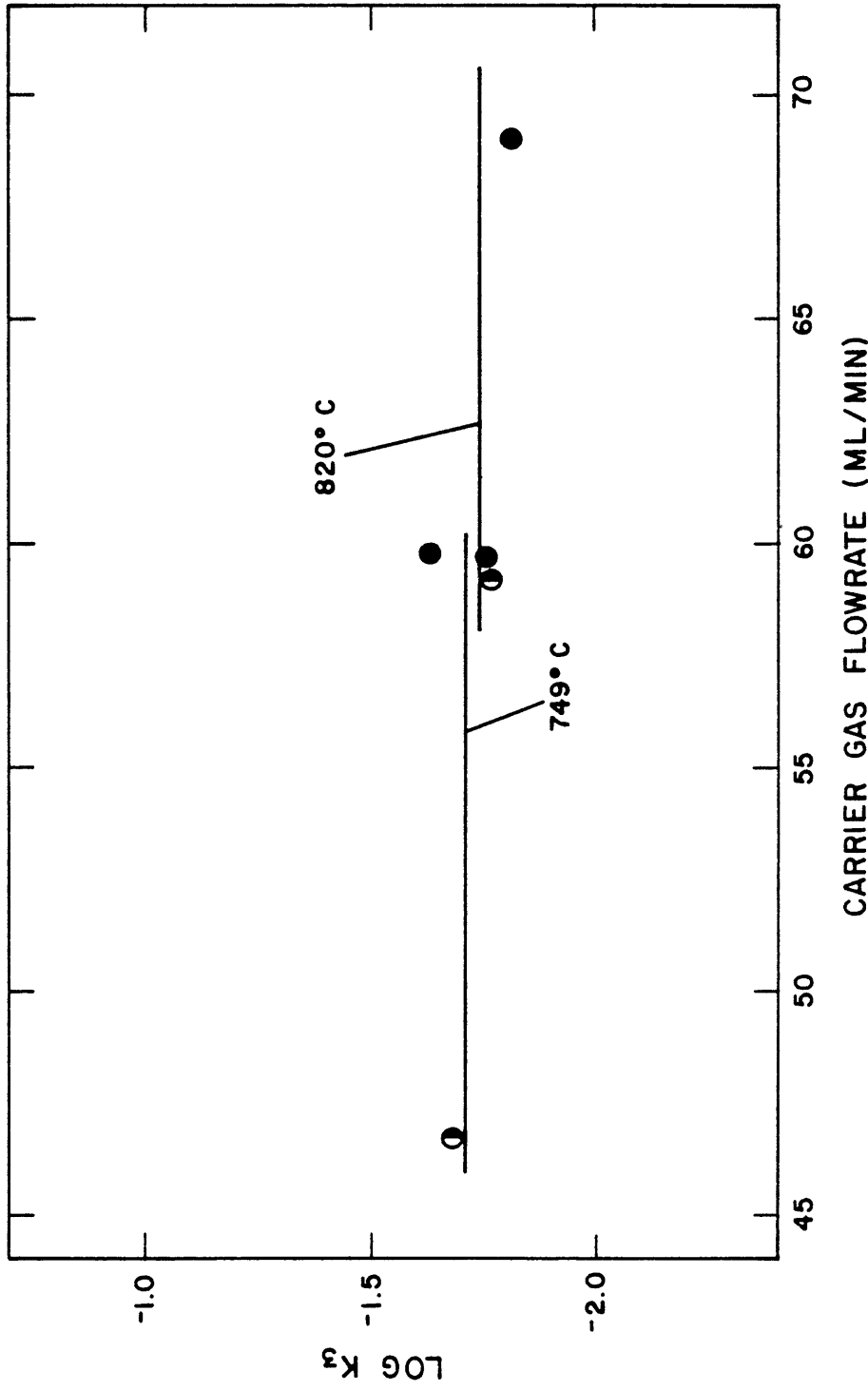


FIGURE 24 - DETERMINATION OF CARRIER GAS FLOWRATE INDEPENDENCE FOR THE REACTION:  $2AgCl_{(l)} + 1/2K_2Cl_{2(g)} = Ag_2KCl_{3(g)}$



results in Figures 25 and 26 show that the slope of the line (i.e.: the value of y) is indeed zero. Therefore, it is safe to assume that chlorine is not a reactant in Equations 4.8 and 4.9.

## 4.2 Silver Extraction Studies

### 4.2.1 The Silver-Iron-Chlorine System

The rotary kiln reactor was used to conduct the silver extraction experiments on the Ag-Fe-Cl System at 700°C. The initial series of experiments was conducted to determine the best method of generating ferric chloride vapor in the reactor. This vapor then acted as the complexing agent while the carrier gas acted as the chloridizing agent.

Five methods of generating ferric chloride vapor were tried:

1. An HCl carrier gas reacting with reagent grade hematite.
2. An HCl carrier gas reacting with sized natural hematite.
3. An HCl carrier gas reacting with iron powder.
4. A Cl<sub>2</sub> carrier gas and reagent grade FeCl<sub>3</sub>.
5. A Cl<sub>2</sub> carrier gas reacting with reagent grade hematite.

From these tests it was found that the extraction rate was enhanced only when hematite was used as the source of FeCl<sub>3(g)</sub>. Calculations were then made to determine the equilibrium vapor pressures of FeCl<sub>3(g)</sub> which could be

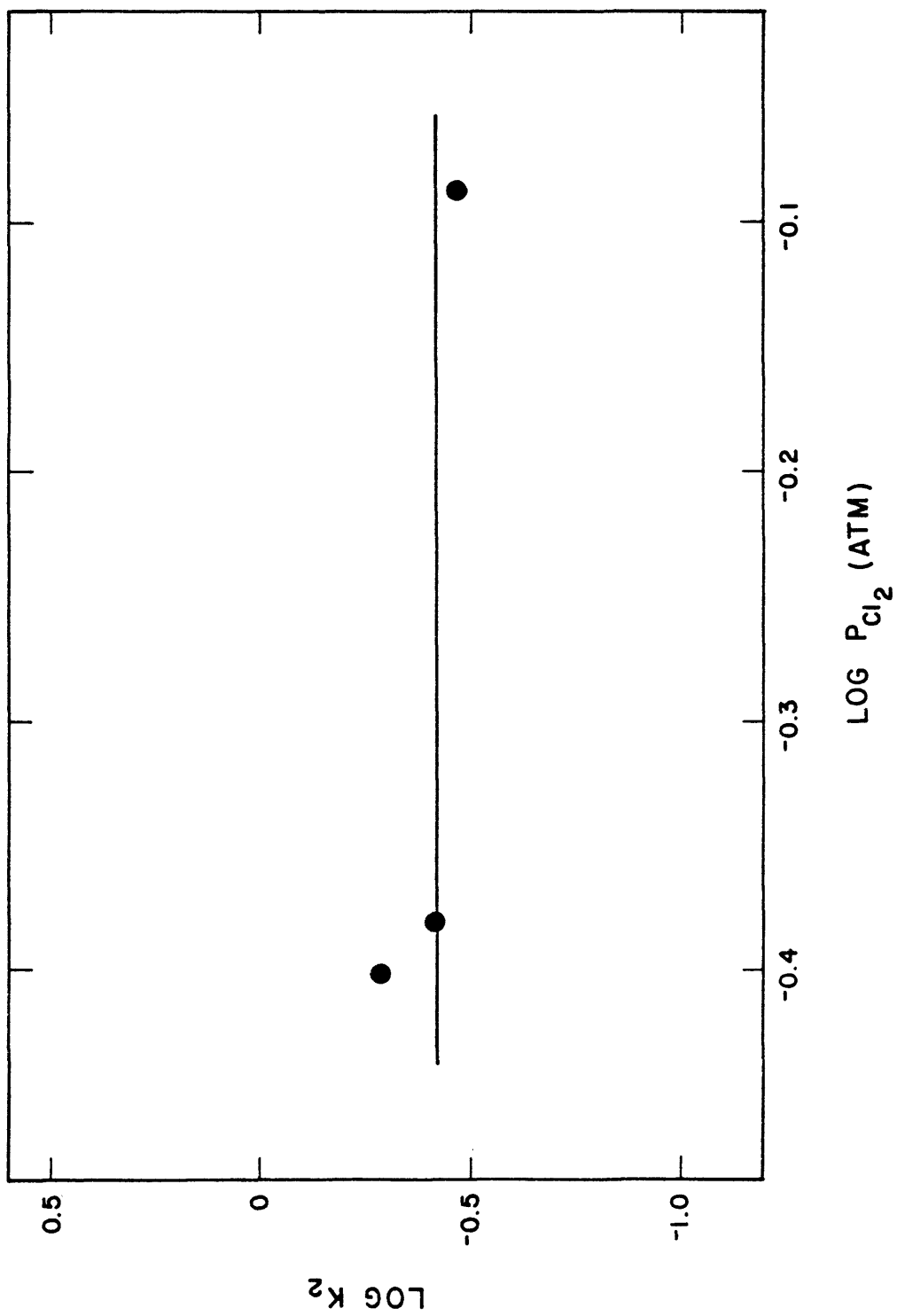


FIGURE 25 - DETERMINATION OF THE EFFECT OF CHLORINE POTENTIAL  
ON LOG K<sub>2</sub> FOR THE REACTION:  $2\text{AgCl}_{(l)} + \text{KCl}_{(g)} = \text{Ag}_2\text{KCl}_3(g)$  AT 820°C

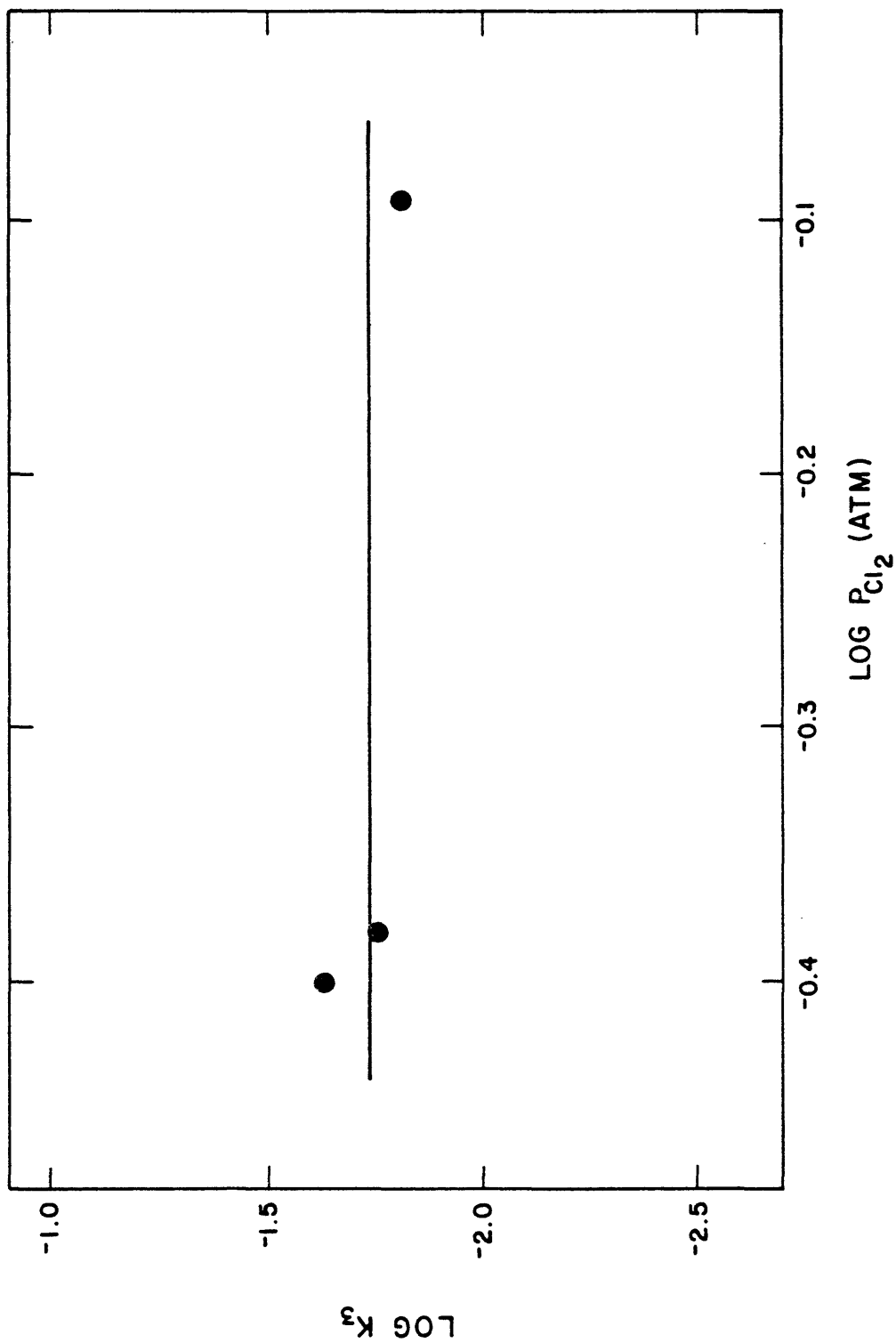
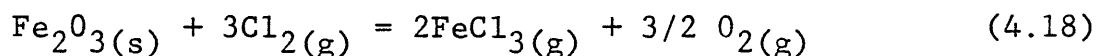
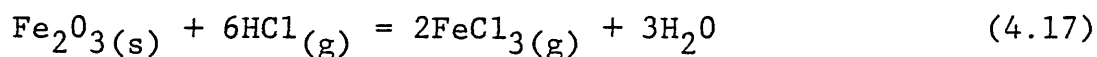


FIGURE 26 - DETERMINATION OF THE EFFECT OF CHLORINE POTENTIAL ON LOG K FOR THE REACTION:  $2AgCl_{(l)} + 1/2K_2Cl_{2(g)} = Ag_2KCl_3(g)$  AT 820°C

expected from the following reactions:



The results of these calculations are presented in Table 4.

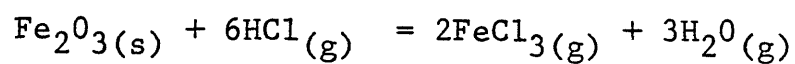
It can be seen that chlorine is the most effective chloridizing agent since it produces the larger partial pressure of  $\text{FeCl}_3(\text{g})$  and thus enhances complexation the most.

Throughout the course of these experiments, the mass balance closure of silver was steadily improved. This was due in part to refining the analysis techniques, but more so to the increase in silver available for extraction. Using a final ore grade of approximately 9.8 T.O. Ag/ton, mass balance closures in excess of 90% were consistently obtained. A summary of the run conditions and results for these tests is given in Table 5.

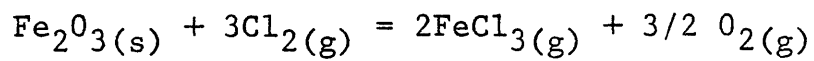
A second series of experiments was conducted to determine the rate of extraction as well as the minimum amount of hematite necessary to achieve better than 90% extraction. In several of these tests, no complexing agent was added to the ore in order to determine a baseline from which to measure the effects of complexation. The run conditions and results for this second series of tests are listed in Table 6, In addition, the results of the

TABLE 4

CALCULATIONS OF  $\text{FeCl}_3$  PARTIAL PRESSURE GENERATED BY  
 CHLORINATION OF HEMATITE:  $T = 727^\circ\text{C}$ ;  $P_T = 624 \text{ mm Hg}$



% HCl (in)	% H <sub>2</sub> O (in)	$P_{\text{FeCl}_3}$ (mm Hg)	(out)
18	0	3.0	
18	1.0	1.4	
30	0	5.5	
30	1.0	2.5	



% Cl (in)	% O <sub>2</sub> (in)	$P_{\text{FeCl}_3}$ (mm Hg)	(out)
100	0	26.9	

TABLE 5  
 SUMMARY OF RUN CONDITIONS AND RESULTS FROM TESTS CONDUCTED  
 TO DETERMINE THE BEST METHOD OF GENERATING  $\text{FeCl}_3$  VAPOR

Run No.	Runtime (min)	Available Ag, (mg)	Complexing Method	% Extraction Heads vs. Tails	Mass Balance Closure % Ag Recovered
2	33	16.7	1	70	52
4	30	12.3	1	79	46
5	30	17.5	1	72	54
7	30	23.3	2	18	89
9	30	23.3	2	35	75
12	60	23.8	2&3	39	75
14	60	23.8	4	63	64
15	60	23.8	4	57	69
16	60	23.8	4&5	92	81
18	30	44.58	4&5	71	91
20	45	44.58	4&5	90	98
21	30	44.58	5	70	99
22	60	44.58	5	94	89

Complexing Methods:

1. HCl gas reacting with reagent grade hematite
2. HCl gas reacting with sized natural hematite
3. HCl gas reacting with iron powder
4. Chlorine gas and  $\text{FeCl}_3$
5. Chlorine gas reacting with reagent grade hematite

TABLE 6  
SUMMARY OF RUN CONDITIONS AND RESULTS OF TESTS CONDUCTED TO DETERMINE  
THE RATE OF EXTRACTION AND MINIMUM CONCENTRATION OF HEMATITE

Run No.	Runtime (min)	Available Ag, (mg)	%Fe <sub>2</sub> O <sub>3</sub> Added	Volatiles Collected	% Extraction Based On Heads vs. Tails	Mass Bal. Closure % Ag Recovered
16	60	23.8	5.8	73	92	81
17	30	44.6	0	5	12	93
18	30	44.6	10.9	62	71	91
19	30	44.6	0	7	15	92
20	45	44.6	9.8	87	90	98
21	30	44.6	9.8	75	76	99
22	60	44.6	10.0	83	94	89
23	60	44.6	0	20	36	84
24	60	53.7	5.1	88	95	93
25	60	53.7	1.0	62	74	89
26	60	53.7	2.0	69	93	76

Carrier Gas Flowrate = 750 ml/min

tests are plotted in Figures 27 and 28.

From these tests, it was found that when an ore which assayed at least 9 T.O. Ag/ton was mixed with 2%  $\text{Fe}_2\text{O}_3$  and reacted with chlorine gas, the percent extraction and silver mass balance closure both exceeded 90%.

#### 4.2.2 The Silver-Potassium-Chlorine System

Extraction tests on the Ag-K-Cl system were conducted in both a rotary kiln reactor and packed bed reactor. The initial experimental block included tests to determine extraction rates and minimum complexing agent requirements. Potassium chloride vapor was generated in both reactors by mixing reagent-grade potassium chloride crystals with the ore and then conducting the extraction tests at  $750^\circ\text{C}$ .

Problems were encountered during complexing tests conducted in the rotary kiln. When the furnace temperature reached  $400\text{-}450^\circ\text{C}$ , the ore became sticky and agglomerated on the walls of the reactor. Furthermore, when the tail samples were analyzed, virtually none of the available silver had been removed.

A second series of tests were then conducted using a packed bed reactor. It was hoped that if the ore still agglomerated, it might remain permeable enough for the chlorine and potassium chloride vapors to diffuse through it and react with the metallic silver in the ore. However,



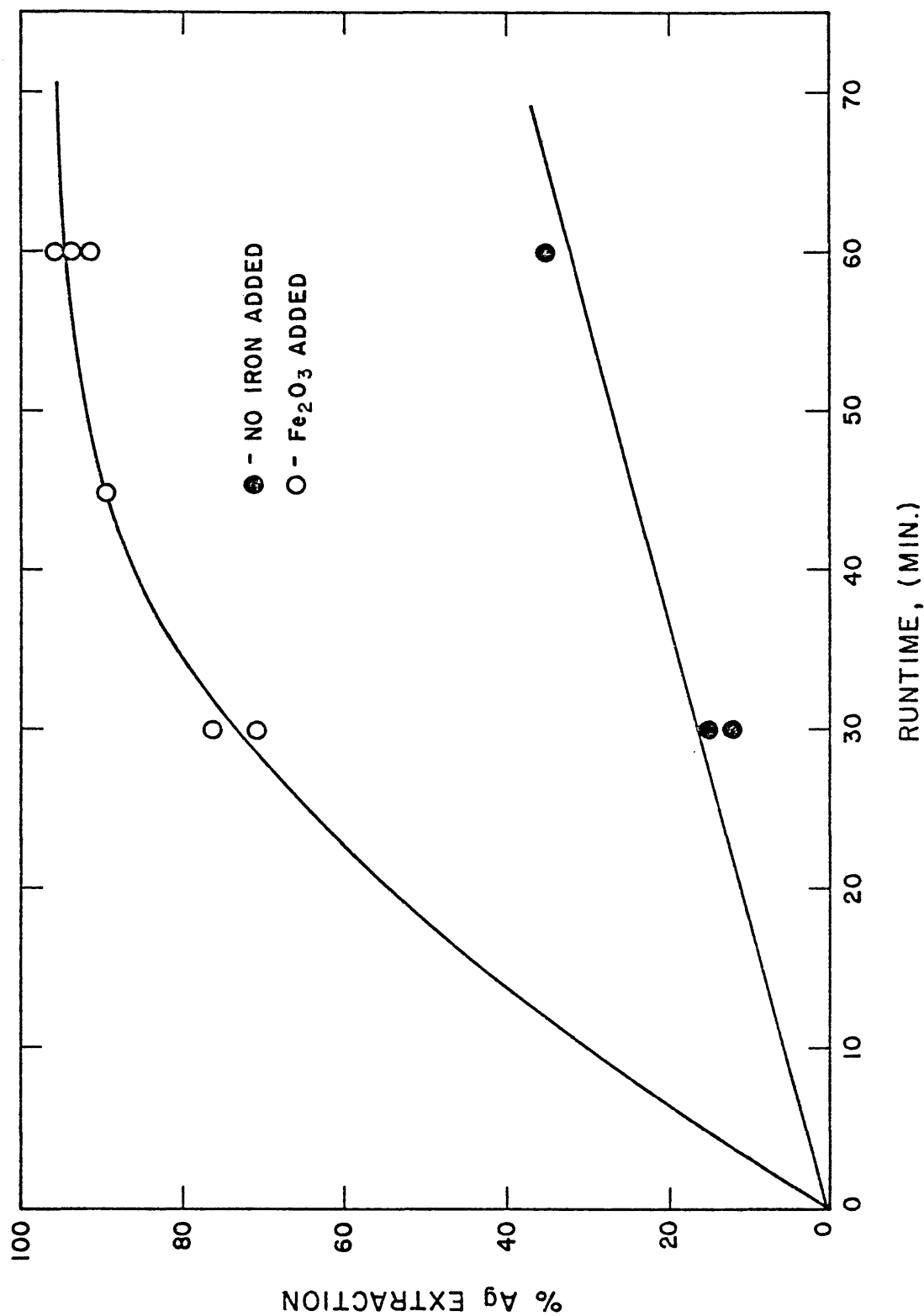


FIGURE 27 - EXTRACTION CURVE FOR THE VAPOR PHASE EXTRACTION OF SILVER FROM SYNTHETIC ORE: T=700° C; AgCl-FeCl<sub>3</sub> SYSTEM

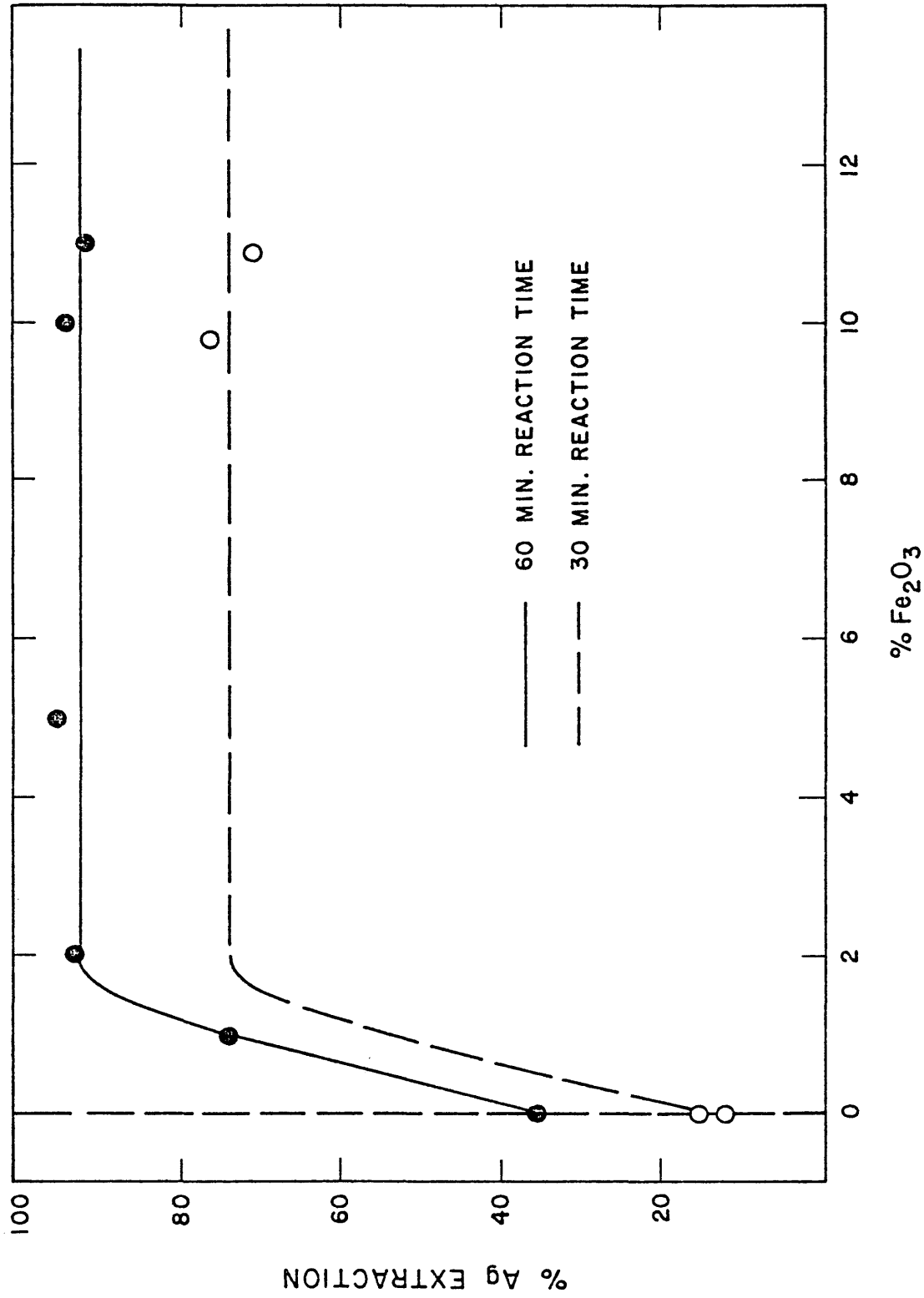


FIGURE 28- SILVER EXTRACTION AT 700° C AS A FUNCTION OF Fe<sub>2</sub>O<sub>3</sub> CONCENTRATION

when the reactor was removed from the furnace, the charge was found to be fused in place and a tails analysis again showed no silver removed from the ore.

No further tests were performed on this system to determine either the cause of agglomeration or the poor extraction rates. A summary of the run conditions and the results is given in Table 7.

TABLE 7

SUMMARY OF RUN CONDITIONS AND RESULTS FROM EXTRACTION TESTS  
CONDUCTED ON THE Ag-K-Cl SYSTEM

Run No.	Experimental Apparatus	Carrier Gas Flowrate(ml/min)	Runtime (hrs)	% KCl Added	% Extraction Heads vs. Tails	Comments
1	Rotary Kiln	750	1	0	62	
2	Rotary Kiln	750	1	5.8	6	charge agglomerated
3	Rotary Kiln	750	1	0	31	
4	Rotary Kiln	750	1	5	0	charge agglomerated
5	Rotary Kiln	750	1	see note	-	" " "
6	Packed Bed	75	2	0	0	
7	Packed Bed	75	12	0	29	
8	Packed Bed	75	12	5	0	charge sintered in place
9	Packed Bed	75	12	0	20	
10	Packed Bed	75	3	3	-	run terminated-broken reactor
11	Packed Bed	75	12	3	0	charge sintered in place

Note: Complexing agent added to tray suspended above bed

## 5. DISCUSSION OF RESULTS

### 5.1 Thermodynamic Studies

In order to calculate the pressure of the complex species, vaporization data for the reaction:



was needed over the temperature range of interest. This was obtained experimentally. A least squares regression of the experimental data produced a best-fit line (See Figure 18) from which the values at  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated. From the van't Hoff Equation (4.12):

$$\Delta H^\circ = -2.303 \times R \times \text{least squares slope}$$

and since

$$\Delta G^\circ = -R T \ln K = \Delta H^\circ - T \Delta S^\circ:$$

$$\Delta S^\circ = 2.303 \times R \times \text{least squares intercept}$$

It should be noted that though Figure 18 is a plot of  $\log P_{\text{AgCl}}$  versus  $1/T$ , the van't Hoff Equation applies because the activity of pure molten silver is assumed to be 1. Therefore, when the logarithm is taken of the equilibrium expression:

$$K = \frac{P_{\text{AgCl}_{(\text{g})}}}{a_{\text{AgCl}_{(\ell)}}} \quad (5.2)$$

the resulting expression becomes:

$$\text{Log } K = \text{Log } P_{\text{AgCl}(g)} - 0 \quad (5.3)$$

A summary of the thermodynamic quantities calculated from the experimental results is given in Table 8.

In order to provide a quantitative comparison of the data generated in this study with that of Rupert<sup>(12)</sup> and Bloom, et al.<sup>(21)</sup>, the values of  $\Delta H^{\circ}_R$  and  $\Delta G^{\circ}_R$  calculated at 800°C for each study are presented in Table 9.

Rupert's<sup>(12)</sup> data was generated over the temperature range 657-799°C using a transpiration apparatus similar to the one used in this study. His value of  $\Delta G^{\circ}_R$  is in excellent agreement with the value generated in this study, however, his value of  $\Delta H^{\circ}_R$  is off by approximately 6 kcal. In analyzing Rupert's raw data, it was noticed that his heat of reaction could be changed as much as 8 kcal by shifting one data point within the limits of his experimental error. Therefore, it is quite probable that the difference in these two heat values is due solely to the scatter in his data.

The data of Bloom, et.al.<sup>(21)</sup> was determined by the boiling point method for the temperature range 1028-1260°C. In order to compare it with the data from this study, it was necessary to extrapolate it 350° using a least squares

TABLE 8

## SUMMARY OF THE THERMODYNAMIC FUNCTIONS FOR

THE REACTION:  $\text{AgCl}_{(l)} = \text{AgCl}_{(g)}^*$ ;  $T = 1000\text{-}1150^\circ\text{C}$

$$\Delta H^{\circ} = 47331 \pm 2314^{**} \text{ cal} \cdot \text{mole}^{-1}$$

$$\Delta S^{\circ} = +26.97 \pm 0.23^{**} \text{ cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$$

$$\Delta G_{\dagger}^{\circ} = 47331 - 26.97 T (+2561) \text{ cal} \cdot \text{mole}^{-1}$$

\* Assuming  $\Delta C_p = 0$

\*\* Assuming an  $\alpha$  error of 0.05

TABLE 9  
COMPARISON OF THERMODYNAMIC VALUES FROM SEVERAL SOURCES

FOR THE REACTION:  $\text{AgCl}(\ell) = \text{AgCl}(\text{g})$   $T = 800^\circ\text{C}$

	This Study	Rupert (12)	Bloom, et al. (21)*
$\Delta H^\circ_R$ (cal · mole <sup>-1</sup> ) =	+ 47331	+ 41346	+ 47525
$\Delta G^\circ_R$ (cal · mole <sup>-1</sup> ) =	+ 18418	+ 18310	+ 19453

\* Extrapolated from 1028°C



regression (assuming  $\Delta C_p = 0$ ). As can be seen in Table 9, the values of  $\Delta H_R^\circ$  obtained in this study and the study by Bloom, et.al. are in excellent agreement but the values of  $\Delta G_R^\circ$  are slightly off. This difference could be attributed to the extrapolation, but it is more likely that the samples Bloom, et al. used were not sufficiently purified. An error of this type would lower the mole fraction of the silver chloride and according to Raoult's Law:

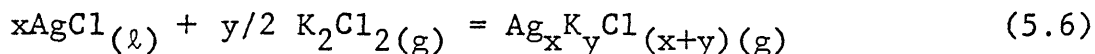
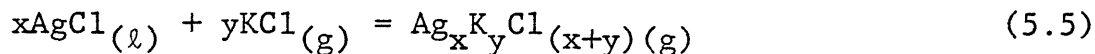
$$\lim_{x_i \rightarrow 1} P_i = x_i P_i^\circ \quad (5.4)$$

cause a decrease in the measured vapor pressure.

From this comparison, it was decided that the data generated in this study was the most accurate over this temperature range and, therefore, should be used as a baseline for the complexation studies.

The experimental results from these studies clearly show that the apparent vapor pressure of silver chloride is enhanced by the formation of an Ag-K-Cl complex species. This complex species was proposed to be  $\text{Ag}_2\text{KCl}_3$  for several reasons. From the transpiration experiments it was found that the chlorine carrier gas did not enter into the reaction. This meant that there was no change in the valence state of either silver or potassium. Therefore, the complexation reactions for the potassium chloride monomer and dimer

had to be of the form:



where  $x$  and  $y$  may take on only integer values. Secondly, when the values of  $x$  and  $y$  were both assumed to 1, insufficient potassium had been transported to account for the additional silver transported. This meant that the value of  $x$  had to be greater than the value of  $y$  to satisfy the mass balance constraints. Of the three complex gaseous species observed by Svedburg<sup>(10)</sup>, only the  $\text{Ag}_2\text{KCl}_2^+(g)$  ion would satisfy these requirements (assuming  $\text{Ag}_2\text{KCl}_2^+(g)$  is a fragment of the parent molecule  $\text{Ag}_2\text{KCl}_3(g)$ ). Additional calculations, assuming  $x$  values of 3 and 4 did not result in a better fit of the van't Hoff Equation. Due to experimental scatter in the data, it was not possible to conduct further measurements from which the values of  $x$  and  $y$  could be determined. However, it is felt that the species  $\text{Ag}_2\text{KCl}_3$  is a good choice since many similar gaseous chloride complex species, which have been observed by Schäfer<sup>(17)</sup>, are formed from the combinations of salts in the ratios 1:1, 2:1, or 1:2.

The results of the complexing experiments are plotted according to the van't Hoff Equation in Figures 21 and 22. The values of  $\Delta H_R^\circ$ ,  $\Delta S_R^\circ$ , and  $\Delta G_T^\circ$  for both the monomer and

dimer reactions were calculated from the regressed lines. A summary of these functions along with their respective uncertainties is presented in Table 10.

It can be seen that the heats of formation for these two reactions are quite different. This can be explained by writing the equations for the heats of each reaction:

$$\Delta H_{R_1} = \Delta H_F(\text{Ag}_2\text{KCl}_3) - \Delta H_F(\text{KCl}) - 2 \Delta H_F(\text{AgCl}) \quad (5.7)$$

$$\Delta H_{R_2} = \Delta H_F(\text{Ag}_2\text{KCl}_3) - \frac{1}{2} \Delta H_F(\text{K}_2\text{Cl}_2) - 2 \Delta H_F(\text{AgCl}) \quad (5.8)$$

and subtracting Equation 5.8 from 5.7:

$$\Delta H_{R_1} - \Delta H_{R_2} = -\Delta H_F(\text{KCl}) + \frac{1}{2} \Delta H_F(\text{K}_2\text{Cl}_2) \quad (5.9)$$

An equation is then obtained which relates the difference in the heats of these reactions to known quantities. From the JANAF Thermochemical Tables<sup>(22)</sup>:

$$\Delta H_F \text{ KCl} = 42604 \text{ (cal} \cdot \text{mole}^{-1}\text{)}$$

$$\Delta H_F \text{ K}_2\text{Cl}_2 = 41603 \text{ (cal} \cdot \text{mole}^{-1}\text{)}$$

Upon substitution of these values into Equation 5.5 we obtain:

$$\Delta H_{R_1} - \Delta H_{R_2} = -21802 \text{ (cal} \cdot \text{mole}^{-1}\text{)}$$

Therefore, a difference of approximately 21,802 cal · mole<sup>-1</sup> should be expected in the heats of these reactions. By calculating the difference in the heats obtained

TABLE 10

## SUMMARY OF THE THERMODYNAMIC FUNCTIONS FOR

THE COMPLEXATION REACTIONS; Temperature Range = 998-1153°K

For the reaction:  $2\text{AgCl}(\ell) + \text{KCl}(\text{g}) = \text{Ag}_2\text{KCl}_3(\text{g})^*$ 

$\Delta\text{H}^{\circ}$	=	$-22567 \pm 8774^{**}$	cal · mole <sup>-1</sup>
$\Delta\text{S}^{\circ}$	=	$-21.95 \pm 1.58^{**}$	cal · mole <sup>-1</sup> · °K <sup>-1</sup>
$\Delta\text{G}_T^{\circ}$	=	$-22567 + 21.95 T (+10470)$	cal · mole <sup>-1</sup>

For the reaction:  $2\text{AgCl}(\ell) + \frac{1}{2} \text{K}_2\text{Cl}_2(\text{g}) = \text{Ag}_2\text{KCl}_3(\text{g})^*$ 

$\Delta\text{H}^{\circ}$	=	$-868 \pm 8775^{**}$	cal · mole <sup>-1</sup>
$\Delta\text{S}^{\circ}$	=	$-8.24 \pm 1.58$	cal · mole <sup>-1</sup> · °K <sup>-1</sup>
$\Delta\text{G}_T^{\circ}$	=	$-868 + 8.24 T (+10470)$	cal · mole <sup>-1</sup>

\* Assuming  $\Delta\text{C}_p = 0$ \*\* Assuming an  $\alpha$  error of 0.05

experimentally, a value of  $21,699 \text{ cal} \cdot \text{mole}^{-1}$  is obtained. This was to be expected since the potassium was divided between KCl and  $\text{K}_2\text{Cl}_2$  by using the equilibrium constant. However, this analysis does serve as an independent check on the validity of the transpiration calculations.

Up to this point, all calculations have been based on the assumption that the silver chloride samples were pure and therefore at unit activity. However, due to the presence of potassium chloride vapors above the molten silver chloride samples, it was necessary to confirm this assumption.

To determine if the silver chloride had been contaminated, several samples which had been used during complexing runs were sent to a commercial lab for analysis. The results are presented in Table 11. If Raoultian activity behavior is assumed, which is not unreasonable at such high mole fractions, then the activity of the silver chloride can be approximated by the mole fraction. Therefore, from the results in Table 11, it was concluded that the activity could be assumed to be 1.

The maximum percent increase in the apparent vapor pressure of  $\text{AgCl}_{(g)}$  was calculated for several temperatures over the range of this study. The results, which are presented in Table 12, show the greatest increase occurring

TABLE 11  
 RESULTS FROM THE COMMERCIAL ANALYSIS OF  
 AgCl SAMPLES CONTAMINATED WITH KCl

Sample No.	Wt. % KCl	Wt. % AgCl*	Mole % KCl	Mole % AgCl*
AgCl-1	0.466	99.543	0.243	99.757
AgCl-2	0.344	99.656	0.179	99.821
AgCl-3	0.438	99.562	0.228	99.772

\* By Difference

TABLE 12  
 VAPOR ENHANCEMENT OF  $\text{AgCl}$  (g) THROUGH THE ADDITION OF  $\text{KCl}$  (g)

Temperature $^{\circ}\text{C}$	$P_{\text{AgCl}}^1$ (mm Hg)	$P_{\text{KCl}}^2$ (mm Hg)	$P_{\text{K}_2\text{Cl}_2}^2$ (mm Hg)	$P_{\text{Ag}_2\text{KCl}_3}$ (mm Hg)	Percent Increase	Moles K Transported Per Mole Ag
727	0.03	0.10	0.04	0.14	910%	1.03
827	0.23	0.81	0.37	0.39	340%	1.92

1. From Equation 4.2

2. Data obtained from JANAF Thermochemical Tables (22)

at the lowest temperatures. This is reasonable since the slope of the line in Figure 21 signifies that the stability of the complex species decreases with increasing temperature. However, the highest pressure of the complex does occur at the highest temperature. This is due primarily to the increased vapor pressure of the complexing agents,  $KCl_{(g)}$  and  $K_2Cl_2(g)$ .

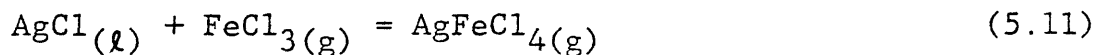
## 5.2 Silver Extraction Studies

### 5.2.1 The Silver-Iron-Chlorine System

Excellent results were obtained from the extraction tests conducted on the Ag-Fe-Cl system. The combination of chlorine as the carrier gas and hematite as the source of the complexing agent achieved the highest rates of extraction. Since the vapor pressure of the complex species is proportional to the vapor pressure of the complexing agent (in this case  $FeCl_3(g)$ ) through the equation:

$$P_{AgFeCl_4} = K \times P_{FeCl_3} \quad (5.10)$$

where K represents the equilibrium constant for the reaction:



it was desirable to achieve the highest  $P_{FeCl_3}$  possible in the rotary kiln. It was found both experimentally and in



thermodynamic equilibrium calculations that  $\text{Cl}_2(\text{g})$  reacting with hematite, as opposed to the reaction of  $\text{HCl}(\text{g})$  with hematite, accomplished this.

In order to quantify the results expected from the vapor pressures of  $\text{FeCl}_3$  generated in the rotary kiln, the value of K in Equation 5.10 was calculated at  $727^\circ$  and  $827^\circ\text{C}$  from the equation:

$$\text{Log } K = \frac{-6993}{T} + 4.6364 \quad (5.12)$$

From Rupert<sup>(12)</sup>

Where:  $T = ^\circ\text{KELVIN}$

The results of these calculations, as well as the percent increase which can be expected in the apparent vapor pressure of  $\text{AgCl}$  are presented in Table 13. Note that although the percent enhancement goes up very slightly with increasing temperature, the actual vapor pressure of the complex increases significantly.

It should be mentioned that one drawback to increasing the volatility of the silver species by complexation is the amount of iron transported with the silver. The condensate from such a process will be predominantly ferric chloride as can be seen by the results of the equilibrium yield calculations also presented in Table 13. However, extraction rates in excess of 90% at only  $700^\circ\text{C}$  make this system look very promising on an industrial scale. Also, if only a 2% hematite addition is needed as a complexing agent for real ores, the cost of such a process might be very attractive. The extraction

TABLE 13  
 VAPOR ENCHANCEMENT OF  $\text{AgCl}_{(g)}$  IN THE ROTARY KILN DUE  
 TO THE EQUILIBRIUM PRESSURE OF  $\text{FeCl}_{3(g)}$

Temperature $^{\circ}\text{C}$	$K_{\text{eq}}^*$	$P_{\text{AgCl}}$ (mm Hg)	$P_{\text{FeCl}_3}$ (mm Hg)	$P_{\text{AgFeCl}_4}$ (mm Hg)	Apparent % Increase in $P_{\text{AgCl}}$	Mole Fe Transported Per Mole Ag
727	.018	0.03	27	0.49	1620	52
827	.067	0.23	68	4.56	1980	14

\* Equilibrium constant for the reaction:  $\text{AgCl}_{(l)} + \text{FeCl}_3(g) = \text{AgFeCl}_4(g)$ ;

$$\text{Log } K_{\text{eq}} = \frac{-6393}{T} + 4.6364 \quad (T = ^{\circ}\text{KELVIN}) \text{ (From Rupert (12))}$$

rates which can be expected from a real ore cannot be accurately estimated from the results obtained with a synthetic ore. It can be assumed that unless the gangue material is extremely permeable and the silver is in the metallic state, the reaction rates might be slower.

Since tests were conducted for the purpose of determining ways in which the volatility of silver could be increased, the recovery of silver from the off-gases was attempted only for the purpose of calculating a silver mass balance. For this process to be considered for commercial application, the method of collecting the volatile silver chlorides should be studied more thoroughly. Of the methods tried in this study, the combination of a water-cooled condenser and a glass-wool filter worked the best. However, 10% of the silver was still lost in the exhaust gases. Henrick and Brennan<sup>(6)</sup> also found this to be a significant problem in their tests on the volatilization of gold chlorides. Factors such as particulate size, solubility, and wettability were all found to be deterrant to the use of conventional gas scrubbers. This was also found to be the case in the initial attempts to scrub the off-gases generated in this study.

### 5.2.2 The Silver-Potassium-Chlorine System

Based upon the results of the equilibrium yield and vapor enhancement calculations presented in tables 12 and 13,

excellent extraction rates had been anticipated for the Ag-K-Cl System. Comparing the Ag-K-Cl and Ag-Fe-Cl Systems at 727°C, it can be seen that the total vapor pressure of silver-bearing species is 300% higher in the Ag-Fe-Cl System. However, the equilibrium yield is much greater in the Ag-K-Cl System. For a given quantity of silver transported, 51 times more iron is required than potassium for the complexation reaction. Furthermore, the iron and potassium will be transported as their chloride vapors along with the silver-bearing species. This results in a significant decrease in the purity of the condensate. Assuming that FeCl<sub>3</sub> and KCl are equally deleterious to any refining process used on the condensate, the use of FeCl<sub>3</sub> as the complexing agent will significantly increase the problem.

At 827°C, the total vapor pressure of silver-bearing species is 770% higher in the Ag-Fe-Cl System than in the Ag-K-Cl System. In addition, the difference in the equilibrium yield between the two systems drops from 51 to 7. This is primarily due to the way in which the equilibrium constants for the complexation reactions in each system vary with temperature.

Unfortunately, confirmation of the predicted rates of extraction in the Ag-K-Cl System was not possible. However, it was assumed that the agglomeration problem was responsible

for the decrease in silver transported during the complexing experiments. In trying to explain the cause of agglomeration, the presence of  $H_2O$  in the system was suspected. From the literature, it was found that  $KCl_{(s)}$  has no waters of hydration. In addition, any moisture in the charge would have been driven off as steam between  $100^\circ$  and  $300^\circ C$  and flushed from the reactor by the  $N_2$  pure gas.

In one rotary kiln experiment, the potassium chloride was placed in a tray and suspended above the bed. The ore still agglomerated, even though the potassium chloride was not in direct contact with it. This gave rise to the assumption that the problem was due to the formation of some low-melting point product of a reaction involving potassium chloride gas. Furthermore, since the synthetic ore and the reactor were both made from  $SiO_2$ , this was suspected as being the other reactant. However, no data could be found to substantiate this assumption.

## 6. INDUSTRIAL APPLICATION OF THIS STUDY

The results from both Rupert's<sup>(12)</sup> work and the extraction tests conducted in this study confirm the enhancement of  $P_{\text{AgCl}}$  due to the formation of a silver-iron chloride complex gaseous species. At  $727^{\circ}\text{C}$ , an apparent increase of 1600% can be expected in the total pressure of silver-bearing species. In addition, it was proven that excellent levels of silver extraction may be obtained in less than 1 hour. Though no tests were conducted at  $827^{\circ}\text{C}$ , an even greater extraction rate is expected since the apparent increase in  $P_{\text{AgCl}}$  climbs to 2000%.

A proposed new scheme for the application of these results involves the extraction of silver from pyritic cinders. A flowsheet for this process is presented in Figure 29.

One industrial process<sup>(23)</sup>, designed for this purpose, uses various salts as the chloridizing agent and requires temperatures in excess of  $1000^{\circ}\text{C}$  to achieve good silver extraction. In addition, the process uses a vertical shaft furnace which requires the feed to be sintered or pelletized prior to charging. This will almost always

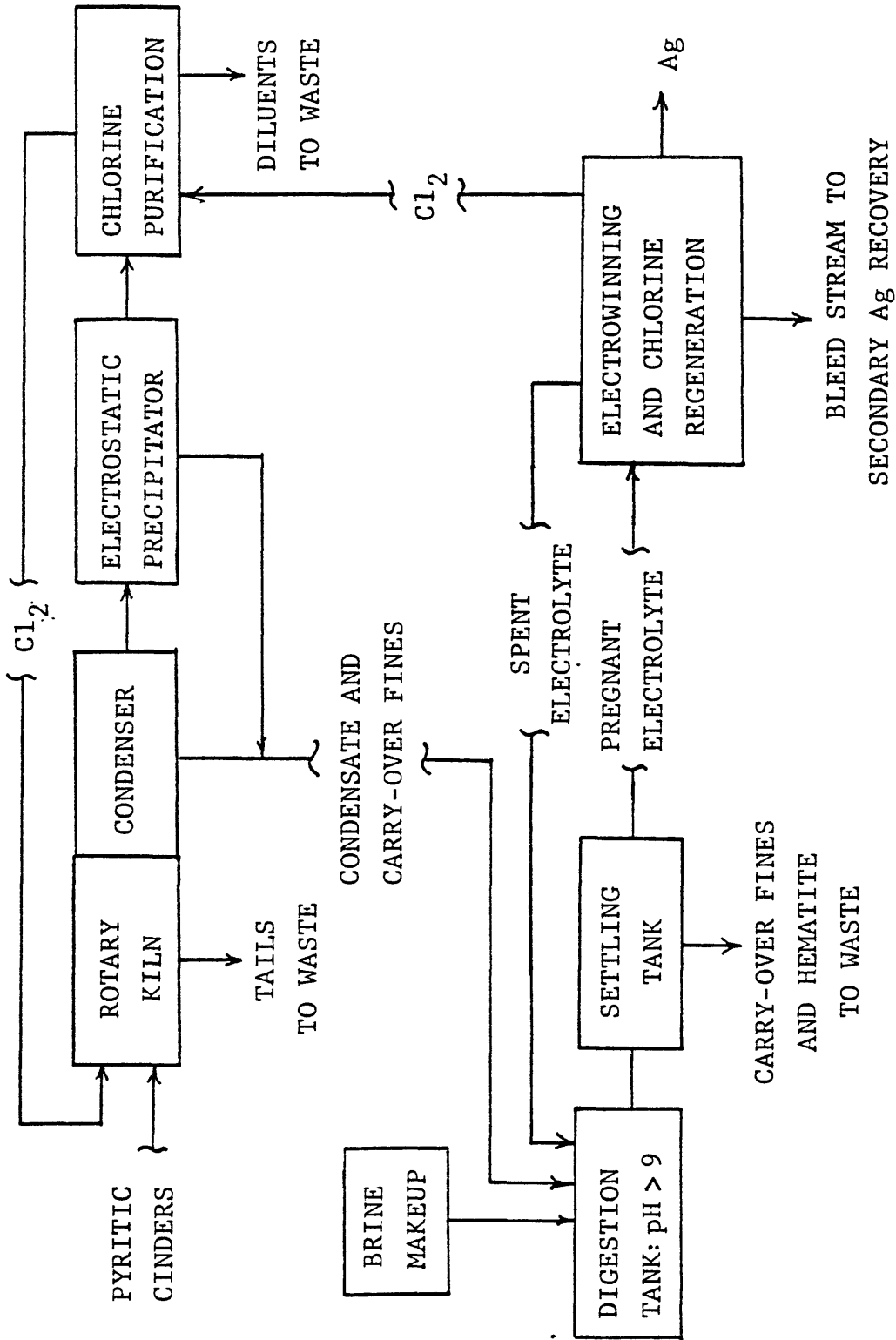


FIGURE 29- FLOWSHEET FOR THE PROPOSED SILVER EXTRACTION PROCESS

cause a reduction in the reaction rate due to the decreased surface area.

This new scheme would use a rotary kiln reactor and a recirculating chlorine gas stream to volatilize the silver as an Ag-Fe-Cl complex. Due to high concentrations of hematite in pyritic cinders, the addition of a complexing agent would not be necessary. A summary of the equilibrium partial pressures of the gaseous species which would be involved in the transport reaction was presented in Table 13.

As the carrier gas is flushed from the kiln it would pass through a water-cooled condenser to affect the condensation of the volatile chlorides. A mechanical device such as a hot auger would be used to scrape the walls of the condenser and remove the condensate from the system. After leaving the condenser, the off-gas would be passed through an electrostatic precipitator which would remove any remaining fume. From the precipitator, the off-gas would have to be put through a purification process. Oxygen generated from the reaction of chlorine and hematite as well as moisture driven from the charge would be removed and the purified chlorine would then be circulated back to the reactor.



The condensate and carry-over fines removed from the condenser and precipitator would be fed to an agitated brine digestion tank. According to Beckstead and Miller<sup>(24)</sup>, by keeping the pH of the leach above 9.3, the ferric chloride will dissolve and reprecipitate as hematite. This will then be removed as a slime with the insoluble carry-over fines. The silver chloride condensate will dissolve and form the ionic species:  $\text{Ag}^+$ ,  $\text{AgCl}_2^-$ ,  $\text{AgCl}_3^{=}$ ,  $\text{AgCl}_4^{=}$ . The total solubility of Ag as these species is presented in Table 13 as a function of brine concentration.

TABLE 14

SOLUBILITY OF Ag (GRAMS/LITER)  
IN CONCENTRATED BRINE

$\text{Cl}^-$ Concentration	Ag Solubility (gr/l.)
1.0 M	0.008
2.0 M	0.043
5.0 M	0.54
10.0 M	4.0

The leach liquor will then be transferred to a modified multi-stage Zadra-type cell in which the silver will be plated out and the chlorine will be regenerated according to the half cell-reactions:

At the cathode:



At the anode:



In Table 14 it can be seen that if a 5.0 M brine solution is used, the electrolyte will contain approximately 0.50 gr/l of solution. According to Mitchell, et al.<sup>(25)</sup>, the Zadra cell will reduce this level of silver to 0.07 gr/l with 80% current efficiency.

Though this scheme has not been tested, several inherent advantages over existing processes must be mentioned:

1. Reactor temperatures of only 700-800°C are necessary.
2. High productivity can be expected due to rapid extraction rates.
3. The use of relatively low flowrates will minimize the problems with carry-over fines.
4. Using a recirculating gas stream prevents the need for scrubbing large volumes of toxic flue-gases and, therefore, makes the process environmentally sound.
5. The process should be quite selective.

## 7. CONCLUSIONS

The transpiration experiments were successful in confirming the existence and measuring the thermodynamic properties of a complex vapor species in the Ag-K-Cl System. The molecularity of the species,  $\text{Ag}_2\text{KCl}_3$  was proposed for several reasons:

1. It has been observed in other studies that complex species are generally formed from the 1:1 or 2:1 combination reactions of salts.
2. In this study, chlorine did not take part in the formation reaction. Therefore, the valence states of silver and potassium both remained as 1.
3. In order to satisfy mass balance constraints, the complex species had to contain more silver than potassium.

Unlike the Ag-Fe-Cl System studied by Rupert<sup>(12)</sup>, the equilibrium constant for the complex species in the Ag-K-Cl System decreases with increasing temperature. However, the equilibrium yield for a process using the Ag-K-Cl System is much more favorable than one using the Ag-Fe-Cl System.

Rotary kiln tests, conducted on the Ag-Fe-Cl System, confirmed the viability of using  $\text{FeCl}_3$  as a complexing agent

for silver extraction schemes. In addition, it was found that by reacting hematite with chlorine, rather than hydrogen chloride, a sufficient pressure of the complexing agent was achieved to cause a sharp increase in the apparent pressure of AgCl.

Unfortunately, confirmation of the predicted rates of extraction on the Ag-K-Cl System was not possible. The addition of potassium chloride to the rotary kiln had caused the synthetic ore to agglomerate, which then prevented any silver from being volatilized. It was proposed that the agglomeration problem was due to the formation of a low-melting point product of a reaction between  $\text{KCl}_{(g)}$  and  $\text{SiO}_{2(s)}$ .

### 8. SUGGESTIONS FOR FURTHER WORK

A thermodynamic study of the vaporization characteristics of the Ag-Al-Cl and Ag-Pb-Cl systems identified by Rupert<sup>(12)</sup> should be conducted. Following this, the flow-reactor mass spectrometer should be used to identify the molecularity of all complex species which have been proposed in the Ag-Fe-Cl, Ag-K-Cl, Ag-Pb-Cl and Ag-Al-Cl systems.

The results of these studies should then be applied to the bench scale extraction of silver using a rotary kiln reactor. As was done with the Ag-Fe-Cl system, tests to determine optimum conditions for extraction and the best method of generating the complexing agent should be conducted.

Further work on the Ag-K-Cl system is also suggested. Emphasis should be focused on preventing the synthetic ore from agglomerating. Once this problem has been solved, the extraction curve for the system should be determined as well as the minimum complexing agent requirement.

Application of these results should then be applied to extraction tests conducted on a variety of real ores to determine the economics of an industrial process.

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APPENDIX A  
TRANSPIRATION CALCULATIONS

The vapor pressure data obtained from the transpiration experiments conducted in this study, was calculated as follows:

System: Pure AgCl

$$\text{Total Moles of Carrier Gas} = \frac{\text{Flowrate} * \text{time} * \text{reactor pressure}}{\text{Gas Constant} * \text{Ambient Temperature}}$$

$$\text{Total Moles of AgCl Transported} = \frac{\text{Weight of Ag Transported}}{107.87}$$

$$\text{Partial Pressure of AgCl} = \frac{\text{Moles AgCl} * \text{Reactor Pressure}}{(\text{Moles AgCl} + \text{Moles Carrier Gas})}$$

System: AgCl - KCl

$$\text{Total Moles of Carrier Gas} = \frac{\text{Flowrate} * \text{time} * \text{reactor pressure}}{\text{Gas Constant} * \text{Ambient Temperature}}$$

$$\text{Total Moles of Ag Transported} = \frac{\text{Weight of Ag}}{107.87}$$

$$\text{Total Moles of K Transported} = \frac{\text{Weight of K Transported}}{39.102}$$

Partial Pressure of AgCl = Obtained From Study of AgCl System

Moles of Ag Transported in Complex = Total Ag - Ag in AgCl

Total Moles of Complex ( $\text{Ag}_2\text{KCl}_3$ ) = 2 \* Moles Ag in Complex

$$\text{Partial Pressure of Complex Species} = \frac{\text{Moles Ag}_2\text{KCl}_3 * \text{Reactor Pressure}}{\text{Total Moles}}$$

Moles of K in the Complex = Moles of Complex

Moles K left as KCl and  $K_2Cl_2$  = Total Moles K - Moles Complex

To determine the distribution of potassium between the monomer and dimer, it was necessary to solve the following equations simultaneously:

$$\text{Moles K} = \text{Moles KCl} + 2 * \text{Moles } K_2Cl_2$$

$$K_{\text{equilibrium}} = \frac{P_{K_2Cl_2}^{\frac{1}{2}}}{P_{KCl}}$$

By combining these two equations, the following equation in one unknown was obtained:

$$2 * K_{\text{eq}} * \text{Moles } K_2Cl_2 + C * \text{Moles } K_2Cl_2^{\frac{1}{2}} - K_{\text{eq}} * \text{Moles K} = 0$$

An interval halving routine then found the moles of  $K_2Cl_2$  which satisfied this equation.

Then:

$$\text{Moles of KCl} = \text{Moles K} - 2 * \text{Moles } K_2Cl_2$$

$$P_{KCl} = \frac{\text{Moles KCl}}{\text{Total Moles}} * \text{Reactor Pressure}$$

$$P_{K_2Cl_2} = \frac{\text{Moles } K_2Cl_2}{\text{Total Moles}} * \text{Reactor Pressure}$$

$$K_{\text{eq}} \text{ (from reactor of monomer)} = \frac{P_{Ag_2KCl_3}}{P_{KCl}}$$

$$K_{\text{eq}} \text{ (from reactor of dimer)} = \frac{P_{Ag_2KCl_3}}{P_{K_2Cl_2}^{\frac{1}{2}}}$$

APPENDIX B  
COMPUTER PROGRAM USED TO REDUCE  
THE TRANSPIRATION DATA

A computer program was written in BASIC to perform the calculations presented in appendix A. The program required the input of:

1. The Transpiration Run Number
2. The Reactor Temperature
3. The Ambient Temperature
4. The Reactor Pressure
5. The Carrier Gas Flowrate
6. The Runtime
7. The Weight of Silver Transported
8. The Weight of Potassium Transported

From these inputs, the total moles of all species, the partial pressures of all species, and the equilibrium constants for the monomer and dimer reactions were calculated. A listing of the program and a sample of the output are presented on the following pages.

## Sample Program Output

```

RUN
*****
*
*                                COLORADO SCHOOL OF MINES                                *
*                                DEPARTMENT OF METALLURGICAL ENGINEERING                *
*                                GOLDEN, COLORADO 80401                                *
*
* PROGRAM AUTHOR: WILLIAM A. MAY                                                       *
* PROGRAM TITLE:  TRANSPIRATION DATA REDUCTION - AG2KCL3                            *
* COURSE:        GRADUATE THESIS                                                       *
*
*****
***** DATA INPUT SECTION *****

COMPLEXATION RUN #?1
RUN TEMP IN K??998
ROOM TEMP IN K??295.9
TOTAL PRESSURE IN MMHG??622.2
TOTAL FLOWRATE IN ML/MIN??59.0
RUNTIME IN MIN??240
MG OF AG TRANSPORTED??3.69
MG OF K TRANSPORTED??0.49

***** RESULTS SECTION *****

    TRANSPIRATION RUN # AGKCL-1

    TOTAL MOLES OF CARRIER GAS =                .477735912
    TOTAL MOLES OF AG TRANSPORTED =              3.42078428E-05
    TOTAL MOLES OF K TRANSPORTED =              1.25313283E-05

    CALCULATED MOLES OF AGCL =                   1.98691135E-05
    CALCULATED MOLES OF KCL IN EQUIL. =          5.07255519E-06
    CALCULATED MOLES OF K2CL2 IN EQUIL. =        1.44704245E-07
    CALCULATED MOLES OF AG2KCL3 =                7.16936464E-06

    PARTIAL PRESSURE OF AGCL =                   3.40492081E-05ATM.
    PARTIAL PRESSURE OF KCL =                    8.6927123E-06ATM.
    PARTIAL PRESSURE OF K2CL2 =                  2.47973084E-07ATM.
    PARTIAL PRESSURE OF AG2KCL3 =                1.22859628E-05ATM.

    LOG PARTIAL PRESSURE OF AGCL =               -4.46708805ATM.
    LOG PARTIAL PRESSURE OF KCL =                -5.05993294ATM.
    LOG PARTIAL PRESSURE OF K2CL2 =              -6.60440015ATM.
    LOG PARTIAL PRESSURE OF AG2KCL3 =            -4.90970612AMT.

    LOG K FOR MONOMER REACTION =                 .15022682ATM.
    LOG K FOR DIMER REACTION =                  -1.60750604ATM.

    REACTOR TEMP: 10000/T =                     10.0200401

```

## Program Listing

```

1000 PRINT '*****
***'
1010 PRINT '*'
    '*'
1020 PRINT '*'                COLORADO SCHOOL OF MINES
    '*'
1030 PRINT '*'                DEPARTMENT OF METALLURGICAL ENGINEERING
    '*'
1040 PRINT '*'                GOLDEN, COLORADO 80401
    '*'
1050 PRINT '*'
    '*'
1060 PRINT '*'                PROGRAM AUTHOR: WILLIAM A. MAY
    '*'
1070 PRINT '*'                PROGRAM TITLE:  TRANSPIRATION DATA REDUCTION - AG2KCL3
    '*'
1080 PRINT '*'                COURSE:        GRADUATE THESIS
    '*'
1090 PRINT '*'
    '*'
1100 PRINT '*****
***'
1110 PRINT
1120 PRINT '***** DATA INPUT SECTION *****'
1130 PRINT
1140 PRINT 'COMPLEXATION RUN #': INPUT N
1150 PRINT 'RUN TEMP IN K?': INPUT T1
1160 PRINT 'ROOM TEMP IN K?': INPUT T2
1170 PRINT 'TOTAL PRESSURE IN MMHG?': INPUT P1
1180 PRINT 'TOTAL FLOWRATE IN ML/MIN?': INPUT F1
1190 PRINT 'RUNTIME IN MIN?': INPUT S1
1200 PRINT 'MG OF AG TRANSPORTED?': INPUT W1
1210 PRINT 'MG OF K TRANSPORTED?': INPUT W2
1220 REM
1230 REM MOLES OF CARRIER GAS
1240 REM
1250 M1 = (F1 * S1 * (273.15 / T2) * (P1 / 760)) / 22400
1260 REM
1270 REM MOLES OF AG AND K TRANSPORTED
1280 REM
1290 M6 = W1 / (1000 * 107.87)
1300 M7 = W2 / (1000 * 39.102)
1310 REM
1320 REM PRESSURE OF AGCL
1330 REM
1340 P2 = 10 ^ (( - 10226 / T1) + 5.7786)
1350 REM
1360 REM MOLES OF AGCL
1370 REM
1380 M2 = P2 * 760 * M1 / P1
1390 REM
1400 REM WEIGHT OF AG TRANSPORTED DUE TO AGCL
1410 REM
1420 W3 = M2 * 107.87 * 1000
1430 REM
1440 REM WEIGHT OF AG TRANSPORTED DUE TO COMPLEX

```

```

1450 REM
1460 W4 = W1 - W3
1470 REM
1480 REM MOLES OF COMPLEX ASSUMING 2 AG ATOMS IN COMPLEX
1490 REM
1500 M3 = W4 / (1000 * 215.74)
1510 REM
1520 REM PRESSURE OF COMPLEX IN ATM.
1530 REM
1540 P3 = (M3 / M1) * (P1 / 760)
1550 REM
1560 REM WT OF K CONSUMED IN COMPLEX
1570 REM ASSUMING 1 K ATOM IN COMPLEX
1580 REM
1590 W5 = M3 * 39.102 * 1000
1600 W6 = W2 - W5
1610 IF W2 > W5 THEN 1700
1620 PRINT 'INSUFFICIENT K FOR EQUILIBRIUM.....'
1630 PRINT
1640 PRINT 'HERE'S THE PROBLEM... '
1650 PRINT
1660 PRINT 'THERE WERE *W2*MG. OF K TRANSPORTED.'
1670 PRINT 'FROM THIS, *W5*MG. WERE NEEDED FOR THE COMPLEX.'
1680 PRINT 'THIS LEFT A DEFICIT OF *W6*MG. OF K'
1690 GOTO 2380
1700 REM
1710 REM CALCULATION OF K SPECIES PRESSURES
1720 REM
1730 M8 = M7 - M3
1740 C = (M1 / (P1 / 760)) ^ 0.5
1750 K1 = (4764 / T1) - 3.0155
1760 K2 = 10 ^ K1
1770 REM
1780 REM INTERVAL HALVING ROUTINE
1790 REM
1800 V2 = .1
1810 V1 = 0
1820 D1 = (V2 - V1) / 2
1830 M5 = V1
1840 FOR I = 1 TO 3
1850 F1 = 2 * K2 * M5 + C * M5 ^ 0.5 - M8 * K2
1860 IF I = 1 THEN 1980
1870 IF F2 / F1 < 0 THEN 1930
1880 F2 = F1
1890 M5 = M5 + D1
1900 NEXT I
1910 PRINT 'SOLUTION TO INTERVAL HALVING IS NOT IN RANGE...'
1920 GOTO 2380
1930 IF ABS (D1 / M5) < 0.0001 THEN 1970
1940 M5 = M5 - D1
1950 D1 = D1 / 2
1960 GOTO 1840
1970 M4 = M8 - 2 * M5
1980 P4 = (M4 / M1) * (P1 / 760)
1990 P5 = (M5 / M1) * (P1 / 760)
2000 L1 = LOG (P2) / 2.303
2010 L2 = LOG (P3) / 2.303
2020 L3 = LOG (P4) / 2.303

```

```

2030 L4 = LOG (P5) / 2.303
2040 REM
2050 REM CALCULATION OF EQUILIBRIUM CONSTANTS
2060 REM
2070 K3 = L2 - L3
2080 K4 = L2 - (0.5 * L4)
2090 REM
2100 PRINT
2110 PRINT "***** RESULTS SECTION *****"
2120 PRINT
2130 PRINT "    TRANSPIRATION RUN # AGKCL-'N
2140 PRINT
2150 PRINT "    TOTAL MOLES OF CARRIER GAS =           *M1
2160 PRINT "    TOTAL MOLES OF AG TRANSPORTED =         *M6
2170 PRINT "    TOTAL MOLES OF K TRANSPORTED =         *M7
2180 PRINT
2190 PRINT "    CALCULATED MOLES OF AGCL =             *M2
2200 PRINT "    CALCULATED MOLES OF KCL IN EQUIL. =    *M4
2210 PRINT "    CALCULATED MOLES OF K2CL2 IN EQUIL. =  *M5
2220 PRINT "    CALCULATED MOLES OF AG2KCL3 =         *M3
2230 PRINT
2240 PRINT "    PARTIAL PRESSURE OF AGCL =             *P2*ATM.*
2250 PRINT "    PARTIAL PRESSURE OF KCL =              *P4*ATM.*
2260 PRINT "    PARTIAL PRESSURE OF K2CL2 =           *P5*ATM.*
2270 PRINT "    PARTIAL PRESSURE OF AG2KCL3 =         *P3*ATM.*
2280 PRINT
2290 PRINT "    LOG PARTIAL PRESSURE OF AGCL =         *L1*ATM.*
2300 PRINT "    LOG PARTIAL PRESSURE OF KCL =          *L3*ATM.*
2310 PRINT "    LOG PARTIAL PRESSURE OF K2CL2 =       *L4*ATM.*
2320 PRINT "    LOG PARTIAL PRESSURE OF AG2KCL3 =     *L2*ATM.*
2330 PRINT
2340 PRINT "    LOG K FOR MONOMER REACTION =          *K3*ATM.*
2350 PRINT "    LOG K FOR DIMER REACTION =            *K4*ATM.*
2360 PRINT
2370 PRINT "    REACTOR TEMP: 10000/T =               *(10000 / T1)
2380 END

```

J

APPENDIX C  
STATISTICAL METHODS USED TO ANALYZE  
THE TRANSPIRATION DATA

The data obtained from the transpiration experiments was regressed using both a least squares linear regression as suggested by Natrella<sup>(26)</sup> and Himmelblau<sup>(27)</sup>, and an absolute-value criteria regression written by the author. Due to the scatter in the data generated during the complexation experiments, it was felt that the least squares criteria would place too much emphasis on the most widely scattered points. This occurs because the least squares regression squares both positive and negative deviations in order to sum the total deviation from the mean. If one data point is widely scattered and possibly spurious, its weight on the regression is disproportionately increased by squaring it.

This is not the case with an absolute-value regression. This method finds the set of parameters which will minimize an objective function based upon the sum of the absolute values of the differences between Y observed and Y calculated. The function was:

$$\phi = Y_i \text{ observed} - (b_0 - b_1 x_i)$$



A search routine was written in BASIC for an Apple Plus-II microprocessor which incremented  $b_0$  and  $b_1$  until a minimum  $\phi$  was obtained.

Once the parameters for the best-fitting line were determined, the line was tested to determine if it fit the data within the limits of experimental error. The following hypothesis were proposed:

$H_0$  : The regression does not fit the data within the limits of experimental error.

$H_1$  : The regression does fit the data within the limits of experimental error.

To test the null hypothesis ( $H_0$ ), an F-statistic was implemented from Himmelblau<sup>(24)</sup> using a type 1 error of 5%. This means that statistically, there is only a 5% chance that we are wrong if we reject the null hypothesis.

Next, a confidence interval was constructed around the regressed line using the formula:

$$\pm W = (2F)^{\frac{1}{2}} \times S_y \times \left( \frac{1}{N} + \frac{(X-\bar{X})^2}{S_{xx}} \right)^{\frac{1}{2}}$$

from Natrella<sup>(23)</sup>

where:  $w = \frac{1}{2}$  the width of the confidence interval

$S_y$  = the standard deviation of the data in the Y direction

X = the independent variable

N = the number of data sets

- $\bar{X}$  = the grand mean in the x direction
- $S_{xx}$  = the sum of the squares of the deviations  
from the grand mean in the X direction
- F = the F-statistic for the desired confidence  
level based upon ( 2, n-2 ) degrees of  
freedom.

To plot this interval, the value of w was either added or subtracted from the calculated value of y at each value of the independent variable. A listing and sample printout of the program used to perform the regression and statistical analysis are included in this appendix.

## Sample Program Output

```

*****
*
*           COLORADO SCHOOL OF MINES
*   DEPARTMENT OF METALLURGICAL ENGINEERING
*           GOLDEN, COLORADO  80401
*
* PROGRAM AUTHOR:  WILLIAM A. MAY
* PROGRAM TITLE:   LINEAR REGRESSION - ABSOLUTE VALUE CRITERIA
* WRITTEN FOR:    EMPIRICAL MODELING MT-520
*
* COMMENT:  THIS PROGRAM WILL REGRESS A SET OF DATA TO FIT A
*           LINEAR, EXPONENTIAL, OR LOGARITHMIC FUNCTION.
*           THE REGRESSION IS BASED UPON THE ABSOLUTE VALUE
*           CRITERIA AND USES A DIRECT SEARCH ROUTINE.
*
*           IN ADDITION, A STATISTICAL ANALYSIS IS PERFORMED
*           ON THE DATA.
*           1. THE REGRESSION IS TESTED FOR FIT WITHIN
*              EXPERIMENTAL ERROR.
*           2. A 95% CONFIDENCE BAND IS CALCULATED AROUND THE
*              REGRESSED LINE.
*
*****

***** DATA INPUT SECTION *****

WHAT MODEL ARE YOU TRYING TO FIT?
  FOR LINEAR...TYPE 1
  FOR EXPONENTIAL...TYPE 2
  FOR LOGARITHMIC...TYPE 3?1

HOW MANY DATA SETS ARE THERE?4

FOR THE STATISTICAL ANALYSIS, PLEASE INPUT:
  1. THE VARIANCE OF THE DUPLICATE EXPERIMENTS ?1.03
  2. THE F-STATISTIC BASED UPON F(2,2) DEGREES OF FREEDOM?3.41
  3. THE T-STATISTIC BASED UPON T(N-2) DEGREES OF FREEDOM?2.11

INPUT THE INDEPENDENT AND DEPENDENT (X THEN Y) VARIABLES.
  XI(1)=?3.45
  YI(1)=?7.73

  XI(2)=?8.69
  YI(2)=?13.31

  XI(3)=?13.92
  YI(3)=?21.44

  XI(4)=?18.11
  YI(4)=?32.65

```

\*\*\*\*\* RESULTS SECTION \*\*\*\*\*

\*\*\* LEAST SQUARES REGRESSION \*\*\*

ASSUMING THE MODEL  $Y = AX + B...$

BEST ESTIMATES: A= 1.66745642  
B= .369612538

THIS REGRESSION YIELDS:

X	Y	+ OR -
3.45	6.12233717	5.86269555
8.69	14.8598088	3.74391999
13.92	23.5806058	3.88450703
18.11	30.5672482	5.60044961

STANDARD DEVIATION = 6.95326771

\*\*\* ABSOLUTE VALUE REGRESSION \*\*\*

INITIAL VALUE OF THE OBJECTIVE FUNCTION = 7.38082924  
FINAL VALUE OF THE OBJECTIVE FUNCTION= 7.21936553

ASSUMING THE MODEL  $Y = AX + B...$

BEST ESTIMATES: A= 1.51368144  
B= .369612538

THIS REGRESSION YIELDS:

X	Y	+ OR -
3.45	5.59181352	5.86269555
8.69	13.5235043	3.74391999
13.92	21.4400582	3.88450703
18.11	27.7823835	5.60044961

STANDARD DEVIATION = 14.1555582

\*\*\* STATISTICAL RESULTS \*\*\*

H0: THE REGRESSION DOES NOT FIT WITHIN THE EXPERIMENTAL ERROR  
H1: THE REGRESSION FITS WITHIN THE EXPERIMENTAL ERROR

RESULTS: ACCEPT THE NULL HYPOTHESIS

THE UNCERTAINTY IN THE SLOPE = .504951787  
THE ERROR IN THE ENTHALPY = 23106.9018CAL./MOLE

]

## Program Listing

```

1000 PRINT '*****'
1010 PRINT '*'
1020 PRINT '*
                                COLORADO SCHOOL OF MINES
                                *'
1030 PRINT '*
                                DEPARTMENT OF METALLURGICAL ENGINEERING
                                *'
1040 PRINT '*
                                GOLDEN, COLORADO 80401
                                *'
1050 PRINT '*'
1060 PRINT '* PROGRAM AUTHOR: WILLIAM A. MAY
                                *'
1070 PRINT '* PROGRAM TITLE: LINEAR REGRESSION - ABSOLUTE VALUE CRITERIA
                                *'
1080 PRINT '* WRITTEN FOR: EMPIRICAL MODELING MT-520
                                *'
1090 PRINT '*'
1100 PRINT '* COMMENT: THIS PROGRAM WILL REGRESS A SET OF DATA TO FIT A
                                *'
1110 PRINT '* LINEAR, EXPONENTIAL, OR LOGARITHMIC FUNCTION.
                                *'
1120 PRINT '* THE REGRESSION IS BASED UPON THE ABSOLUTE VALUE
                                *'
1130 PRINT '* CRITERIA AND USES A DIRECT SEARCH ROUTINE.
                                *'
1140 PRINT '*'
1150 PRINT '* IN ADDITION, A STATISTICAL ANALYSIS IS PERFORMED
                                *'
1160 PRINT '* ON THE DATA.
                                *'
1170 PRINT '* 1. THE REGRESSION IS TESTED FOR FIT WITHIN
                                *'
1180 PRINT '* EXPERIMENTAL ERROR.
                                *'
1190 PRINT '* 2. A 95% CONFIDENCE BAND IS CALCULATED AROUND THE
                                *'
1200 PRINT '* REGRESSED LINE.
                                *'
1210 PRINT '*'
1220 PRINT '*****'
1230 PRINT
1240 DIM X(50),Y(50)
1250 DIM XI(50),YI(50)
1260 DIM W(50)
1270 GOTO 1800
1280 REM
1290 REM SUBROUTINES
1300 REM
1310 Q = 0: FOR I = 1 TO N:Q = Q + ABS (YI(I) - (A * X(I) + B)): NEXT I: RETURN
1320 Q = 0: FOR I = 1 TO N:Q = Q + ABS (YI(I) - EXP (A * X(I) + B)): NEXT I: R
RETURN
1330 Q = 0: FOR I = 1 TO N:Q = Q + ABS (YI(I) - 10 ^ (A * X(I) + B)): NEXT I: R
RETURN
1340 PRINT : PRINT 'THIS REGRESSION YIELDS:'
1350 PRINT : PRINT 'X','Y','+ OR -'
1360 PRINT : RETURN
1370 SD = 0: FOR I = 1 TO N:SD = SD + (YI(I) - (A * X(I) + B)) ^ 2: NEXT I:SD =
SD / (N - 2): RETURN
1380 SD = 0: FOR I = 1 TO N:SD = SD + (YI(I) - EXP (A * X(I) + B)) ^ 2: NEXT I:
SD = SD / (N - 2): RETURN
1390 SD = 0: FOR I = 1 TO N:SD = SD + (YI(I) - 10 ^ (A * X(I) + B)) ^ 2: NEXT I:
SD = SD / (N - 2): RETURN
1400 FOR I = 1 TO N: PRINT X(I),A * X(I) + B,W(I): NEXT I: RETURN
1410 FOR I = 1 TO N: PRINT X(I),A * X(I) + B, EXP (A * X(I) + B),W(I): NEXT I:
RETURN
1420 FOR I = 1 TO N: PRINT X(I),A * X(I) + B,10 ^ (A * X(I) + B),W(I): NEXT I:
RETURN
1430 FOR I = 1 TO N:X(I) = XI(I):Y(I) = YI(I): NEXT I: RETURN
1440 FOR I = 1 TO N:X(I) = XI(I):Y(I) = LOG (YI(I)): NEXT I: RETURN
1450 FOR I = 1 TO N:X(I) = LOG (XI(I)) / 2.302585:Y(I) = LOG (YI(I)) / 2.3025
85: NEXT I: RETURN
1460 PRINT

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```

1470 PRINT '*** STATISTICAL RESULTS ***'
1480 PRINT
1490 PRINT 'H0: THE REGRESSION DOES NOT FIT WITHIN THE EXPERIMENTAL ERROR'
1500 PRINT 'H1: THE REGRESSION FITS WITHIN THE EXPERIMENTAL ERROR'
1510 PRINT
1520 IF (SD / S1) < S2 THEN PRINT '      RESULTS: REJECT THE NULL HYPOTHESIS':
RETURN
1530 PRINT '      RESULTS: ACCEPT THE NULL HYPOTHESIS': RETURN
1540 FA = 0:FB = 0:Q2 = Q1:D = D / 4: GOTO 2270
1550 FA = 0:FB = 0:D = D / 4: GOTO 2270
1560 PRINT : PRINT 'ITERATIONS HAS EXCEEDED 30': GOTO 2430
1570 XT = 0:YT = 0:XY = 0:D2 = 0:D3 = 0: FOR J = 1 TO N
1580 XT = XT + XI(J):YT = YT + YI(J)
1590 XY = XY + XI(J) * YI(J)
1600 D2 = D2 + XI(J) ^ 2:D3 = D3 + YI(J) ^ 2
1610 NEXT J
1620 XH = XT / N:YH = YT / N
1630 D1 = XT * YT / N
1640 SX = XY - D1
1650 D4 = XT ^ 2 / N:D5 = YT ^ 2 / N
1660 D6 = D2 - D4:D7 = D3 - D5
1670 D8 = SX ^ 2 / D6
1680 D9 = D7 - D8
1690 E1 = D9 / (N - 2)
1700 SY = E1 ^ (0.5)
1710 E2 = E1 / D6
1720 E3 = E2 ^ 0.5
1730 E4 = S3 * E3
1740 E5 = E4 * 45760.61
1750 FOR J = 1 TO N
1760 W(J) = (2 * S2) ^ (0.5) * SY * (1 / N + (XI(J) - XH) ^ 2 / D6) ^ (0.5)
1770 NEXT J
1780 RETURN
1790 PRINT : PRINT : PRINT
1800 PRINT '***** DATA INPUT SECTION *****'
1810 PRINT
1820 PRINT 'WHAT MODEL ARE YOU TRYING TO FIT?'
1830 PRINT '      FOR LINEAR...TYPE 1'
1840 PRINT '      FOR EXPONENTIAL...TYPE 2'
1850 PRINT '      FOR LOGARITHMIC...TYPE 3': INPUT M
1860 PRINT
1870 PRINT 'HOW MANY DATA SETS ARE THERE?': INPUT N
1880 PRINT
1890 PRINT 'FOR THE STATISTICAL ANALYSIS, PLEASE INPUT:'
1900 PRINT '      1. THE VARIANCE OF THE DUPLICATE EXPERIMENTS ': INPUT S1
1910 PRINT '      2. THE F-STATISTIC BASED UPON F(2,'N - 2') DEGREES OF FREEDOM'
;: INPUT S2
1920 PRINT '      3. THE T-STATISTIC BASED UPON T(N-2) DEGREES OF FREEDOM': INP
UT S3
1930 PRINT
1940 PRINT 'INPUT THE INDEPENDENT AND DEPENDENT (X THEN Y) VARIABLES.'
1950 FOR R = 1 TO N
1960 PRINT '      XI('R')=': INPUT XI(R)
1970 PRINT '      YI('R')=': INPUT YI(R)
1980 PRINT
1990 NEXT R
2000 PRINT CHR$(12)
2010 PRINT '***** RESULTS SECTION *****'

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2020 PRINT
2030 PRINT '*** LEAST SQUARES REGRESSION ***'
2040 PRINT
2050 ON M GOSUB 1430,1440,1450
2060 X1 = 0:Y1 = 0: FOR I = 1 TO N
2070 X1 = X1 + X(I):Y1 = Y1 + Y(I): NEXT I
2080 X1 = X1 / N:Y1 = Y1 / N
2090 T = 0:D = 0: FOR I = 1 TO N
2100 T = T + ((X(I) - X1) * (Y(I) - Y1))
2110 D = D + (X(I) - X1) ^ 2: NEXT I
2120 A = T / D:B = Y1 - A * X1
2130 PRINT 'ASSUMING THE MODEL Y = AX + B... '
2140 PRINT : PRINT '      BEST ESTIMATES: A= 'A
2150 PRINT '      B= 'B
2160 GOSUB 1340
2170 GOSUB 1570
2180 ON M GOSUB 1400,1410,1420
2190 ON M GOSUB 1370,1380,1390
2200 PRINT : PRINT 'STANDARD DEVIATION = 'SD
2210 PRINT
2220 PRINT
2230 PRINT '*** ABSOLUTE VALUE REGRESSION ***'
2240 ON M GOSUB 1310,1320,1330
2250 PRINT : PRINT 'INITIAL VALUE OF THE OBJECTIVE FUNCTION = 'Q
2260 C = 0:Q2 = Q:Q1 = Q:B1 = B:A1 = A:D = .05:FA = 0:FB = 0
2270 IF C > 30 THEN 1560
2280 B = B + D * B: ON M GOSUB 1310,1320,1330
2290 IF Q < Q1 THEN Q1 = Q:B1 = B:FB = 1: GOTO 2270
2300 B = B1: IF FB = 1 THEN 2340
2310 B = B - D * B: ON M GOSUB 1310,1320,1330
2320 IF Q < Q1 THEN Q1 = Q:B1 = B: GOTO 2310
2330 B = B1
2340 A = A + D * A: ON M GOSUB 1310,1320,1330
2350 IF Q < Q1 THEN Q1 = Q:A1 = A:FA = 1: GOTO 2340
2360 A = A1: IF FA = 1 THEN 2400
2370 A = A - D * A: ON M GOSUB 1310,1320,1330
2380 IF Q < Q1 THEN Q1 = Q:A1 = A: GOTO 2370
2390 A = A1
2400 C = C + 1
2410 IF ABS ((Q2 - Q1) / Q2) > .000001 THEN 1540
2420 IF C < 5 THEN 1550
2430 PRINT 'FINAL VALUE OF THE OBJECTIVE FUNCTION= 'Q1
2440 PRINT : PRINT 'ASSUMING THE MODEL Y = AX + B... '
2450 PRINT : PRINT '      BEST ESTIMATES: A= 'A
2460 PRINT '      B= 'B
2470 GOSUB 1340
2480 GOSUB 1570
2490 ON M GOSUB 1400,1410,1420
2500 ON M GOSUB 1370,1380,1390
2510 PRINT : PRINT 'STANDARD DEVIATION = 'SD
2520 GOSUB 1460
2530 PRINT : PRINT 'THE UNCERTAINTY IN THE SLOPE = 'E4
2540 PRINT 'THE ERROR IN THE ENTHALPY = 'E5'CAL./MOLE'
2550 END

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]

APPENDIX D  
CHEMICAL ANALYSIS TECHNIQUES

Transpiration Studies

The condensate from the off-gas condenser was leached and analyzed according to the following procedure:

After removing the condenser assembly from the transpiration apparatus, both the condenser and sleeve were placed in an 18-in. by 1½-in. pyrex test tube filled with a 30% solution of  $\text{NH}_4\text{OH}$  + 1% KCN. This solvent was found to work satisfactorily in dissolving both the AgCl and KCl condensates. After leaching for two hours, the condenser assembly was rinsed with a wash bottle filled with the solvent and the rinse solution was added to the leach liquor. This was then diluted to 500 ml with additional solvent. Triplicate samples were then diluted into the working range of the atomic absorption spectrophotometer. This range is 2-5 ppm for silver and 0.5 to 2 ppm for potassium. If both silver and potassium were being analyzed (as was the case with all complexing runs) two sets of triplicate samples were made. All dilutions were performed with the same solvent so that matrix effects would be eliminated. In addition, the silver and potassium standards were made



using this same solvent.

For each sample being analyzed, ten A-A readings were taken and averaged to obtain the metal ion concentration of that sample. Each of the three samples were then averaged and this final value was used to calculate the weight of metal which had been transported.

#### Extraction Studies

The head sample analysis of the synthetic ore was performed by splitting out duplicate 25-30 gram samples of the roasted ore and leaching them in boiling aqua regia (3 parts hydrochloric acid and 1 part nitric acid). Each sample was weighed to the nearest 0.01 gram and leached for 2 hours with a magnetic stirrer hot plate. The leach liquor was then diluted to 250 ml with a 10% nitric acid solution. Further dilutions to obtain an Ag concentration between 2 and 5 ppm for the A-A was also done with the 10% nitric solution. The A-A analysis was then performed as described previously. Results were reported as mg Ag/gr. ore.

The tails samples from the Ag-Fe-Cl studies were leached in the same manner as the head samples except that after leaching, all dilutions were made with a 30% solution of  $\text{NH}_4\text{OH}$  + 1% KCN. This caused the iron in solution to precipitate as iron hydroxide, which then settled to the bottom. A-A analysis was then performed as described previously.

The tails samples from the Ag-K-Cl studies were leached for 2 hours in a 30% solution of  $\text{NH}_4\text{OH}$  + KCN. A magnetic stirrer was used to keep the ore in suspension during the digestion. After leaching, the leach liquor was diluted and analyzed in the same manner as previously described for the condensate from the transpiration studies.

The condensate from the extraction studies was also leached and analyzed using the same procedure as described for the transpiration studies.

BIOGRAPHICAL NOTE

The author was born in Middletown, New York, on June 4, 1948. He attended primary and secondary schools in Pine Bush, New York, and graduated from Pine Bush Central High School in June, 1966.

After serving in the United States Army, in which he worked as a clerk/driver for the Army Operations Center, U.S. Southern Command Headquarters, Fort Amador, Canal Zone, he returned to Middletown. He attended Orange County Community College in Middletown and received an Associates degree in Computer Science in 1973. The author attended the Colorado School of Mines from 1976 to 1979, earning the degree of Bachelor of Science in Metallurgical Engineering. Upon completion of this degree he plans to reside in Ann Arbor, Michigan, where he has accepted a position as Research Engineer for Climax Molybdenum of Michigan.

The author is a member of the American Institute for Mining, Metallurgical, and Petroleum Engineers (AIME), and the newly formed extractive metallurgy chapter of the American Society for Metals (ASM).