"Cold" Plasma Processing of Local Planetary Ores for Oxygen and Metallurgically Important Metals

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Abstract

In the previous progress reports for 1988-89 and 1989-90, the utilization of a "cold" or nonequilibrium plasma in chlorination processing was discussed along with the results of some preliminary experiments. This report is a continuation of that discussion, but is focused on the progress that has been achieved in the past 12 months. During that period TiO_2 has been successfully chlorinated at temperatures between 700 and 900°C without the aid of carbon. In addition to these initial experiments a technique has been developed for determining the temperature of a specimen in a plasma. Development of that technique has required evaluating the emissivity of TiO_2, ZrO_2 and $FeOTiO_2$, and analyzing the specimen temperature in a plasma as a function of both power absorbed by the plasma and the pressure of the plasma. We have also calibrated the mass spectrometer with $TiCl_4$ and CCl_4 vapor and are now prepared to report all future results in terms of partial pressures.

Introduction

During the first two reporting periods funding for this work was provided by the Space Engineering Research Center (SERC). During the latest period, our primary source of funding has been through the U.S. Bureau of Mines' Pyrometallurgy Generic Center at the University of Missouri at Rolla (contract # MU-USDI-G1175129 and MU-USDI-G1105129). We wish to gratefully acknowledge their support.

Support from the Bureau of Mines has not altered our basic perspective, namely, to investigate the feasibility of using a "cold" or non-equilibrium plasma in the enhancement of reaction rates and in the biasing of the thermodynamics of reactions that would not proceed if conventional means were employed. There are many reasons to explore the potential of this new technology for both terrestrial and extraterrestrial applications. However, our attention is focused on the latter in the discussion which follows.

Material requirements at a Lunar base will be varied and demanding, and can possibly be likened to that in the present day nuclear industry. The extent of requirements will depend on the critical nature of the components and/or systems involved. The demand for materials will, initially, be met by importing them from Earth. Ultimately, the great expense of transporting materials from the Earth to the Moon will dictate that general construction materials be produced from

extraterrestrial sources. Eventually as the Lunar base progresses more ambitious efforts will be undertaken to achieve greater self sufficiency with regards to materials.

Not only will there be a demand for materials at a Lunar base, there will be a demand for materials that can meet a wide range of mechanical, electrical, optical, and chemical requirements. There has been a tendency to focus on iron, produced as a by-product at lunar oxygen production facilities, as a primary construction material. Unfortunately high purity iron is susceptible to brittle failure. Iron experiences a lowering of absorbed impact energy with decreasing temperature. That phenomenon is referred to as "ductile-brittle" transition. At low temperatures a crack or surface imperfection in the iron can propagate faster than plastic deformation can occur, so that little energy is absorbed. At higher temperatures cracking is preceded by energy consuming deformation.

Just before dawn on the lunar surface, temperatures dip as low as 123 K. At that temperature high purity iron will be subject to failure by cleavage fracture through any and all impacts. This condition can be alleviated by alloying the iron.

This example demonstrates that there will be a need for recovery of multiple elements to produce materials that can be used in the Lunar environment. Except for the iron oxide in illmenite, the Lunar soil is composed of refractive oxides. New techniques, accordingly, will be necessary to recover elements other than Fe.

We have proposed the use of a nonequilibrium plasma as one technique that may have potential for recovery of metallurgically important metals from refractory oxides. Since the reactive environment is created by an electromagnetic field one apparatus can be used in the processing of multiple feed materials. The intent of the present work is to examine the feasibility of using a non-equilibrium plasma in the chemical processing of materials.

In conventional processing reactants are heated until the chemical potential of the desired reaction is negative, and the temperature is high enough to ensure rapid reaction rates. In a cold plasma energy is used to produce radicals and heat. Radicals are produced by reducing the pressure, such that electrons, responding to electromagnetic radiation, are accelerated until they have sufficient energy to liberate bound electrons, break bonds and excite both ions and neutral species upon impact. Radicals formed in this manner from adsorbed gaseous species are available for reaction with the underlying substrate.

In the experimental program refractory metal oxides have been chlorinated without carbon as a reducing agent. A microwave induced plasma has been used to create monatomic chlorine that has been used to chlorinate both rutile and silica at temperatures below 900°C. The monatomic chlorine has a high chemical potential, and, as a result, can participate in reaction where diatomic chlorine can not.

Experiments are planned to, also, examine the feasibility of utilizing a cold plasma in hydrogen reduction of refractory metal oxides. The use of hydrogen has several distinct

advantages. Monatomic hydrogen, like monatomic chlorine, is highly reactive. However, monatomic hydrogen (unlike monatomic chlorine) when reacted with a refractory oxide produces both solid and gaseous products. By continuing to flush the reactor with fresh gaseous reactant, the back reaction can be prevented.

Experimental Apparatus

The construction of the experimental apparatus was, essentially, completed during the last reporting period. We have, however, added an electronic package that allows for determination of a power used to generate the plasma. We now have the capability to measure both the plasma's efficiency in absorbing the microwaves and the efficiency of which energy is converted to microwaves.

Plasma Characterization

A cold plasma is typically characterized by the composition of the gas, the plasma density (pressure), power absorbed by the plasma, and a geometrical factor or characteristic length. Characterization becomes complex when a solid specimen is inserted into the plasma. There are no established procedures to follow like the Gibbs phase rule. The complexity of a plasma is represented by the temperatures involved. In a cold plasma there is the electron temperature, the ion temperature, the temperature of neutrals and the temperature of the solid specimen. They are all different. In establishing the state of the plasmas employed in this investigation, the standard parameters noted above have been fixed, the size and shape of the solid specimen set, and the specimen temperature monitored during an experiment.

Measuring any temperature in a plasma is a difficult task. In a plasma, free electrons have a continuum of energy states. The electrons can absorb and emit energy at any wavelength, and, as such, it is unlikely that a solid body in a plasma could be characterized as a grey body. Because of that situation a single color optical pyrometer was employed in lieu of a two color unit. The optical pyrometer is used to monitor radiant emissions at 600 nm to determining the solid specimen temperature.

A number of preliminary experiments were required before the temperature of a solid specimen could be determined in the plasma. Proper use of the optical pyrometer required measuring the emissivity of the specimens. The task was accomplished using a resistance wound furnace, a thermocouple and the optical pyrometer. The experiments were conducted from 600°C to 1000°C and the results of that work are shown in Figure 1. Those results reveal that the emissivity of TiO_2, ZrO_2 and $FeTiO_3$ increase only slightly over the temperature range noted.

With knowledge of the emissivity of the specimens, the effect of the plasma on temperature readings could be deduced. The temperature of a solid specimen in the plasma was monitored. Once the specimen reached a constant temperature the plasma was extinguished by turning the power off to the microwave generator. The temperature of the solid specimen was continually

monitored as it cooled. The resulting data and a least squares routine for a polynomial fit were used to predict the temperature of the specimen in the plasma as shown in Figure 2. The error in the temperature readings was found to increase as both the power absorbed and pressure decreased.

These experiments were conducted at a range of power settings and plasma densities. some of the results of this work are presented in a three dimensional plot shown in Figure 3a and as a contour map in Figure 3b. The graphs reveal that the solid specimen temperature is a strong function of the power absorbed and a weaker function of the pressure (or density) of the plasma. These experiments were conducted with a nitrogen plasma and then later spot checked with a N_2 - 10% Cl_2 plasma. The chlorine was found to only slightly effect the temperature readings obtained with the nitrogen plasma. The extend of the effect is presented in Table I.

Plasma - Solid Reactions

A series of experiments have been conducted to test the general hypothesis that a cold plasma can be used to bias thermodynamics with the formation of radicals.

Rutile has been reacted in a nitrogen-chlorine plasma at pressures of 17 to 30 Torr and power absorption levels of 0.35 to 1.0 KW. These conditions correspond to rutile reaction temperatures of 665°C to 850°C. The mass spectrometer was used to monitor the extent of metal chloride formation. Some of the results of those experiments are presented in figure 4. Those results reveal that chlorides of Ti and Si are readily formed in the plasma, even though conventional thermodynamics indicates that the chlorides of these metals can not be formed at the conditions employed (see Figure 4). The presence of monatomic chlorine in the plasma makes the reactions possible.

The source of silicon for the silicon chlorides reported in Figure 5 is the specimen holder and the walls of the plasma confinement chamber.

Equipment Calibration

During the last few months we have assembled a transportation device in order to calibrate the signal from the mass spectrometer. The apparatus consists of two baths, the primary bath consisting of mineral oil and the other of ice and water. The evaporating fluid was placed in two bubblers in series as shown in Figure 6. A combination stirrer and heater was used to circulate the mineral oil around the bubbler. A nitrogen carrier gas was passed through a copper coil (not shown in the figure) immersed in the bath before entering the bubblers. The saturated gas upon leaving the bubbler was immediately passed through an expansion valve to prevent condensation. The gas then entered the mass spectrometer or exited through a secondary roughing pump.

The primary bath could be either heated or cooled. To cool the mineral oil, ice water was circulated through a second copper coil immersed in the oil. Mineral oil was used in the primary bath to guard against any accidental contact between water and $TiCl_4$ liquid. Those two compounds react vigorously yielding HCl vapor. The temperature of the primary bath was monitored using a

partial immersion thermometer.

Both $TiCl_4$ and CCl_4 were used in the calibration of the signal from the mass spectrometer. The carrier gas was found to be easily saturated with the vapors of those compounds at gas flow rates of 30 to 100 ml/min. All of the experiments were conducted at a flow rate of 50 ml/min. The results of the calibration experiments are presented in Figures 7 and 8.

The measured vapor pressure of $TiCl_4$ was consistently found to be greater than that predicted by data in the literature as shown in Figure 7. It is, however, encouraging to note that the slope of the lines (and therefore the calculated values of the heat of vaporization) are approximately equal. Analysis of the signal received from the mass spectrometer suggested that $TiCl_4$, $TiCl_3$ and $TiCl_2$ were all present in the vapor as parent molecules. The concentrations of both $TiCl_3$ and $TiCl_2$ were well above that which is predicted by thermodynamic data. Large concentrations of hydrogen and HCl were also detected. The results from the mass spectrometer suggest that the liquid $TiCl_4$ was contaminated.

As a result of the problems associated with the $TiCl_4$, carbon tetrachloride was used to calibrate the signal from the mass spectrometer. The results of that work are presented in Figure 8. At room temperature and above the results of the present work compare favorably with data published by K.K. Kelley. The discrepancy in the value obtained in the present work at 6°C and the calculated value is probably associated with a nonthermal equilibrium condition. A 10°C discrepancy between the bath temperature and the fluid temperature would account for the difference. There is a substantial difference in the measured vapor pressure of CCl_4 in the present work to that calculated from the HSC data base. The values for the vapor pressure of CCl_4 obtained from HSC have involved extrapolation of specific heat data.

That extrapolation leads to a normal boiling point temperature for CCl_4 more than 40°C higher than the accepted value of 77°C. No such discrepancy exists with K.K. Kelley's data.

Table I. Difference in Specimen Temperature in Nitrogen and Nitrogen - Chlorine Plasmas

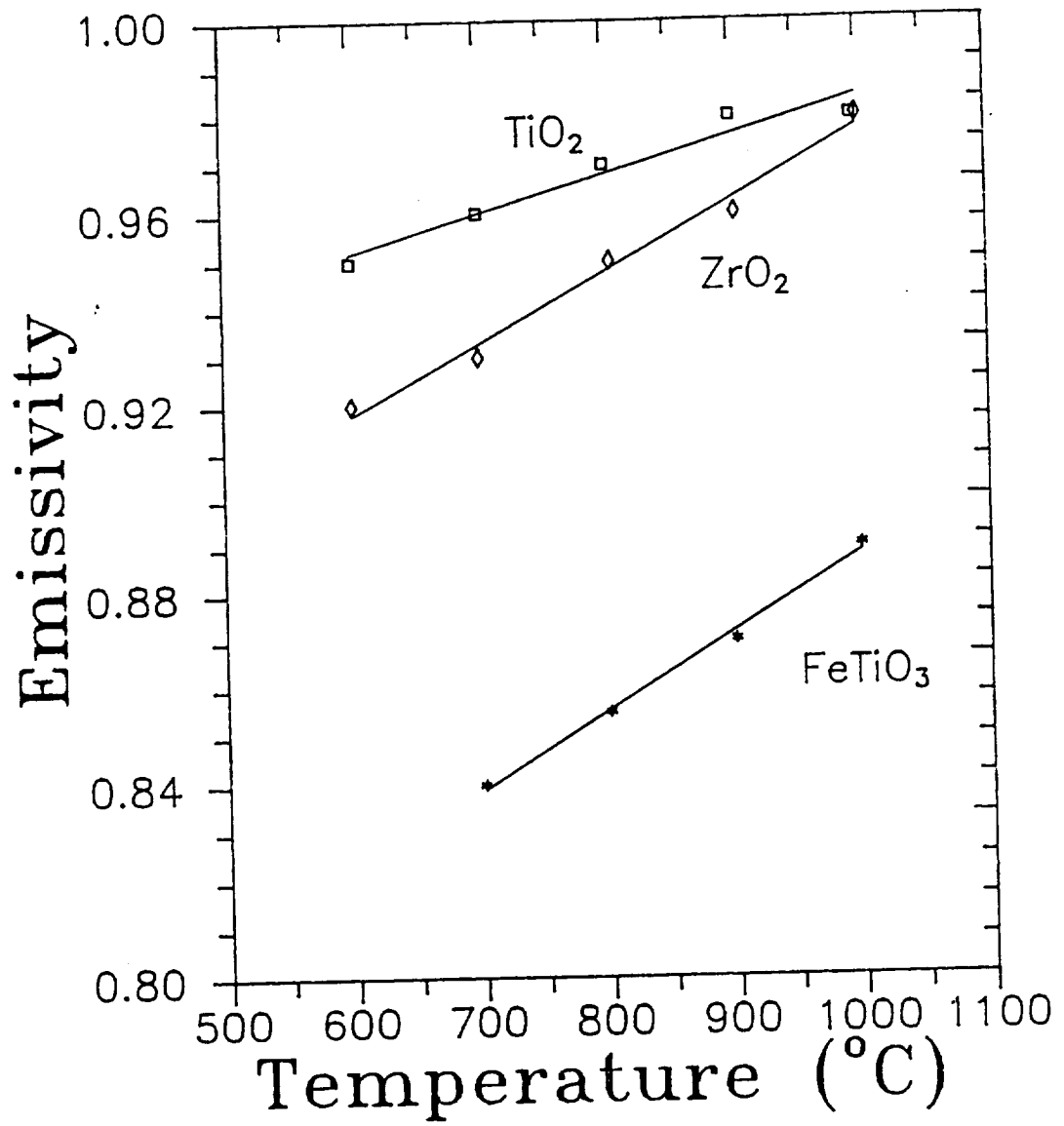| Press. (Torr)	Power (KW)	
	0.5	1.0
	ΔT	ΔT
13	1°C	---
28	---	3°C

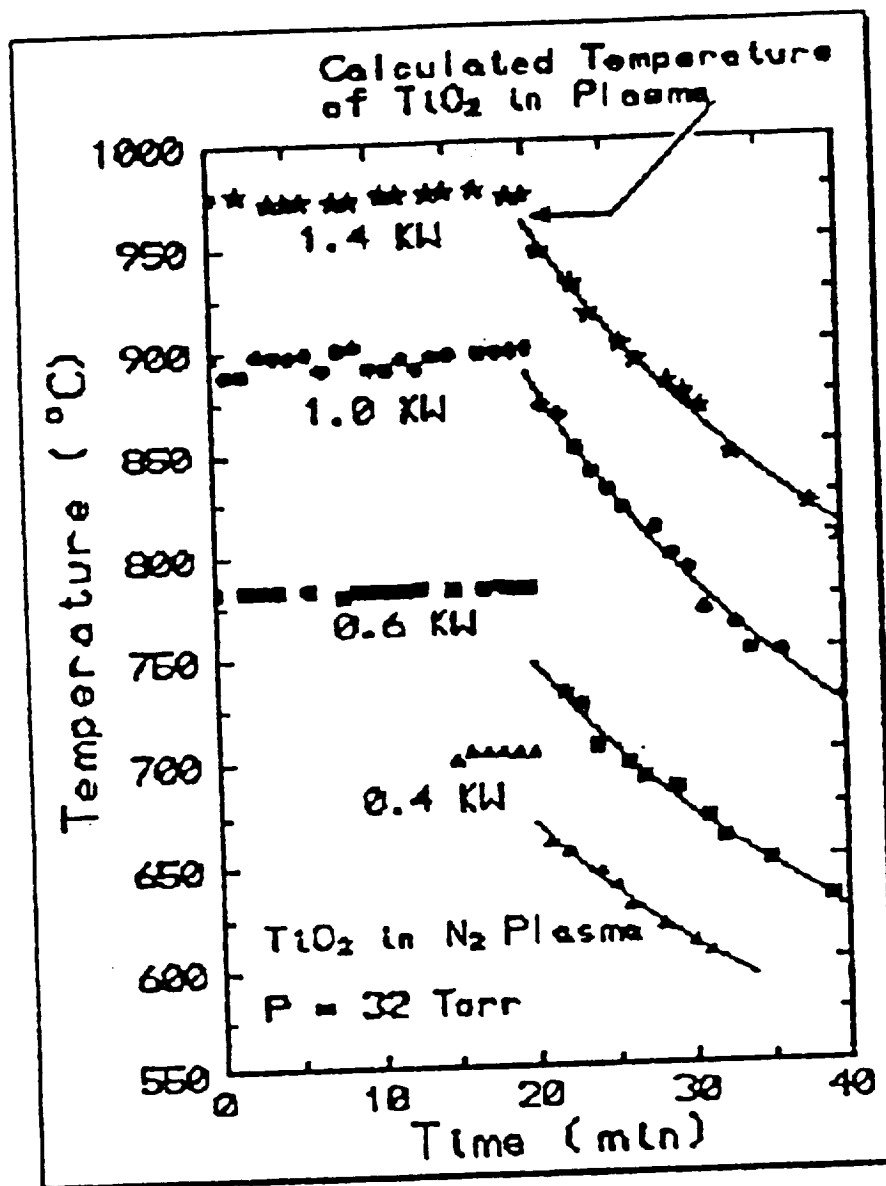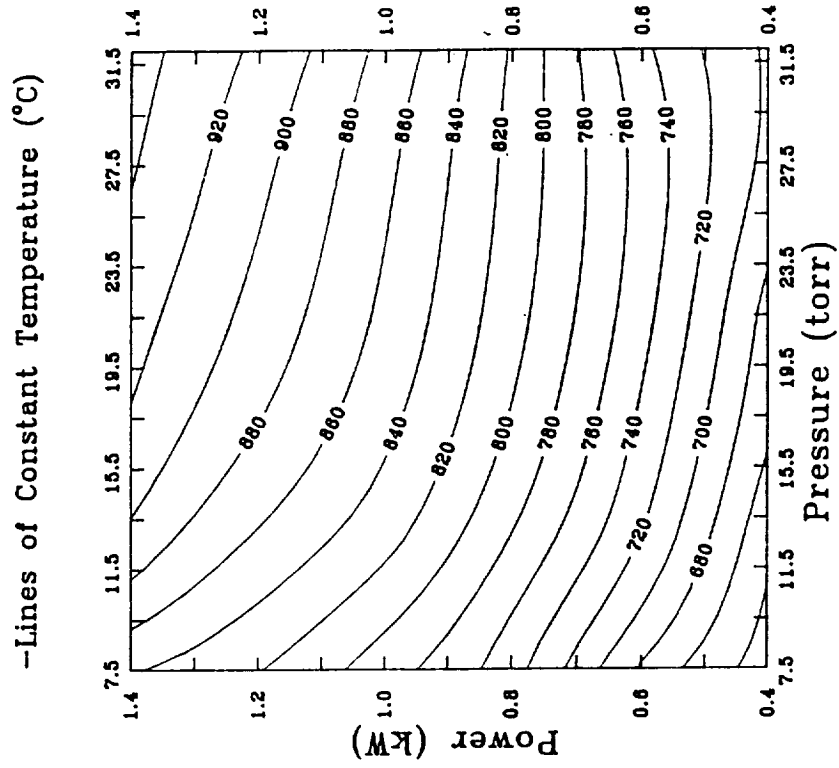Figure 1 -   Measured values of the emissivity for oxides.

Figure 2 -   Actual temperature of specimen determined by monitoring temperature before and after plasma extinguished.

TiO$_2$ in N$_2$ Plasma

TiO$_2$ in N$_2$ Plasma
—Lines of Constant Temperature (°C)

(a)

(b)

Figure 3 -   Temperature of rutile specimen in N$_2$ plasma as a function of power and plasma pressure: (a) three dimensional plot, (b) isothermal contours.
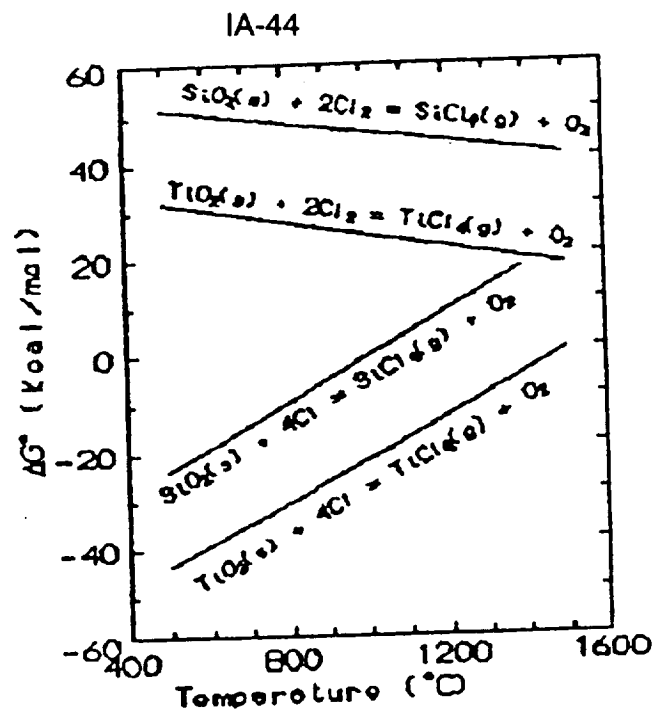
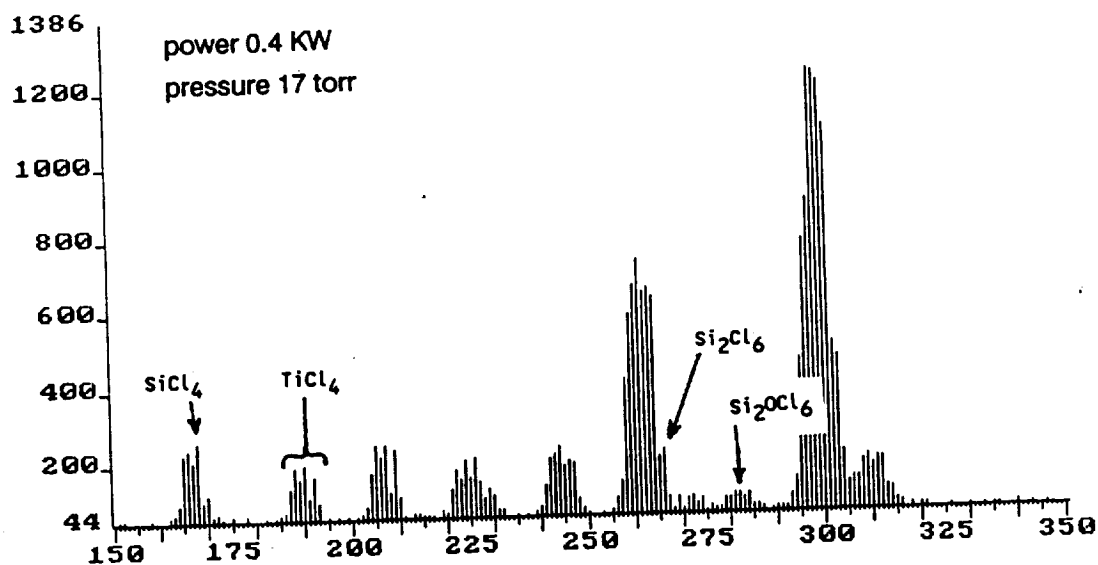Figure 4 -   Standard Gibbs energy data for formation of chlorides.

Figure 5 -   Experimental results from mass spectrometer.

APPARATUS FOR MASS-SPECTROMETER CALIBRATION USING TiCl$_4$

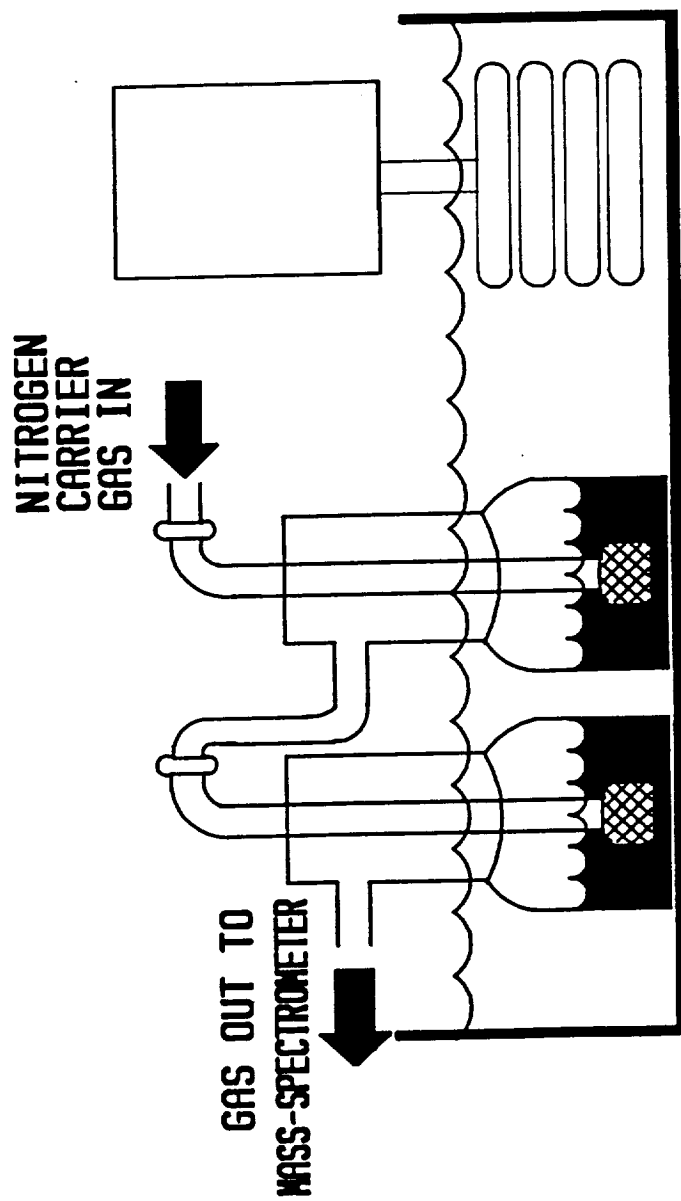NITROGEN CARRIER GAS IN

GAS OUT TO MASS-SPECTROMETER

Figure 6 -   Transportation apparatus, diagram does not show cooling coils, secondary bath or coil for preconditioning nitrogen before entering bubblers.
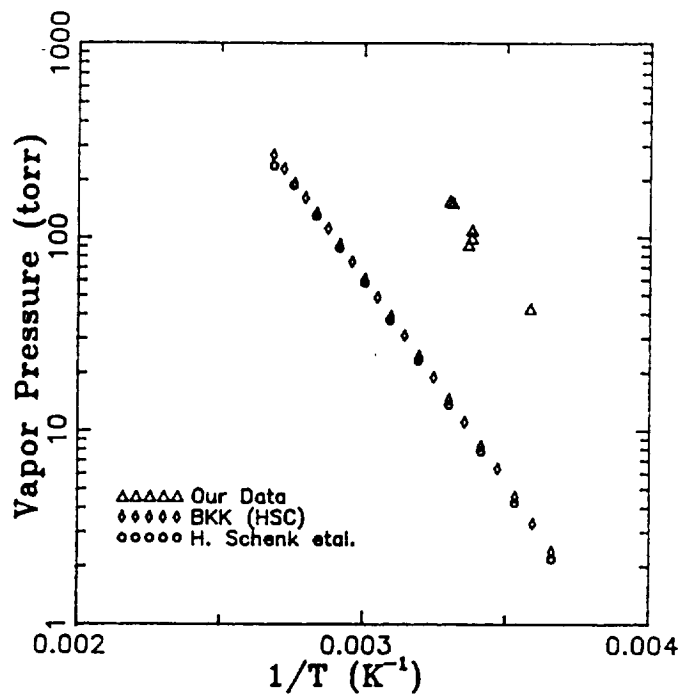
Vapor Pressure of TiCl$_4$

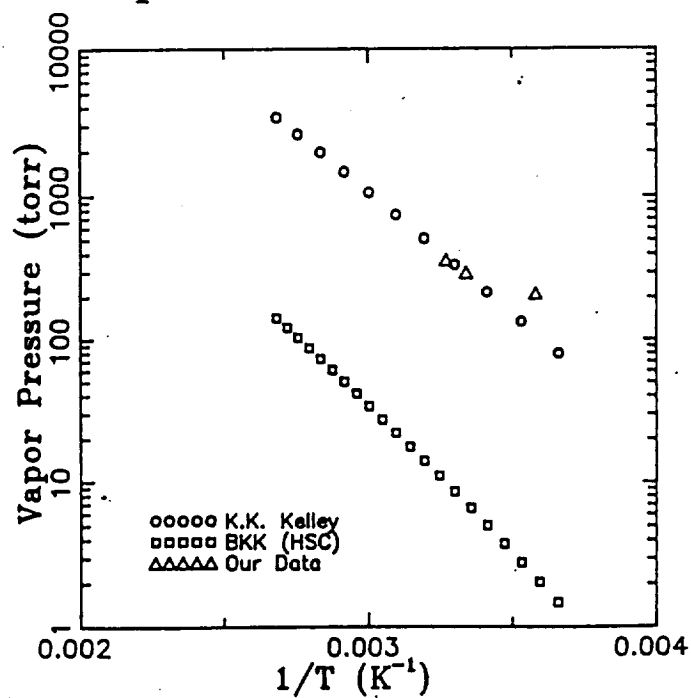Figure 7 -   Comparison of vapor pressure measurements for TiCl$_4$.

Vapor Pressure of CCl$_4$

Figure 8 -   Comparison of vapor pressure measurements for CCl$_4$.