

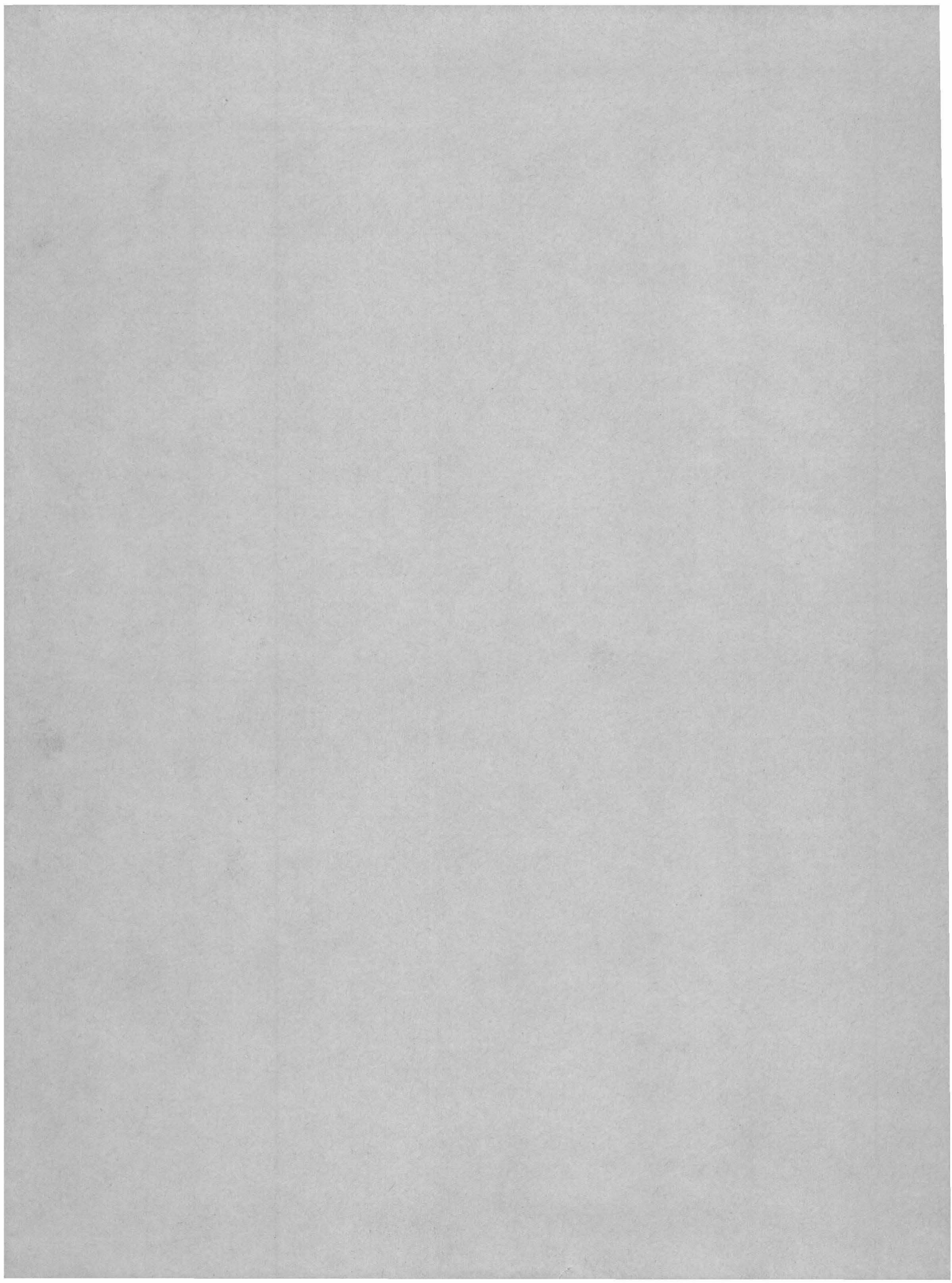
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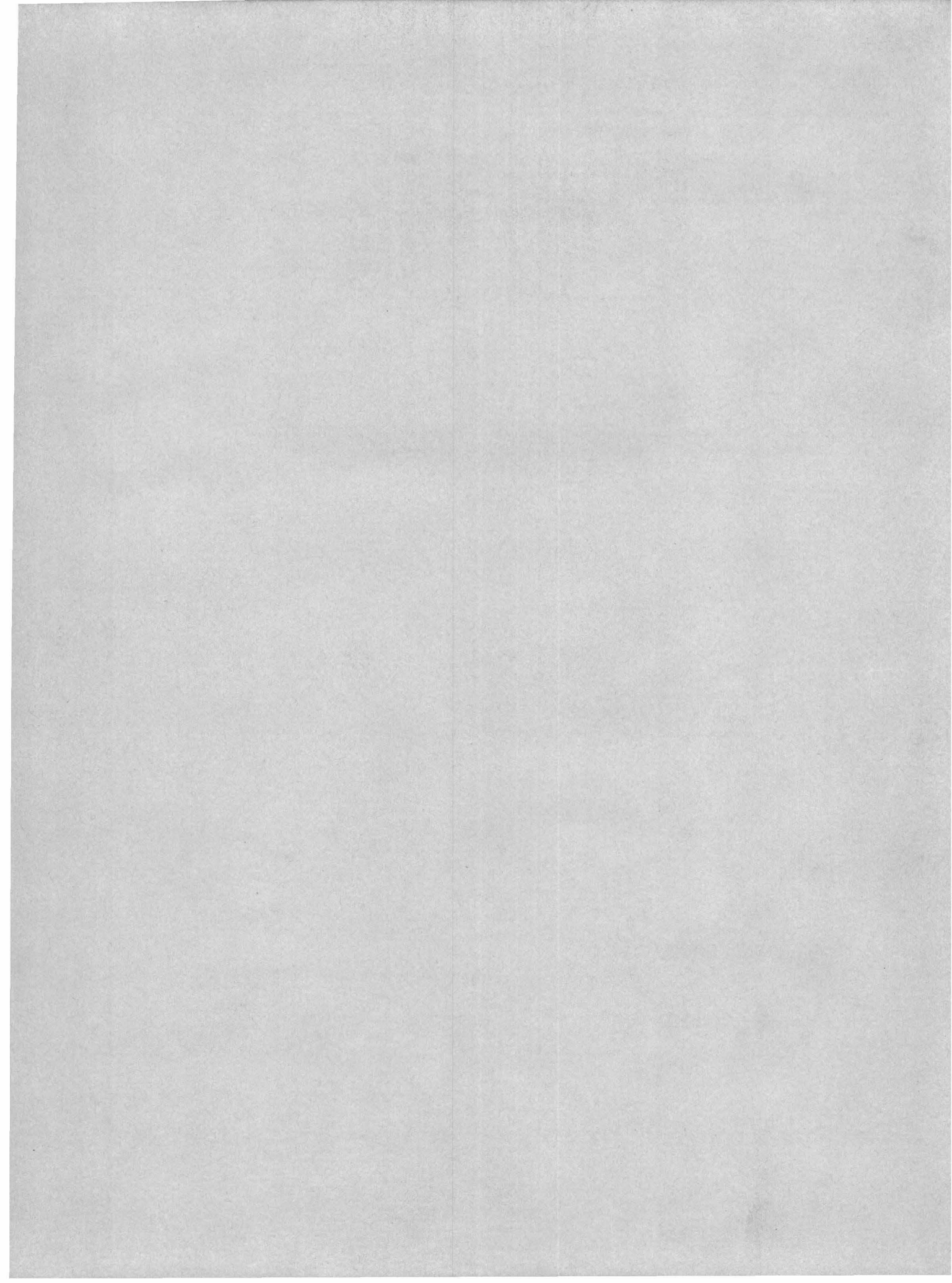
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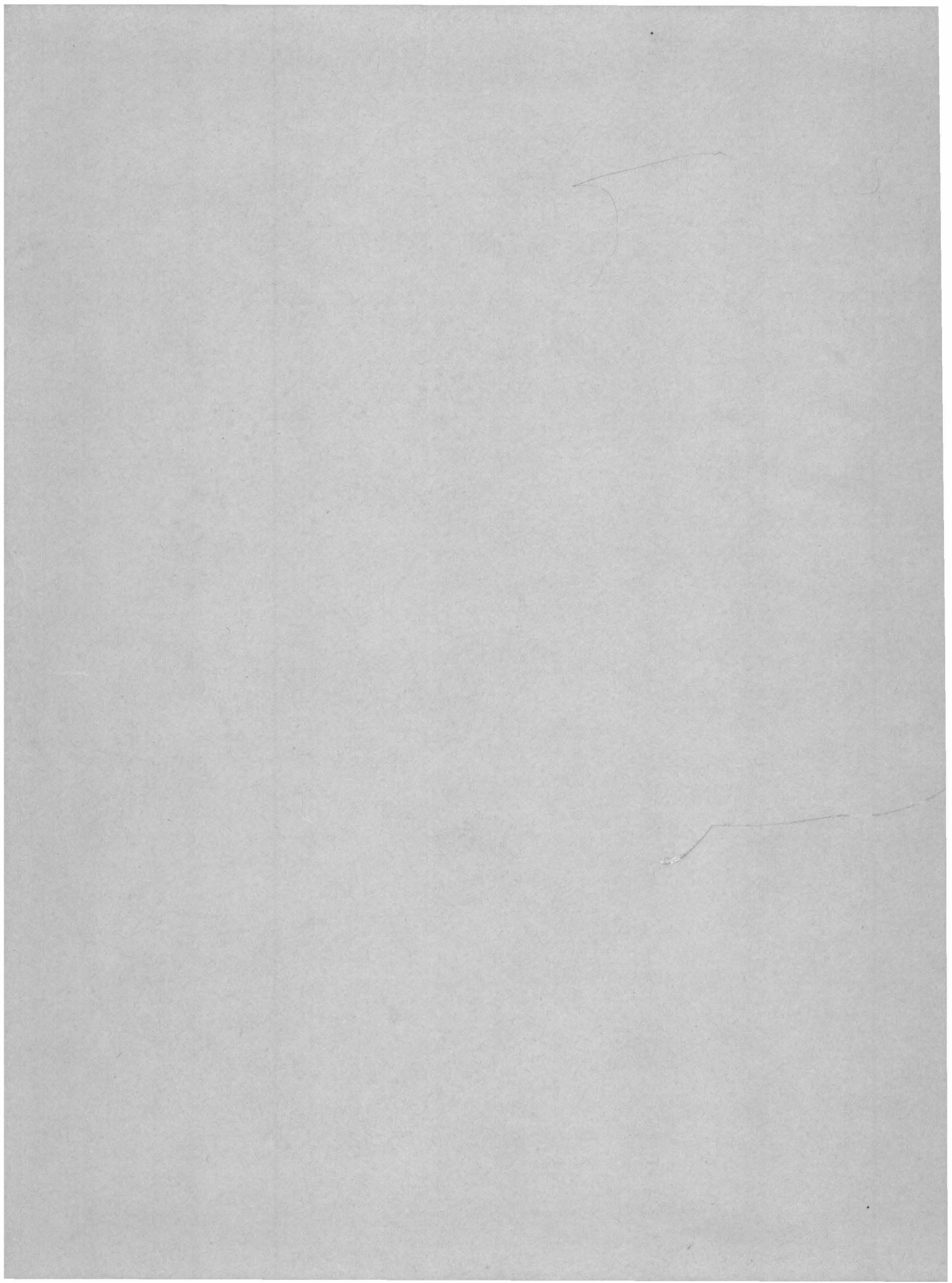


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THE GETTERING PROPERTIES  
OF TITANIUM AND ZIRCONIUM  
AT ELEVATED TEMPERATURES

A THESIS SUBMITTED TO THE GRADUATE SCHOOL OF THE  
UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT  
OF THE REQUIREMENTS FOR THE DEGREE OF  
MASTER OF SCIENCE  
IN CHEMISTRY  
JANUARY 1966

By

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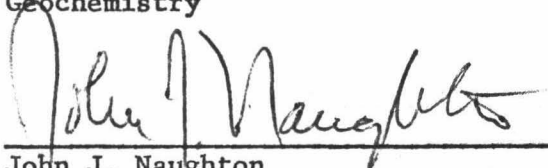
We certify that we have read this thesis and that in our opinion it is satisfactory in scope and quality as a thesis for the degree of Master of Science in Chemistry.

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## I. INTRODUCTION

In the development of vacuum technique it was recognized that the establishment of a vacuum in a sealed-off tube was considerably aided by the use of gas sorbing materials. These materials, which are known as getters, remove gases by means of physico-chemical processes such as adsorption, diffusion, and chemical reaction.<sup>1</sup>

An ideal getter might be defined as a material with an infinite irreversible capacity for absorbing all gases which come in contact with its surface, with this ideal getter ultimately reducing the pressure in an ideal closed system to zero. Needless to say, this getter does not exist; however a number of materials have been shown to be quite useful in this application.

### A. Historical Review and Background

The practice of using getters in sealed-off vacuum bulbs dates back to 1894, when Malignani<sup>3</sup> painted red phosphorus onto the inside of the exhaust tube of a carbon filament lamp. Its use resulted in a considerable decrease in pressure of residual gases.<sup>4</sup> Subsequently other chemicals were introduced for the same purpose, and came to be known as getters or clean-up reagents for gases. Gettering has progressed from this early start to a common industrial method of producing high vacua in a large number of electronic devices.

Metals in many shapes and forms can serve as getters. The two most useful types are vaporized or "flashed" metallic films and bulk metals.<sup>5</sup> Bulk getters are distinguished from "flashed" getters in that the limiting capacity of the bulk

getter usually depends upon the mass of the getter and not on the surface area.<sup>6</sup>

There is currently great interest in the use of the metals titanium (Ti) and zirconium (Zr) as bulk getters and the discussion below is limited to these metals. Although these perform differently, the gas mechanisms of sorption are quite similar. At room temperature the reactions of gases with a bulk getter are usually limited to surface effects. Once adsorption on the surface is complete, the rate of formation of a surface-reaction product may be the process that controls the rate of gettering. In this case the limiting rate is established by the diffusion of an atom or ion through the reaction product. In the high temperature region the rate of gettering depends upon the rate of gas diffusion into the bulk of the metal. Small quantities of gas that are dissolved by the metal reside as atoms or ions at interstitial positions in the metal lattice.<sup>7</sup>

The gas phase reactions of the metals Ti and Zr are interesting both from a scientific and from a technical point of view for the following reasons:<sup>8,9</sup> (a) The metals are rather unreactive at room temperature to both liquid and gas phase corrosion reactions. However, at elevated temperatures, the metals react readily with hydrogen, the halogens, oxygen, nitrogen, carbon, boron, silicon, and sulfur. (b) The reaction products are soluble in the metals. (c) The solubility of the reaction products may greatly change the physical properties of

the metal. In fact, many of the difficulties associated with the reduction, refining, working, and use of these metals may be due to these gas phase reactions. (d) The metals have high melting points (Ti 1680°C, Zr 1860°C) and have many uses in equipment operating at high temperature.

Ti- and Zr-gas reactions have been studied at both elevated and reduced pressures, and at various temperatures by several techniques. These previous methods of study involved specially constructed getter bulbs containing iodide titanium rings with molybdenum and nickel supports. A platinum-platinum 10% rhodium thermocouple was used for temperature measurements with heating of the getter taking place by induced radio frequency current.<sup>10</sup>

Another study on gettering rates of Ti and Zr involved working under constant volume conditions and recording the decrease in pressure with time. Various temperatures were maintained by means of an eddy current induction heater and were measured with a nickel-nickel chromium thermocouple.<sup>11</sup>

Gulbransen and Andrew<sup>12</sup> used a vacuum microbalance in conjunction with a vacuum system fitted with a zircon furnace tube to make their measurements on Ti- and Zr-gas reactions.

Other investigators<sup>13</sup> have employed intermittent gas admission to Zr at various temperatures, and a capillary leak<sup>14, 15</sup> method has been reported in which a calibrated capillary flowmeter was used to introduce gas continuously at a very slow rate into a chamber containing the Zr at a preset

temperature. Getter temperature was maintained at high temperatures by high frequency induction and at low temperatures with an electrically heated oven. The pressure measurements in these various systems were taken with a McLeod Gauge or a Bayard-Alpert ionization gauge.

Brennan<sup>16</sup> has used emission microscopy for the study of absorption of drypton on the metals Ti and Zr to calculate the number of surface metal atoms available to sorb the gases in contact with the metal.

#### B. Object of Present Research

The object of this research was to determine the gettering properties of Ti and Zr over a much wider range of temperatures and at much lower pressures than previously was used. The workers cited above have, in general, limited the temperature ranges used to those of interest to the producers of commercial vacuum tubes, that is, room temperature to 400-500°C and pressures in the region of  $10^{-5}$  mm Hg or more. In this study measurements were extended to about 1000°C and into the pressure region usually classed as the ultra-high vacuum region, that is,  $10^{-7}$  mm Hg or less.

Optimum getter temperature for the removal of residual gases was considered to be of particular importance as such information can be of great use at the University of Hawaii in the program of potassium-argon age determination by mass spectrometry. In potassium-argon age determinations background or residual gases must be at a minimum so that the gas sample



introduced for study can be more readily and accurately analyzed. During sample introduction the getter should be operating under conditions to give the optimum removal of unwanted gases. At present the "optimum" operating conditions are only empirically selected for the Ti getter.

The gases studied included hydrogen, oxygen, water vapor, nitrogen, carbon monoxide, carbon dioxide, methane, and argon. These gases are commonly found in high-vacuum systems and are known collectively as the residual gases. To assure a high vacuum it is essential that these gases be removed as completely and efficiently as possible. Gettering provides a means for this residual removal.

#### C. Method of This Research

To make the measurements of the partial pressures in the ultra-high-vacuum region,  $10^{-7}$  mm Hg or less, a detection system known as an omegatron was used (see Figure 1). When used in conjunction with a vibrating reed electrometer, a frequency oscillator, and a strip chart recorder, the omegatron detects the partial pressure of the gases present in the vacuum system (see Figure 2). From these measurements the gas-metal reactions with the metal (Ti or Zr) are deduced at various temperatures.

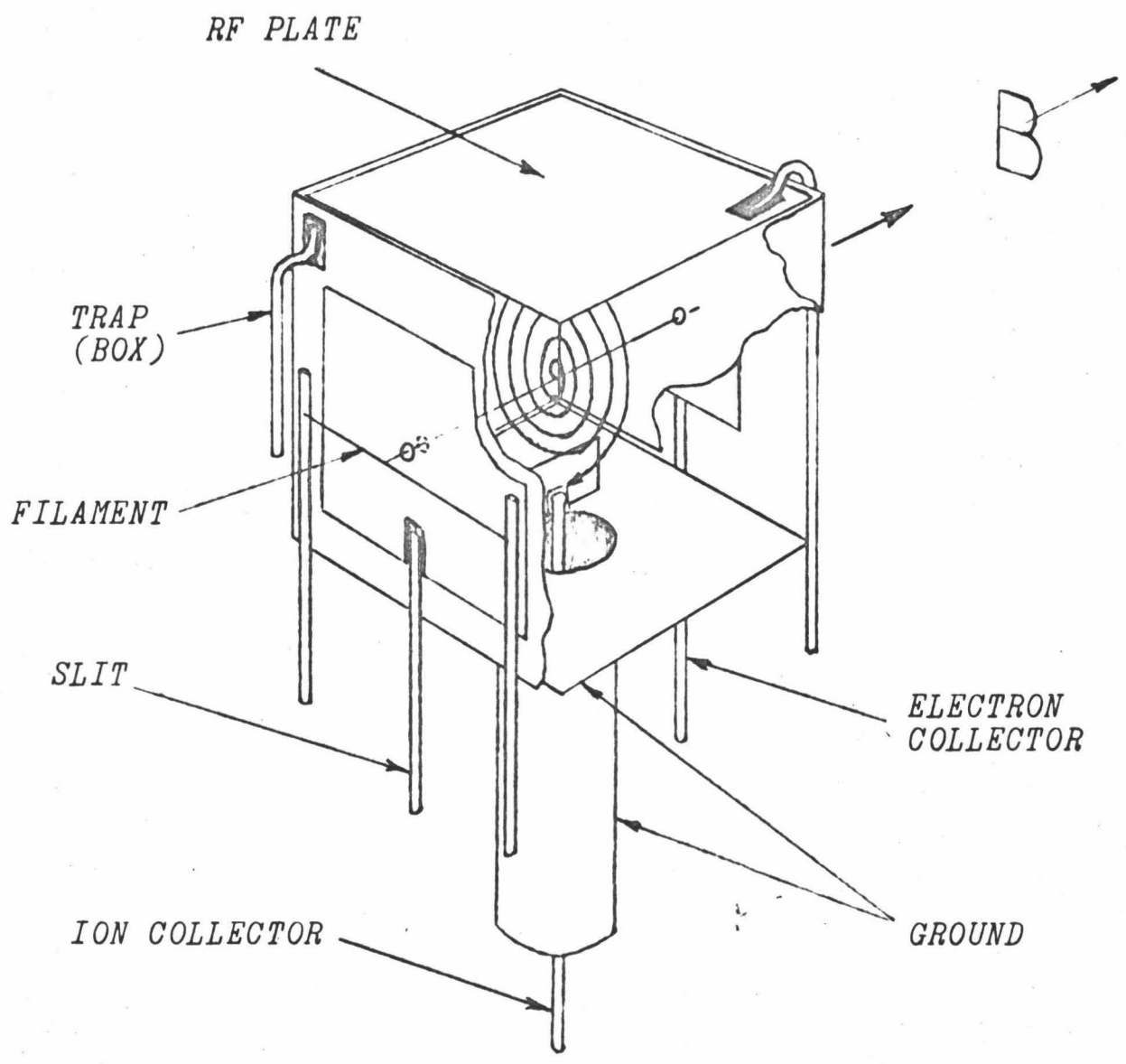
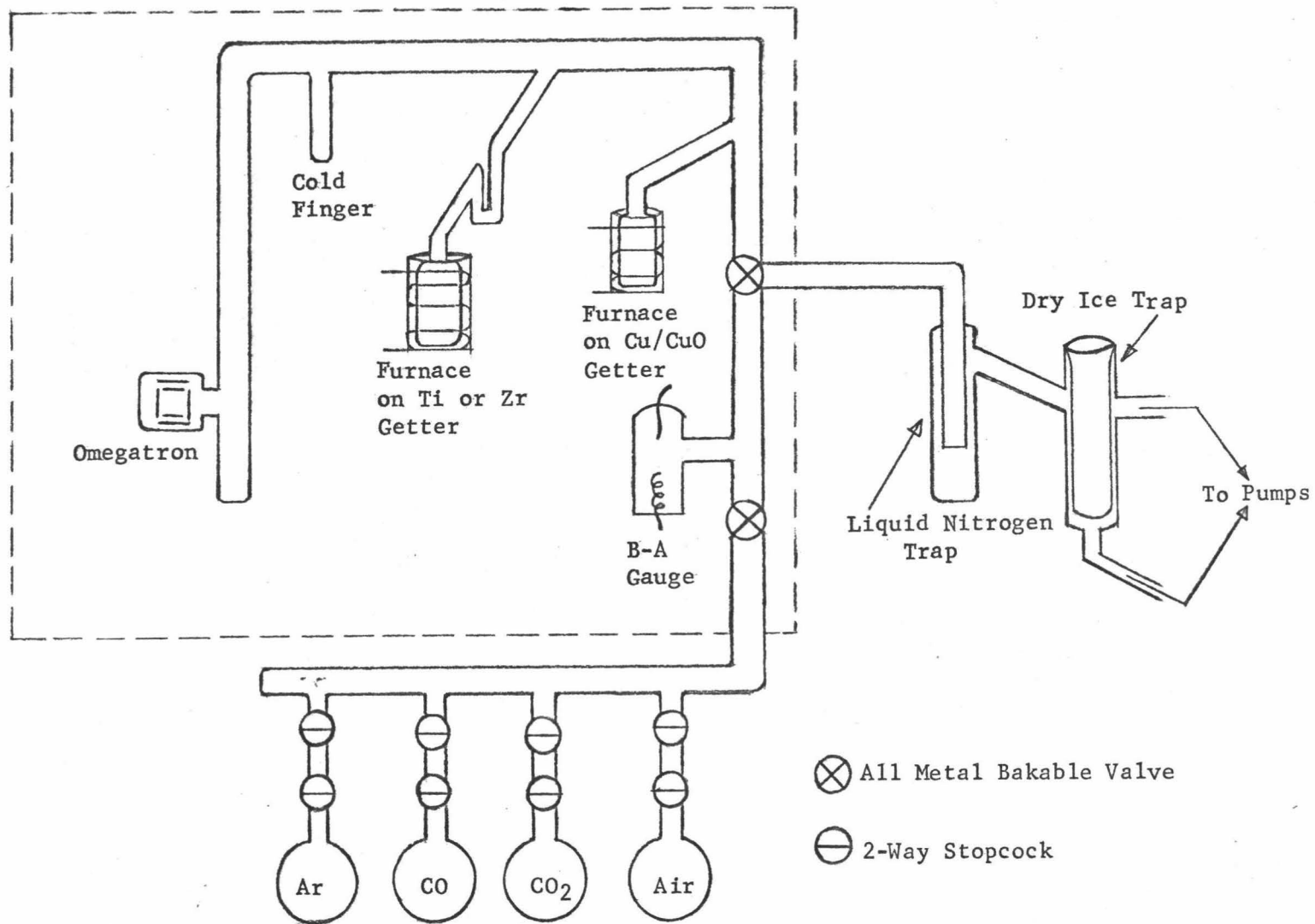


FIGURE 1 - Omegatron

FIGURE 2 - Schematic Diagram of the Ultra-High Vacuum System



## II. EXPERIMENTAL

### A. Description of Apparatus

To study the gettering effects of titanium and zirconium an ultra-high-vacuum system was constructed as shown schematically in Figure 2. While the construction followed the general form as given by Alpert,<sup>17</sup> modifications were made and the essential changes are explained here. The system was mounted on a table approximately 3 feet wide x 4 feet long x 3 feet high constructed of Equipto angles. The top was covered with a piece of  $\frac{1}{2}$  inch thick transite.

The main parts of the high-vacuum system were constructed of Pyrex glass tubing which was supported within a frame constructed of  $\frac{1}{2}$  round, type 302 stainless steel rods. The portion to be baked, shown in Figure 2 within the dashed box, was constructed on top of the table while the remainder of the system was built under or to the side of the table. The oven to fit the top section of the system was constructed in two sections. A top 21" x 28" and three sides, two of which were 15" x 20" and the other 15" x 28", were fabricated of 1" Maranite sheet lined with aluminum foil. The three sides were held together by 3" long bolts with the top resting in place. General Electric 9", 500 watt quartz infrared lamps were attached to the top and to two sides of the oven. No lamp was placed on the third side which faced the omegatron tube. The three heater lamps were wired in parallel and controlled with a 20 ampere Variac. With 10 amperes passing through the lamps

the temperature inside the oven was raised to 250°C in three hours. The fourth side of the oven was a removable bakeout wall and was a sheet of unlined Maranite 21" x 28" x 1".

The valves shown within the dotted line section in Figure 2 are all metal, bakeable, ultra-high-vacuum valves (Granville-Phillips Type C). One of the sections, marked "getter", was made from quartz tubing 20 mm in diameter, closed on one end and connected through a quartz-to-Pyrex graded seal to the remainder of the system. One tube contained 20 grams of 20 mesh copper/copper oxide which had been carefully cleaned and solvent degreased before being added to the tube.

The other getter section was assembled in a similar manner except that 12 grams of -8 + 34 mesh titanium sponge or 12 grams of -10 + 65 mesh zirconium sponge were placed in an inner 30 mm quartz crucible which was then put inside of a 35 mm quartz tube and connected through a quartz-to-Pyrex graded seal to the remainder of the system.

Each getter tube was fitted with a wire wound resistance furnace. The copper/copper oxide getter was degassed at a temperature of 450°C for 24 hours and then operated at 400°C. The titanium and/or zirconium getter was heated to approximately 1050°C for one hour and then cooled to room temperature before each gas to be studied was admitted to the vacuum system.

The sample section was made up of four Pyrex gas bulbs, one of which contained air, and the other three CO, CO<sub>2</sub>, and

Ar, all of mass spectroscopic purity, obtained from the Airco Division of The Matheson Company.

The "working" part of the system consisted of the detector, an omegatron tube in conjunction with a 4000 gauss permanent magnet (Vacunetics OM-101), a Cary 31 vibrating reed electrometer, a Vacunetics OPS-101 power supply, a Hewlett Packard test oscillator model 650A, and a 10 ma Varian G-10 graphic recorder with a chart speed of 11/16" per minute.

The omegatron<sup>18-27</sup> is a well known type of mass analyzer which operates as a miniature cyclotron with crossed electric and magnetic fields and an ionizing electron beam. It has been used successfully by several workers for the measurement of partial pressures.<sup>28-34</sup> Gas molecules ionized by the electron beam follow a spiral path in a plane which is perpendicular to the magnetic field. A radio frequency (RF) field applied perpendicular to the magnetic field is parallel to the plane in which the ionized molecules are moving. The alternating electric RF field accelerates the ion over a portion of its spiral path and retards it over the other portion unless the frequency of the applied RF field is exactly the same as the resonant frequency of the ion of interest. In this case, the ion gains energy over its entire path and spirals outward. An ion collector at the bottom of the electrode box collects these ions and the DC current generated is amplified and measured with a vibrating reed electrometer.

The magnetic field collimates the electron beam and also causes the ions to move in a spiral path. A trapping voltage on the outer electrode structure (box) prevents loss of ions in the axial direction. Qualitative information about the ion species collected is obtained from the frequency at which the ion current appears, while quantitative information is obtained from the size of the ion current generated. The relation between the mass number of the ion, the radio frequency, and the magnetic field strength is given by:<sup>35</sup>

$$f_{Kc} = 1.525 \frac{Bn}{M}$$

where  $f_{Kc}$  = frequency in kilocycles  
 $B$  = magnetic field strength in gauss  
 $n$  = number of electron charges on the ion  
 and  $M$  = mass of the ion in atomic mass units.

Maxima and minima are observed in the ion current generated as the radio frequency is varied, with each peak corresponding to a particular mass-to-charge ratio.

According to the nature of the experimental situation, it is necessary to tailor the operating conditions to give the best possible compromise between sensitivity and resolution. The magnet position generally is the most critical factor in determining resolution. The theoretical resolution is given by the formula:<sup>36</sup>

$$R = \frac{M}{\Delta M} = \frac{DB^2 e}{E_0 M}$$

where

R = theoretical resolution

M = mass of the ion in atomic mass units

$\Delta M$  = width of the peak at half height in a.m.u.

D = distance from the electron beam to the ion collector in cm

B = magnetic field strength in gauss

e = charge of the ion in esu

and  $E_0$  = amplitude of the electric field in volts per cm.

One measure of sensitivity is the ratio of the peak height to pressure, measured on a separate ion gauge (Figure 2); the other is the ratio of the ion current per mm Hg to the electron beam current.<sup>37</sup>

Two omegatrons were used during the course of this experiment. The first was a Vacunetics OT-101 the filament of which burned out after approximately 200 hours of use, and the second, a Sylvania SY-1301, was used to the completion of the research.

Both omegatrons<sup>38,39</sup> were very similar in construction and consisted of materials capable of withstanding a 400°C bakeout. The internal parts displayed in Figure 1 were made of molybdenum with the exception of the stainless steel ion collector shield, the platinum ion collector, tungsten filament and leads, and the tungsten header leads. The envelope was composed of Corning 7720 Nonex glass.



The trapping voltage cage (box) was a 2 cm square box with holes in opposing sides to permit passage of the ionizing electron beam. The beam focusing electrode and the electron collector electrode were both 0.005" molybdenum sheets, 12 mm square. The beam focusing electrode (slit) also had a 0.025" aperture in the center to permit passage of the electron beam. Both of these electrodes were positioned 1 mm from the trapping voltage cage.

Positioned 1 mm in front of the focusing electrode (slit) was the tungsten filament emitter which is 0.0035" tungsten wire 12 mm in length. This wire was positioned to center on the holes in the trapping voltage cage and was pretensioned to eliminate sag during operation. The ion collector shield was welded to the RF ground electrode shown at the bottom of the box. An opening in the RF ground electrode permitted passage of the electrically isolated ion collector lead. Platinum sandwich welds, which reduce brittleness and improve strength, were used on the difficult moly-moly or moly-tungsten junctions. The omegatron header was the standard 8-Pin T-9 design with the ion collector lead positioned in the center of the pin circle and forming the ninth pin. In the Sylvania omegatron the eight outer pins were 0.060" O.D. tungsten and in the Vacunetics omegatron these pins were 0.050" O.D. tungsten. The center pin was 0.040" and 0.060" O.D. tungsten in the Sylvania and Vacunetics models respectively. All connections were made by individual spring clips adjusted to fit the omegatron leads.

The mount was sealed into the envelope such that the tubulation was at right angles to the electron beam. This permitted passage of the tubulation between the pole face of the magnet.

The unit marked "gauge in Figure 2 was a Veeco RG-75P (Vacuum Electronics Company) Bayard-Alpert ionization gauge. This gauge was controlled by a Veeco Ionization gauge control which supplied the operating voltages to the ionization gauge and also contained an electrometer for reading the plate current on a microammeter. This meter was calibrated to read the pressure directly as mm of Hg (equivalent nitrogen pressure).

The section under the table consisted of a mechanical pump (Welch 1405) joined to a three-stage mercury diffusion pump (H. S. Martin Company). Attached to the diffusion pump was a dry ice trap which was in turn connected to a liquid nitrogen trap which was in turn joined to the rest of the system above the table.

#### B. Procedure

The following procedure was used whenever the vacuum system was started after a shut-down, when a new gas sample was added or whenever it became necessary to bake the entire system. The vacuum system was sealed and the mechanical pump was started. After fifteen to twenty minutes the mercury diffusion pump was started and the dry ice and liquid nitrogen traps were filled.

Then the valve bodies were removed from the metal valves, bakeout clamps were installed, the oven was placed over the system and the whole system was baked at 350-400°C for 8 to 12 hours. The oven was then allowed to cool to approximately 100°C and then was reheated to 350-400°C for a second period of 8 to 12 hours. During the last three hours of this second baking period the liquid nitrogen level was lowered to cover only the lower 2 to 3 inches of the trap to remove condensed material to a lower part of the trap, hence preventing as much as possible re-evaporation when the liquid nitrogen level varied.

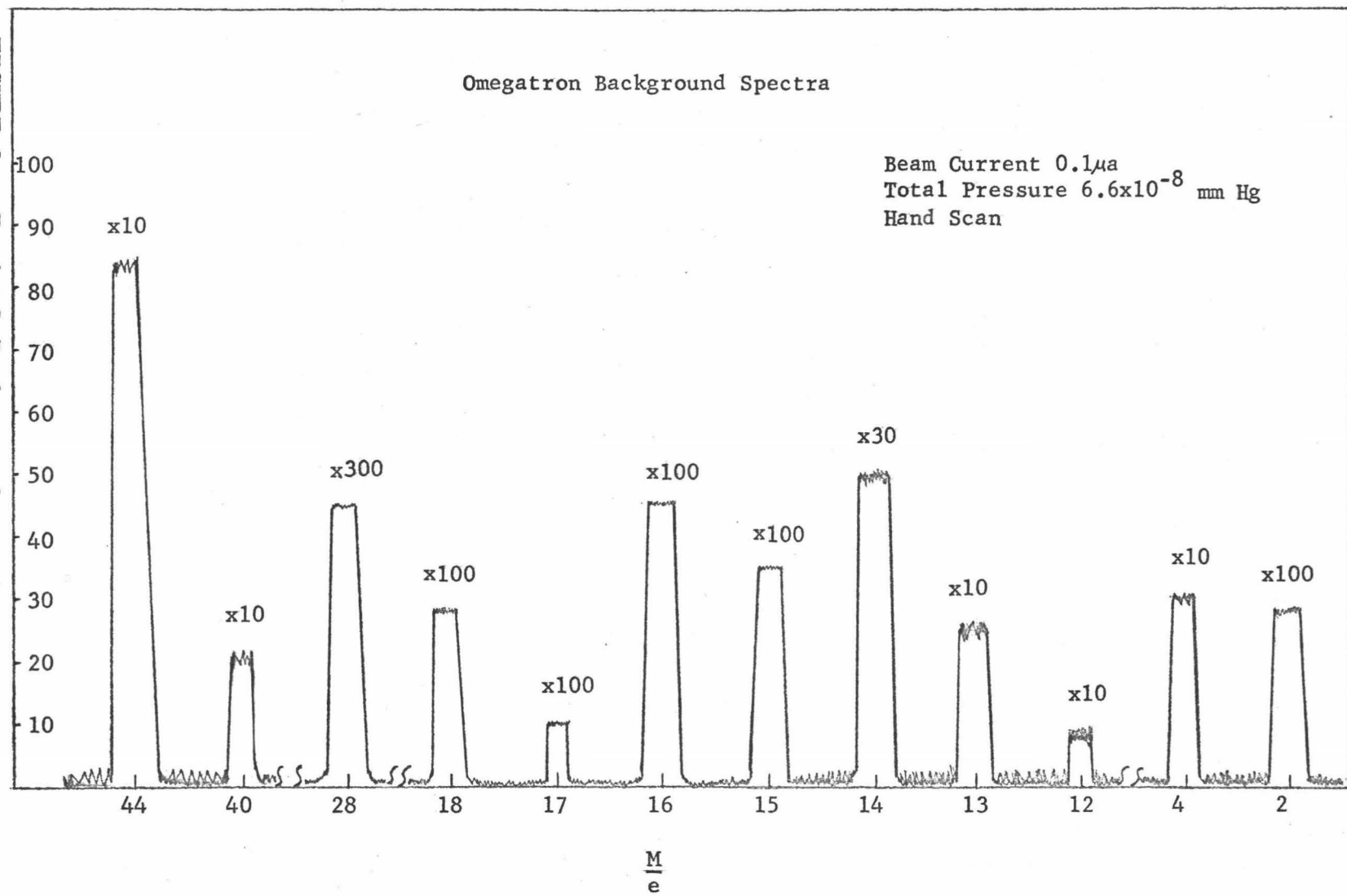
At the completion of the baking period the trap was covered with liquid nitrogen and the oven was turned off but allowed to cool in place until the temperature had dropped to approximately 100°C. The oven was then removed and the metal valve bodies were replaced.

Leads were affixed to the furnaces covering the titanium or zirconium and copper/copper oxide getters. The copper/copper oxide getter was degassed at a temperature of 450°C for 24 hours and was operated at 400°C continually when used. The titanium or zirconium getter was heated at approximately 1050°C for one hour and then was cooled to room temperature before each gas to be studied was admitted into the vacuum system. The ion gauge was turned on and after a few minutes of pumping, the pressure in the system was commonly around  $10^{-8}$  mm Hg.

Table 1  
Operating Values of Omegatrons

	Vacunetics OT 101	Sylvania SY 1301
Filament Circuit		
Heater	1.35 V ac	1.2 V ac
Bias	70 V dc	70 V dc
Beam Current	1 $\mu$ A	0.1 $\mu$ A
Collector	20 V dc	22.5 V dc
Trap	1 V dc	1 V dc
RF Bias	1/8 Revolution Clockwise	1/8 Rev Cw
Output Voltage	1.7 V dc	1.7 V dc

FIGURE 3 - Typical Background Spectra



The metal valves were closed and a background spectrum of the gases in the system was then recorded with the omegatron. For operating values of the component variables of the omegatron see Table 1. The spectrum obtained as in Figure 3 is a plot of ion mass (actually  $M/e$ ) versus concentration (or partial pressure) of each species present in the system.

After the background and its total pressure had been recorded the following method was used to admit the gas to be studied to the system. The stopcock nearest the bulb of gas was opened for a few seconds and closed. The second stopcock was then opened. After opening the second stopcock for a few seconds the metal valve between the gas sample bulbs and the vacuum system was opened for several seconds and closed. The metal valve leading to the pumps was opened and allowed to pump to a vacuum of  $10^{-4}$  mm Hg. The valve to the pump was then closed and the sample gas was again admitted to the system as previously described. After again pumping to a vacuum of  $10^{-4}$  mm and then closing the system to the pumps a third sample of the gas was added to the system and pumped to a pressure of  $10^{-6}$  mm Hg. The metal valve was then closed, the omegatron was turned on and a spectra was obtained with the Ti or Zr getter at room temperature and the Cu/CuO held constant at  $400^{\circ}\text{C}$  for one set of runs or at room temperature for a second set of runs. The omegatron was then turned off, a pressure reading was taken, and the temperature of the getter was raised to  $200^{\circ}\text{C}$  for twenty minutes. A pressure reading was

taken and if it was below  $10^{-4}$  mm Hg ( $10^{-4}$  mm Hg is the maximum pressure permitted for safe operation of the omegatron) the omegatron was again started and a spectrum run.

The temperature of the getter was increased to  $300^{\circ}\text{C}$  for twenty minutes and the pressure was then taken. If the pressure was below  $10^{-4}$  mm Hg the omegatron was turned on and a spectrum taken. In a like manner, a succession of such operations was performed at getter temperatures of  $400$ ,  $500$ ,  $600^{\circ}\text{C}$ , etc. until a final temperature of  $1000^{\circ}\text{C}$  was reached.

The getter temperature was then reduced to  $900$ ,  $800$ ,  $700^{\circ}\text{C}$ , etc. with a pressure check made at each temperature until room temperature was reached with a spectrum run at each of the respective temperatures. If the pressure exceeded  $10^{-4}$  mm Hg at any time, it was reduced to this level or lower before the omegatron was again operated.

After each run was completed the Ti or Zr getter was degassed for one hour at  $1050^{\circ}\text{C}$  and the Cu/CuO getter was degassed for one hour at  $450^{\circ}\text{C}$  with the metal valve leading to the pumps open. The getters were then allowed to cool to room temperature. A pressure reading was taken after a few minutes of pumping by the ion gauge. If the pressure was  $10^{-7}$  mm Hg or less a new gas sample was introduced by the method previously described and the whole process of increasing getter temperature and obtaining spectra was again repeated. If a pressure greater than the  $10^{-7}$  mm Hg range was obtained after

outgassing of the getters the vacuum system was put through a bakeout cycle.

Respective spectra were made for each gas sample with Ti or Zr, with or without Cu/CuO, at rising temperatures of 20, 200, 400, 600, 800, 900, and 1000°C and falling temperatures of 600, 300, and 100°C.

In the runs made with the Cu/CuO getter set at a constant 400°C a cold finger was used and was packed with dry ice or covered with liquid nitrogen contained in a small Dewar flask.

Partial pressure of each particular gas studied was plotted versus the various temperatures of the getters Ti or Zr. Similar plots were also made when the system contained Cu/CuO at 400°C and a cold finger.

### C. Calculations

The resonant frequency of the ion sought may be found from the formula:

$$f_{Kc} = \frac{1.525 Bn}{M}$$

where  $f_{Kc}$  = frequency (Kilocycles)  
 $B$  = magnetic field strength (gauss) at 4000  
 $n$  = number of charges on the ion  
 and  $M$  = mass of the ion (a.m.u.)

The gas ions of primary interest are CO<sub>2</sub>, Ar, O<sub>2</sub>, N<sub>2</sub>, CO, water vapor, CH<sub>4</sub>, and H<sub>2</sub>.

$$\text{for CO}_2^+ \quad f_{Kc} = \frac{(1.525)(4000)(1)}{44} = 139 \text{ Kc}$$



$$\text{for Ar}^+ \quad f_{\text{Kc}} = \frac{(1.525)(4000)(1)}{40} = 153 \text{ Kc}$$

$$\text{for O}_2^+ \quad f_{\text{Kc}} = \frac{(1.525)(4000)(1)}{32} = 191 \text{ Kc}$$

$$\begin{aligned} \text{for N}_2^+ \text{ and} \\ \text{CO}^+ \quad f_{\text{Kc}} = \frac{(1.525)(4000)(1)}{28} = 218 \text{ Kc} \end{aligned}$$

$$\text{for H}_2\text{O}^+ \quad f_{\text{Kc}} = 339 \text{ Kc}$$

$$\text{for CH}_4^+ \quad f_{\text{Kc}} = 382 \text{ Kc}$$

$$\text{and for H}_2^+ \quad f_{\text{Kc}} = 3026 \text{ Kc}$$

In practice, however, the experimental resonant frequencies are found to be those listed in Table 2. From the experimental frequencies the actual field strength of the magnet can be calculated.

$$\begin{aligned} B &= \frac{Mf_{\text{Kc}}}{1.525n} \\ &= \frac{(44)(143)}{(1.525)(1)} = 4130 \text{ gauss} \\ &= \frac{(40)(158)}{(1.525)(1)} = 4140 \text{ gauss} \\ &= \frac{(28)(225)}{(1.525)(1)} = 4130 \text{ gauss} \\ &= \frac{(18)(350)}{(1.525)(1)} = 4130 \text{ gauss} \\ &= \frac{(16)(392)}{(1.525)(1)} = 4120 \text{ gauss} \end{aligned}$$

Hence the actual field strength of the magnet was approximately 4130 gauss instead of the stated value of 4000.

Table 2  
Resonant Frequencies

Gas Ion	Mass(a.m.u.)	Calculated Frequency(Kc)	Experimental Frequency(Kc)
$\text{CO}_2^+$	44	139	143
$\text{Ar}^+$	40	153	158
$\text{O}_2^+$	32	191	197*
$\text{N}_2^+$	28	218	225
$\text{CO}^+$	28	218	225
$\text{H}_2\text{O}^+$	18	339	350
$\text{CH}_4^+$	16	382	394
$\text{H}_2^+$	2	3026	3120

Calculated from experimentally determined field  
strength of 4130 gauss

### III. RESULTS AND DISCUSSION

#### A. Omegatron

Although it was not the direct aim of this research to study the omegatron, certain of its characteristics were investigated during the course of the research and were found to be in agreement with the literature.<sup>40</sup>

Of primary interest in the gas analysis were the peaks below mass 50. To obtain a high resolution of these peaks a permanent magnet of approximately 4000 gauss was used. It would have been possible to use a magnet strength as low as 2000 gauss; however resolution would have been greatly reduced. Other desirable parameters which could have been varied were the RF voltage, the trapping voltage, and the RF bias control. RF voltage can be varied between fairly wide limits, but reduction in this voltage also reduces collected ion current. The Sylvania people working with this type of omegatron have found an RF voltage of 1.7 volts to be the most effective for most gases studied. However, for mass 2, hydrogen, they recommend increasing the RF voltage to 3.0 volts and the trapping voltage to 1.9 volts. The result is an increase in sensitivity and a decrease in resolution. In this research, at the resonant frequency of hydrogen, mass 2, an RF voltage of 2.35 volts was used as this was the maximum obtainable output of the oscillator at this particular frequency. This voltage did prove satisfactory for detection of mass 2 ions. For masses 3,

$H_3^+$ , and 4,  $He^+$ , an output voltage of 3 volts was attainable and proved satisfactory for their detection.

In general, the trapping voltage was set at the recommended 1.0 volt above ground and proved optimum for maximum sensitivity. The RF bias control was used to remove uncollected ions from the ion chamber, but its most pronounced effect was to change the heights of various peaks. The optimum setting for the RF bias changed with different RF voltages. RF bias was found by experimentation to give the best overall sensitivity at 1/8 revolution clockwise.

Recommended beam current for normal operation is 1.0  $\mu a$ . Although greater sensitivity and ionizing potential can be obtained with larger beam currents, stability is seriously affected by space charge effects; thus, 1.0  $\mu a$  has been found to be the practical maximum. For the Vacunetics omegatron tube this value of 1.0  $\mu a$  was used; in the operation of the Sylvania tube the beam current used was 0.1  $\mu a$ . Under the reduced beam current of 0.1  $\mu a$ , molecular collisions were decreased; however, a suitable spectrum was still obtained. The peak heights obtained from the Sylvania tube were increased in direct proportion to the decrease in beam current so that the peak heights of both omegatron tubes could be compared at 1.0  $\mu a$ .

It was suggested that the electron collector bias be set at 22.5 volts in order to minimize beam current fluctuations observed at higher voltages.

The Sylvania tube was employed as a replacement for the Vacunetics tube when its filament burned out before the experimental work was completed. The cause of the filament burn out was thought to be due to a sudden burst in pressure into the  $10^{-4}$  mm Hg range, which is beyond the safe limit of operation for the tube. No apparent difference was noted in the performance of the two tubes.

#### B. Gettering Effects and Reactions

In the determination of the gettering power of Ti and Zr two separate runs were made for each gas: In the first run the Ti or Zr getter alone was used at temperatures ranging from 20-1000°C. The second run utilized not only the Ti or Zr getter but also a cold finger plus the Cu/CuO getter set at a constant temperature of 400°C. From the comparison of these runs it was possible to determine the effect of the cold finger and Cu/CuO getter on each gas tested. Thus it was possible to make a comparison of the gettering effects of Ti and Zr for each of the gases examined as shown below:

##### 1. Carbon dioxide, carbon monoxide, and methane.

In the systems containing the Cu/CuO getter at 400°C an increase in CO<sub>2</sub> was noted along with a decrease in CO. This was most probably due to the following reactions:



Data obtained suggests that it was highly likely that the reaction  $\text{CO} \longrightarrow \text{C} + \frac{1}{2}\text{O}_2$  takes place at a faster

rate than  $\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_2$ . In nearly all systems, the partial pressure of  $\text{CO}_2$  was approximately  $1\frac{1}{2}$  times that of the partial pressure of  $\text{CO}$ . In conjunction with these reactions Ti or Zr metal probably reacted with the products and reactants in the following manner:



Upon study of the methane present in the vacuum system it was found that the content of this gas generally decreased with the increase in temperature. Such an action strongly suggests that  $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$  took place. For the plots of the various systems described above see Figures 4, 5, 6, 7, 10, and 11.

## 2. Water vapor.

The use of the cold finger resulted in a decrease in the amount of water present in the vacuum system.  $\text{Cu}/\text{CuO}$  most probably reacted with hydrogen present in the system

to produce water:  $2\text{CuO} + \text{H}_2 \longrightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O}$ . The water formed was then frozen out by the cold finger. See Figures 8 and 9. Upon inspection of the data for water vapor it was found that the partial pressure of water vapor was greater in the 300-700°C range upon descent from 1000°C than for the range upon ascent to 1000°C. It is postulated that this increase in partial pressure with falling temperature in the 700-300°C range was in part due to the presence of additional hydrogen from the decomposition of methane at 1000°C. This hydrogen in turn was oxidized to water vapor.

At higher temperatures (greater than 600°C) relatively larger amounts of water vapor were found to be present in all systems studied. It is believed that this relative increase in water vapor was due to its desorption from the glass walls of the vacuum system at these elevated temperatures. The gettering effect of Ti or Zr metal results from the oxides and/or hydrides being formed with the metal.



### 3. Hydrogen.

Experimental data obtained showed that the amount of hydrogen present at 600°C on descent from 1000°C was

greater than the amount of hydrogen present at 600°C while increasing to 1000°C. See Figures 12 and 13. Again it is postulated that this increase in partial pressure with falling temperature was in part due to the presence of additional hydrogen from the decomposition of methane. It should be noted that the largest source of hydrogen was most probably due to the decomposition of the Ti or Zr hydride which occurred quite rapidly above 400°C.

When  $H_2^+$  had a partial pressure approaching  $10^{-6}$  mm Hg and greater (approximately 600°C)  $H_3^+$  was also present. This pressure value was multiplied by 1.5 and added to the  $H_2^+$  present when the graphs were made.

$H_3^+$  has been studied by Bajeu and Comsa<sup>41</sup> and is formed in the following manner:  $H_2^+ + H_2 \rightarrow H_3^+ + H$ . The atomic hydrogen (H) produced reacts very rapidly to form molecular hydrogen ( $H_2$ ).

#### 4. Oxygen.

Oxygen is very difficult to detect in a vacuum system possessing any heated filaments as the oxygen can react with the hot filament to form an oxide.<sup>42</sup> In this experiment, two hot filaments were present; one, that of the omegatron, and two, that of the ion gauge. Also adding to the problem of detection, Ti or Zr metal react quite readily with oxygen even at room temperature.<sup>43,44</sup> No detection of  $O_2^+$ , mass-to-charge (M/e) ratio of 32, was observed in this experiment. A peak height at a mass-to-charge ratio



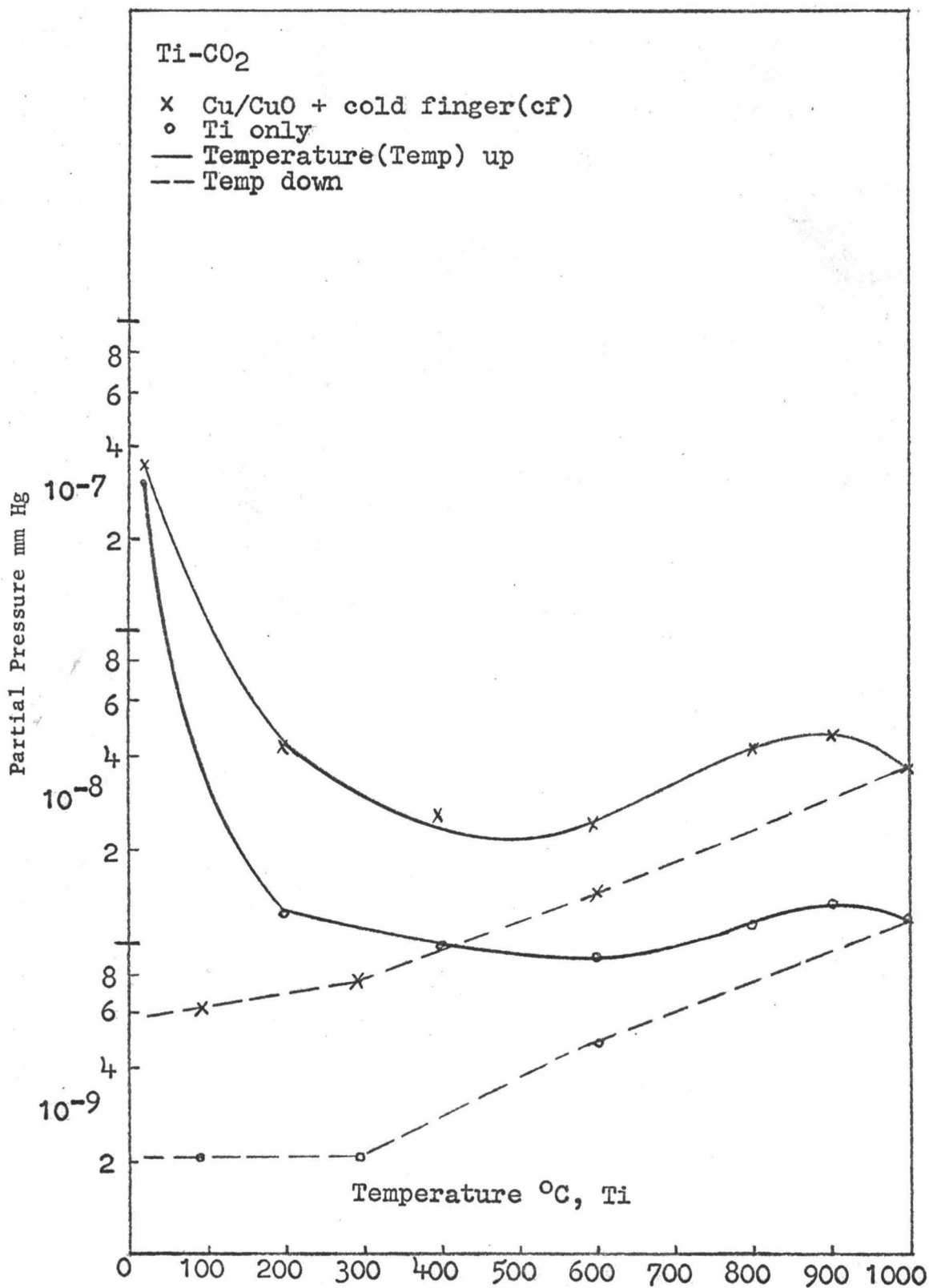


FIGURE 4 - Partial Pressure vs Temperature for Ti-CO<sub>2</sub>

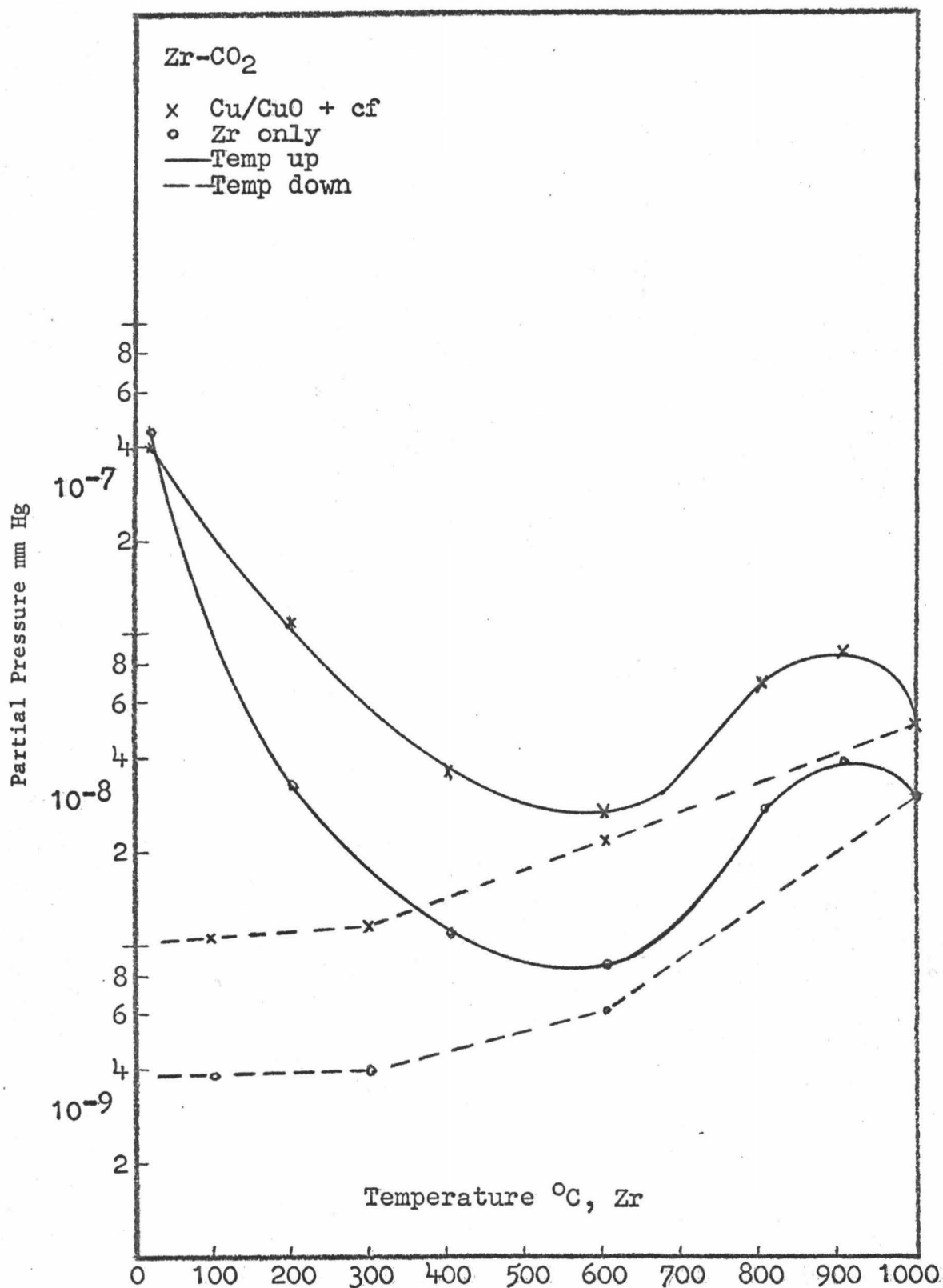


FIGURE 5 - Partial Pressure vs Temperature for Zr-CO<sub>2</sub>

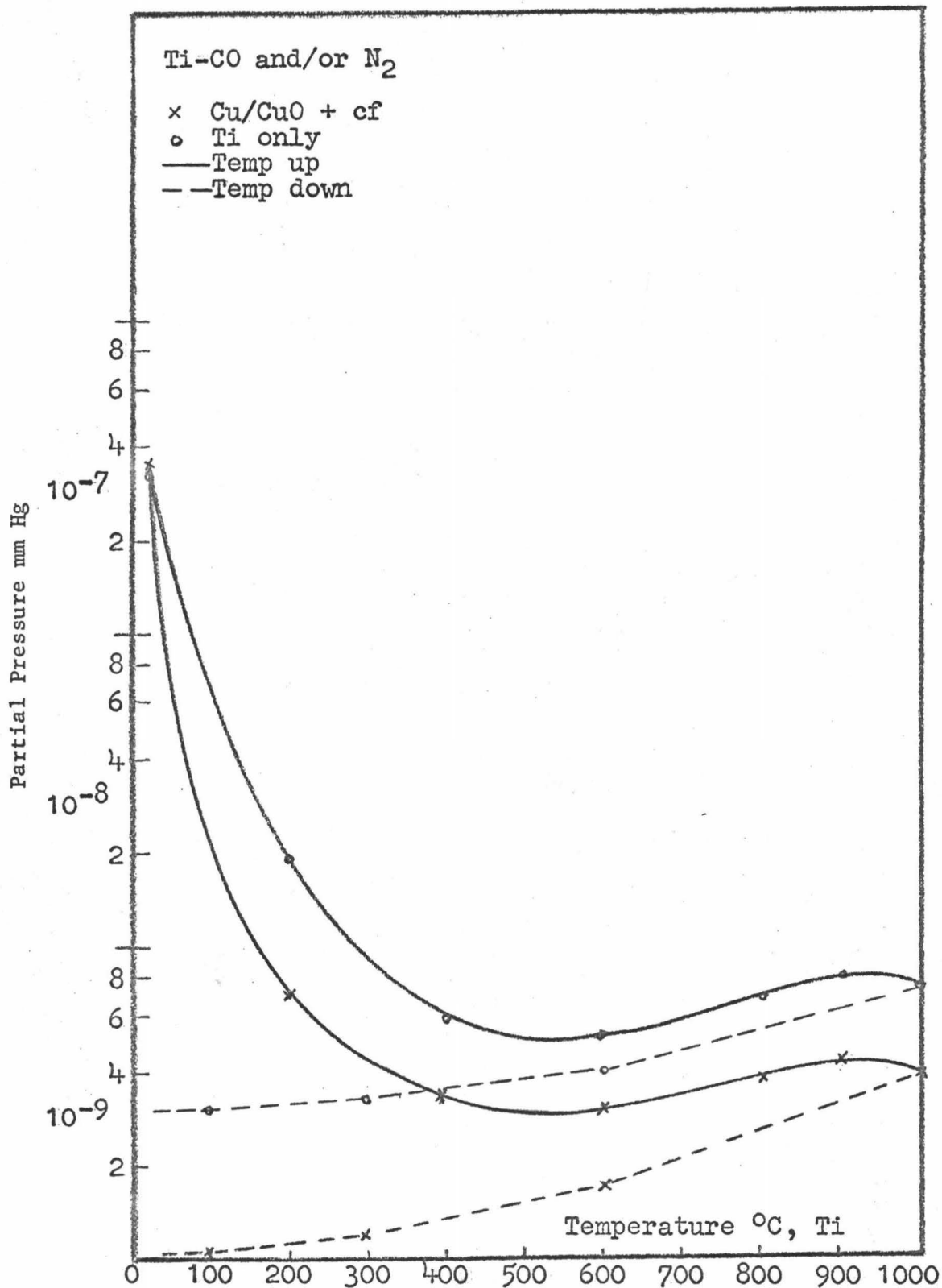


FIGURE 6 - Partial Pressure vs Temperature for Ti-CO &/or N<sub>2</sub>

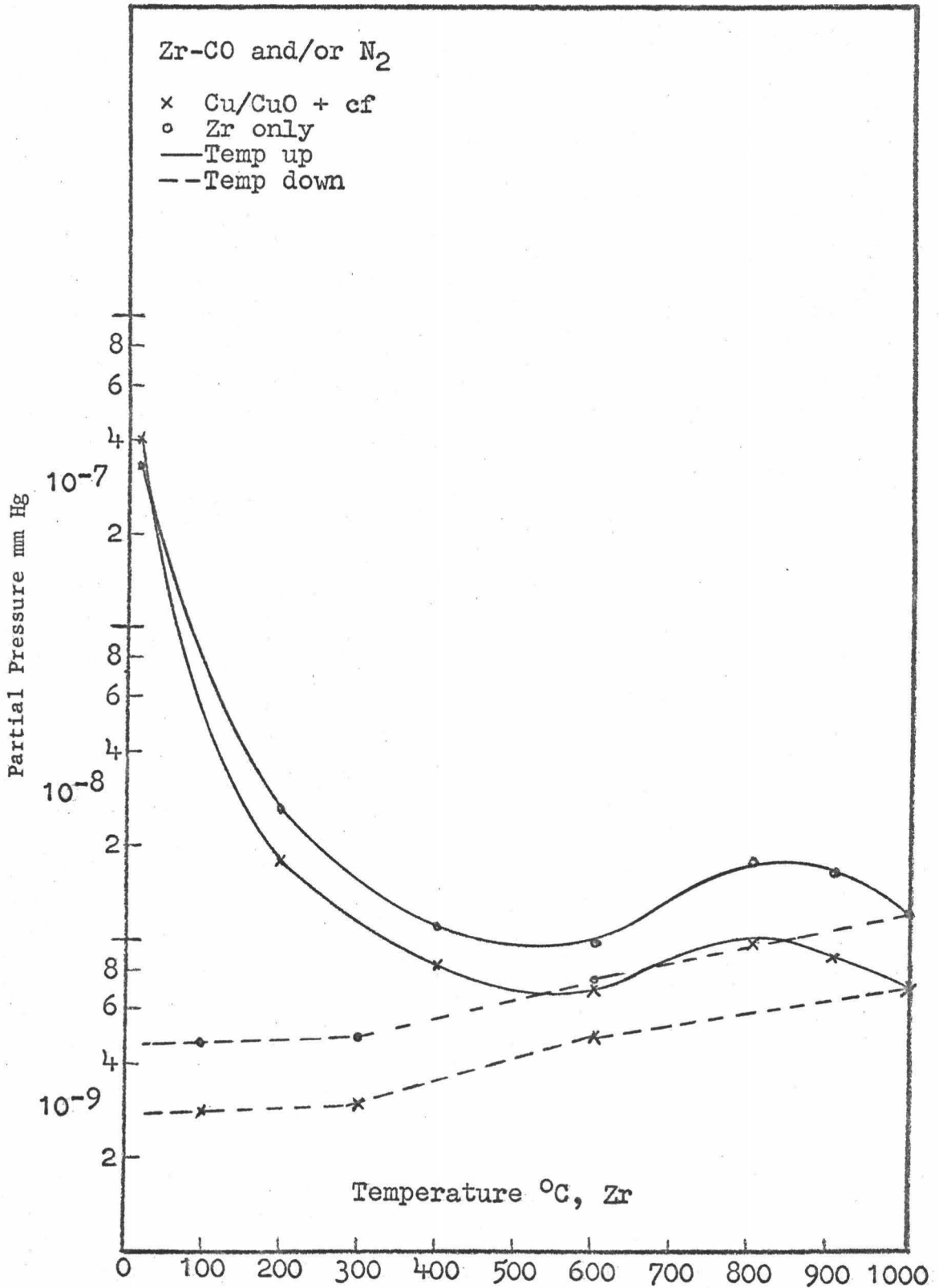


FIGURE 7 - Partial Pressure vs Temperature for Zr-CO &/or N<sub>2</sub>

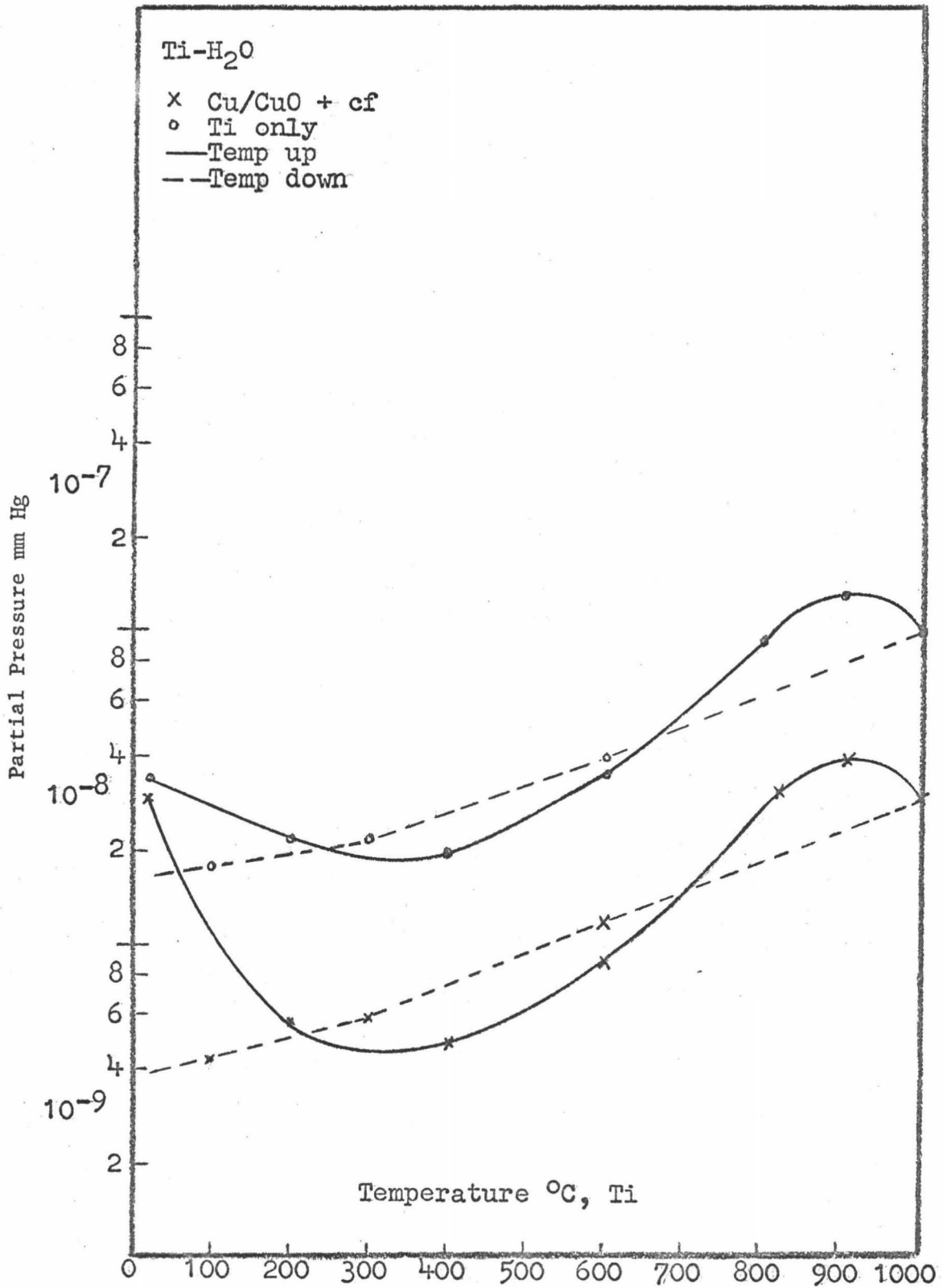


FIGURE 8 - Partial Pressure vs Temperature for Ti-H<sub>2</sub>O

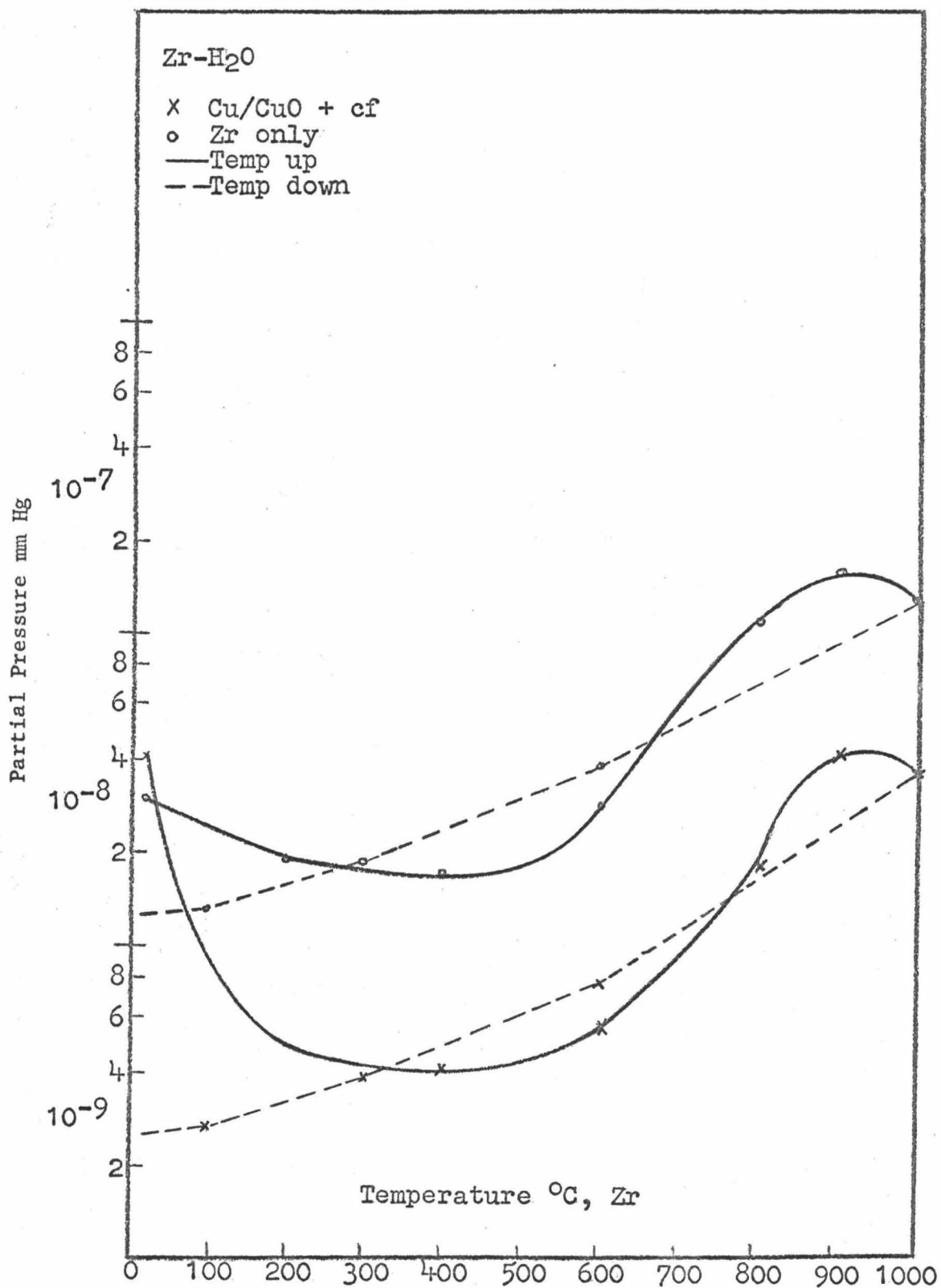


FIGURE 9 - Partial Pressure vs Temperature for Zr-H<sub>2</sub>O

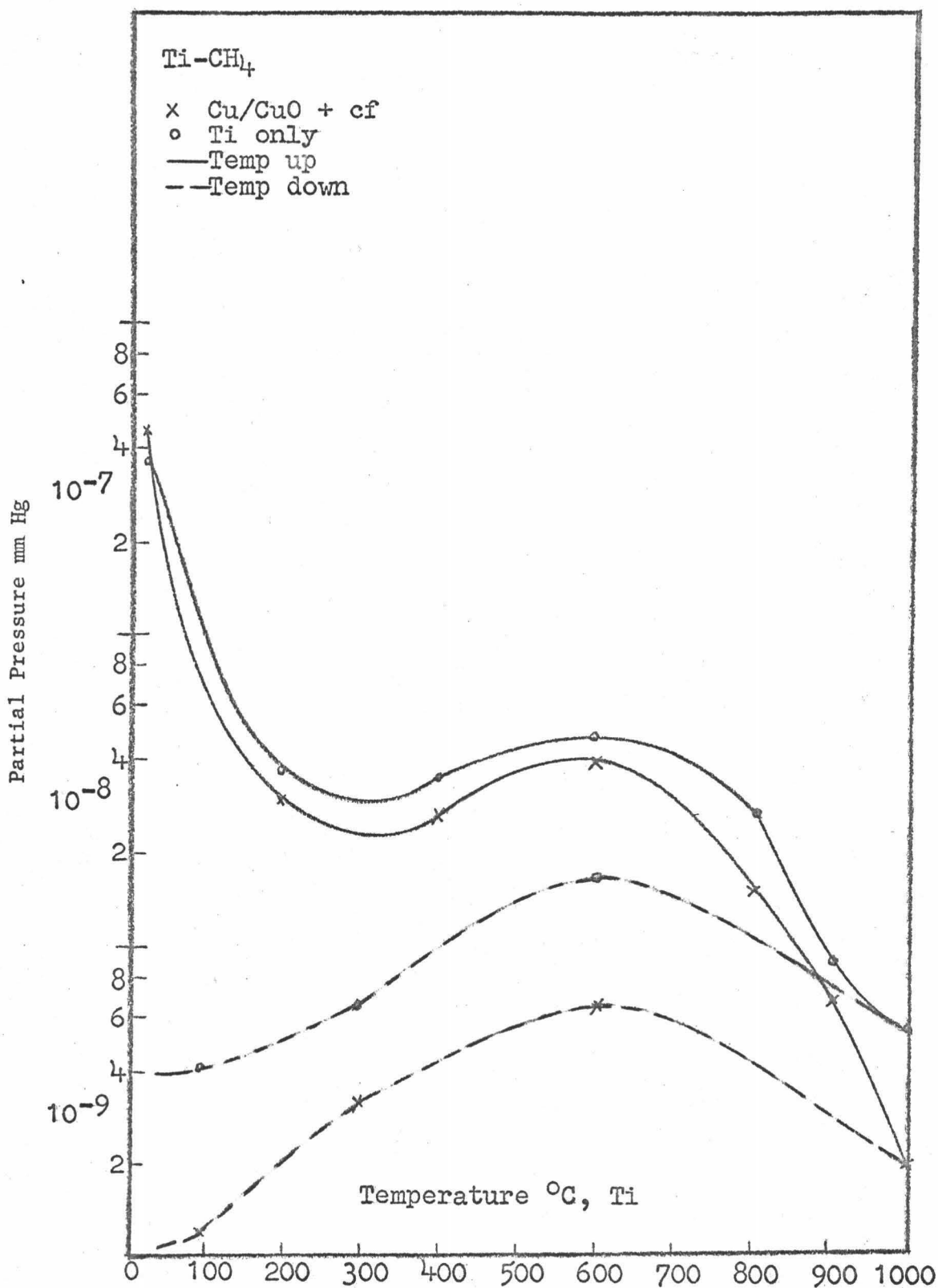


FIGURE 10 - Partial Pressure vs Temperature for Ti-CH<sub>4</sub>

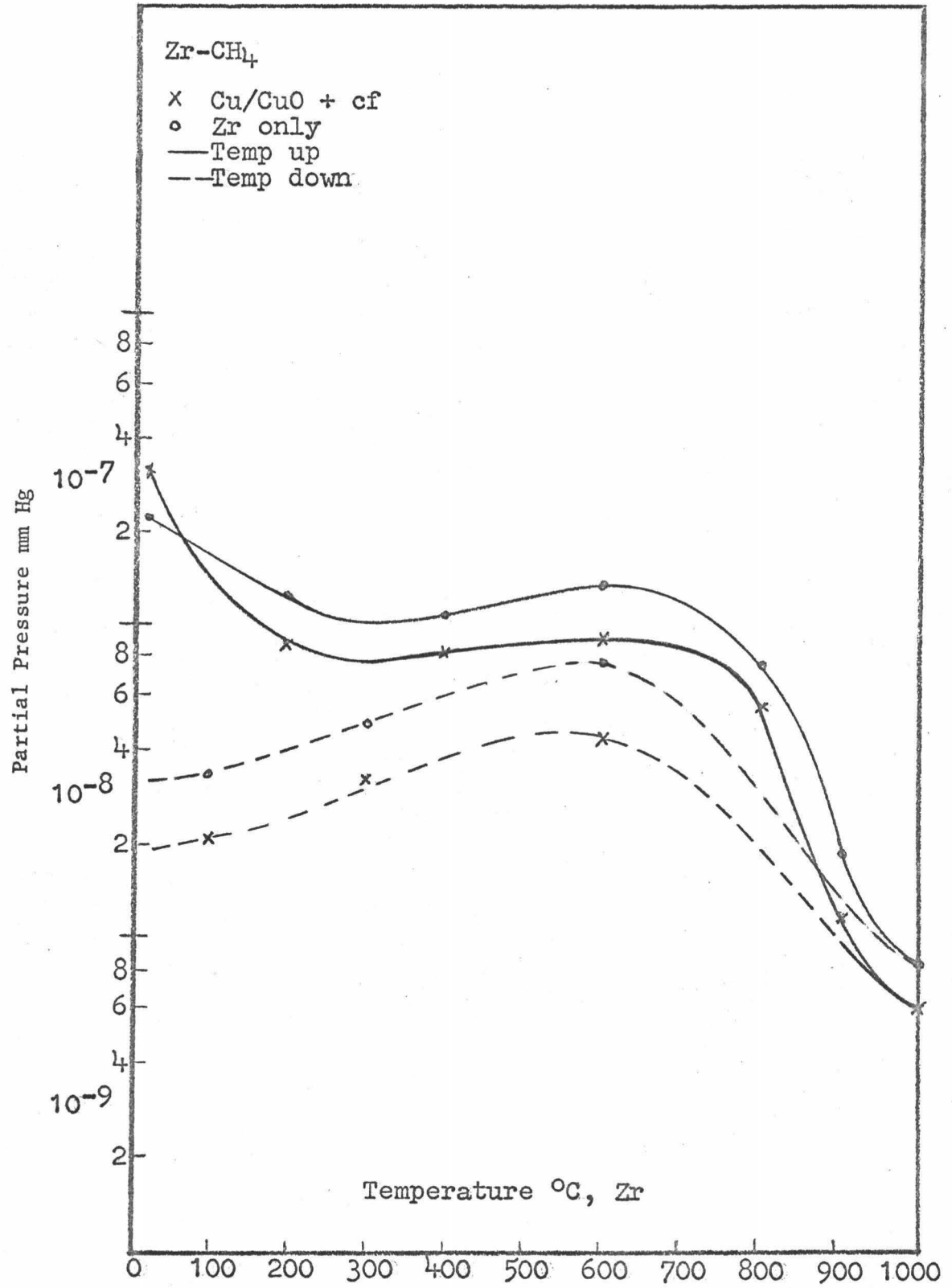


FIGURE 11 - Partial Pressure vs Temperature for Zr-CH<sub>4</sub>



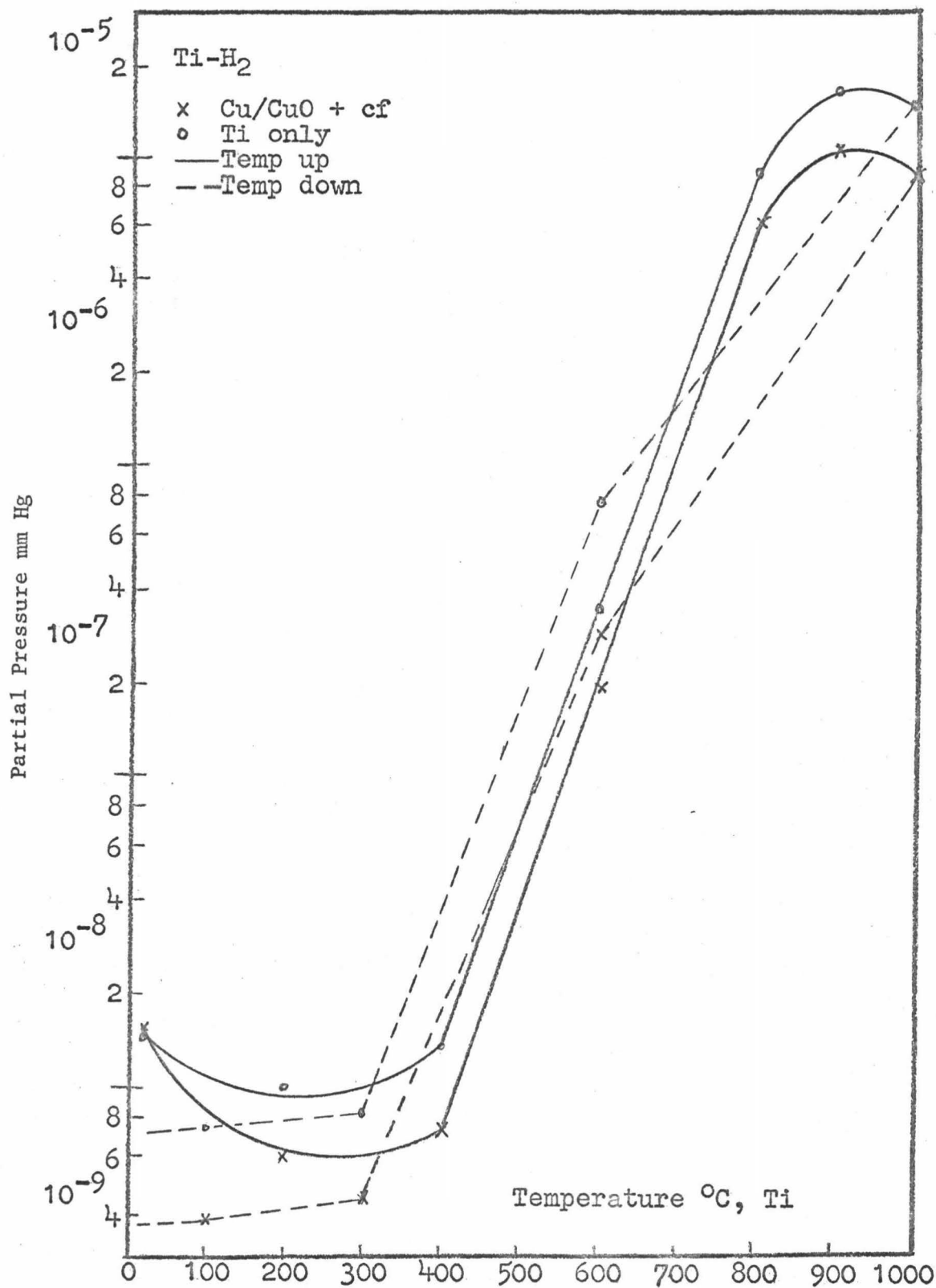


FIGURE 12 - Partial Pressure vs Temperature for Ti-H<sub>2</sub>

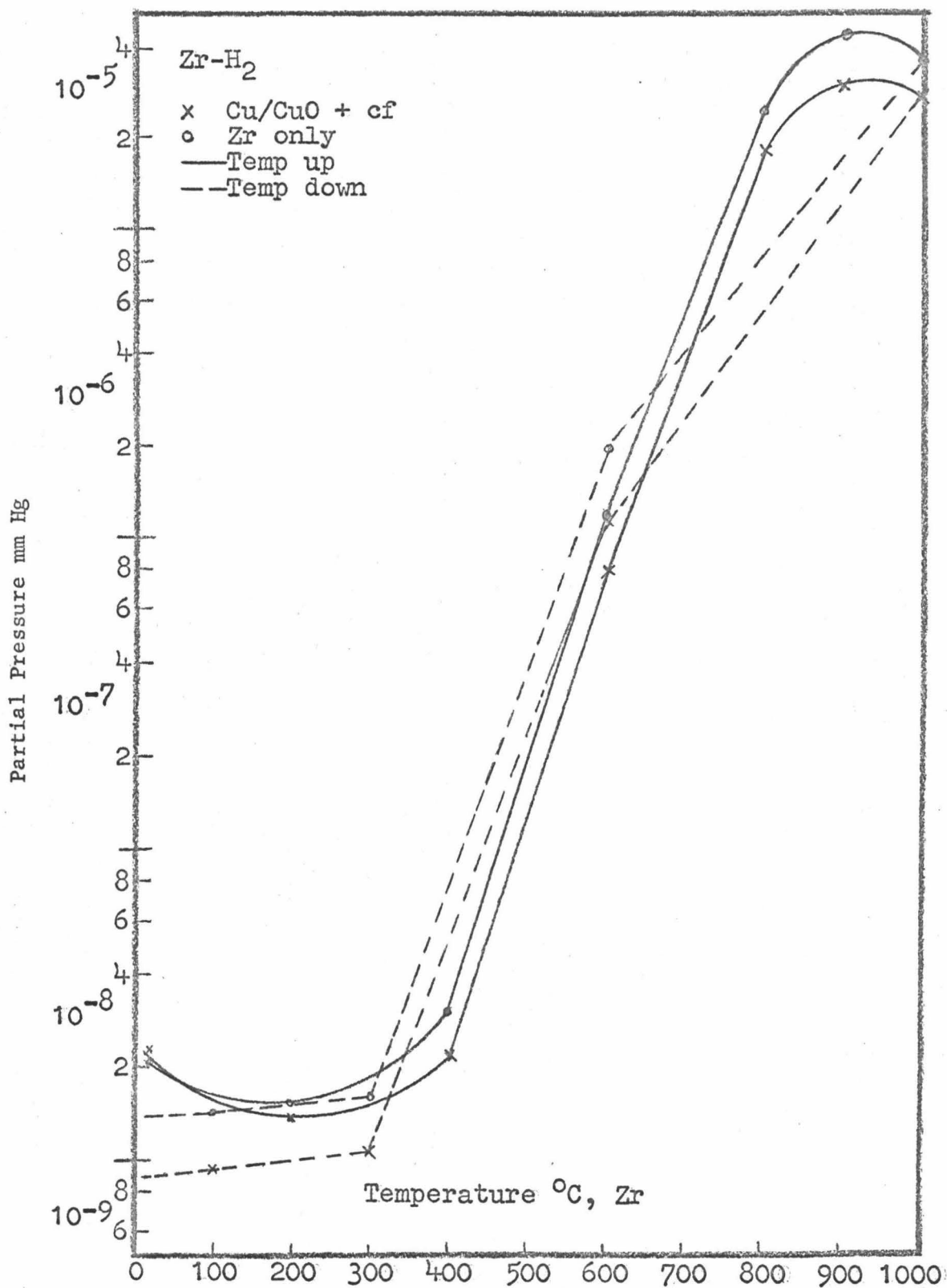
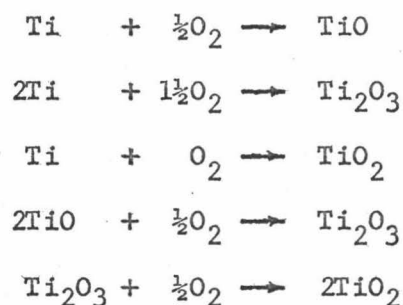


FIGURE 13 - Partial Pressure vs Temperature for Zr-H<sub>2</sub>

of 16 was found ( $O_2^{++}$  ?,  $O^+$  ?) but was attributed to  $CH_4^+$ , M/e 16. This assumption was made because of the fragmentation patterns which occurred. These fragments possessed mass-to-charge ratios of 15 ( $CH_3^+$ ), 14 ( $CH_2^+$ ), 13 ( $CH^+$ ), and 12 ( $C^+$ ) in the correct pattern<sup>45</sup> attributed to methane M/e 16 ( $CH_4^+$ ). Oxygen, M/e 17 ( $^{17}O^+$ ) and oxygen, M/e 18 ( $^{18}O^+$ ) were not believed to be present as  $^{17}O$  constitutes only 0.04% and  $^{18}O$  constitutes 0.2% of all oxygen found in nature. Also in support of this belief was the fact that M/e at 17 and 18 were found to be in the correct ratio for  $OH^+$  M/e 17 and  $H_2O^+$  M/e 18.

Titanium has been found to react with any oxygen present in several different ways.<sup>46</sup>



However, only the tetravalent state of Zr has been found<sup>47</sup> in the reaction of Zr with oxygen:  $Zr + O_2 \longrightarrow ZrO_2$ .

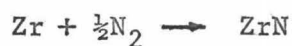
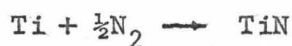
##### 5. Nitrogen.

Nitrogen is hard to distinguish from carbon monoxide in an ultra-high-vacuum system.<sup>48</sup> The peak needed to distinguish between  $N_2^+$ , M/e 28, and  $CO^+$ , M/e 28 is M/e 12 ( $C^+$ ). This peak M/e 12 is generally not large enough to make a valid identification; and adding to this problem is

the interference of M/e 12 ( $C^+$ ) from methane and M/e 12 ( $C^+$ ) from CO. M/e 14 provided no clue for identification either as it may be assigned to M/e 14 ( $N_2^{++}$ ,  $N^+$ ) or M/e 14 ( $CO^{++}$ ). Methane and carbon dioxide can also interfere as M/e 14 ( $CH_2^+$ ) or M/e 14 ( $CO^{++}$ ).

As a check for M/e 28, the vacuum system was flushed with CO several times. The spectra at various getter temperatures were then taken. This same procedure was then followed using air. The data obtained for M/e 28 was then plotted in the manner shown in Figures 6 and 7. In both cases no significant difference was apparent in the shape of the curves obtained for M/e 28. It is therefore concluded that the M/e 28 detected was in all likelihood due to a combination of both CO and  $N_2$ .

Nitride formation has been found<sup>49,50</sup> to occur quite readily at temperatures of a few hundred degrees or more and occurs as follows:



#### 6. Argon.

The getters Cu/CuO, Ti, and Zr have no significant effect on argon. Argon pressure remained relatively constant from 20-800°C. From beyond 800 to 1000°C the pressure increased approximately 4-fold. This rise in pressure was attributed to Ar desorption from the quartz and glass walls of the vacuum system at these elevated temperatures.

Several runs were made to a maximum temperature of 800°C only and no appreciable increase in pressure was observed. See Figures 14 and 15.

#### 7. Helium.

The partial pressure of helium was found to increase as the temperature of the getter was increased from 20 to 1000°C. As with argon, several runs were made to a maximum temperature of 800°C; these runs showed no noticeable difference from those made to 1000°C. See Figures 16 and 17.

It is concluded from Norton's<sup>51</sup> report that this rise in pressure was due to helium permeating from the atmosphere through the glass walls of the vacuum system.

#### 8. General Applicability.

Blumenthal<sup>52</sup> has found a marked increase in the rate of diffusion O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, and C into metallic Ti and Zr due to an allotropic change in crystal structure. This change occurs at 882°C for Ti and 862°C for Zr. It is postulated here that this phase change was the cause of the change in slope in the partial pressure vs temperature range of 800-1000°C.

Previous workers have identified the compounds formed in the reactions with Ti and Zr metal, namely the hydrides, oxides, nitrides, and carbides, by electron and X-ray diffraction analysis.<sup>53,54,55</sup>

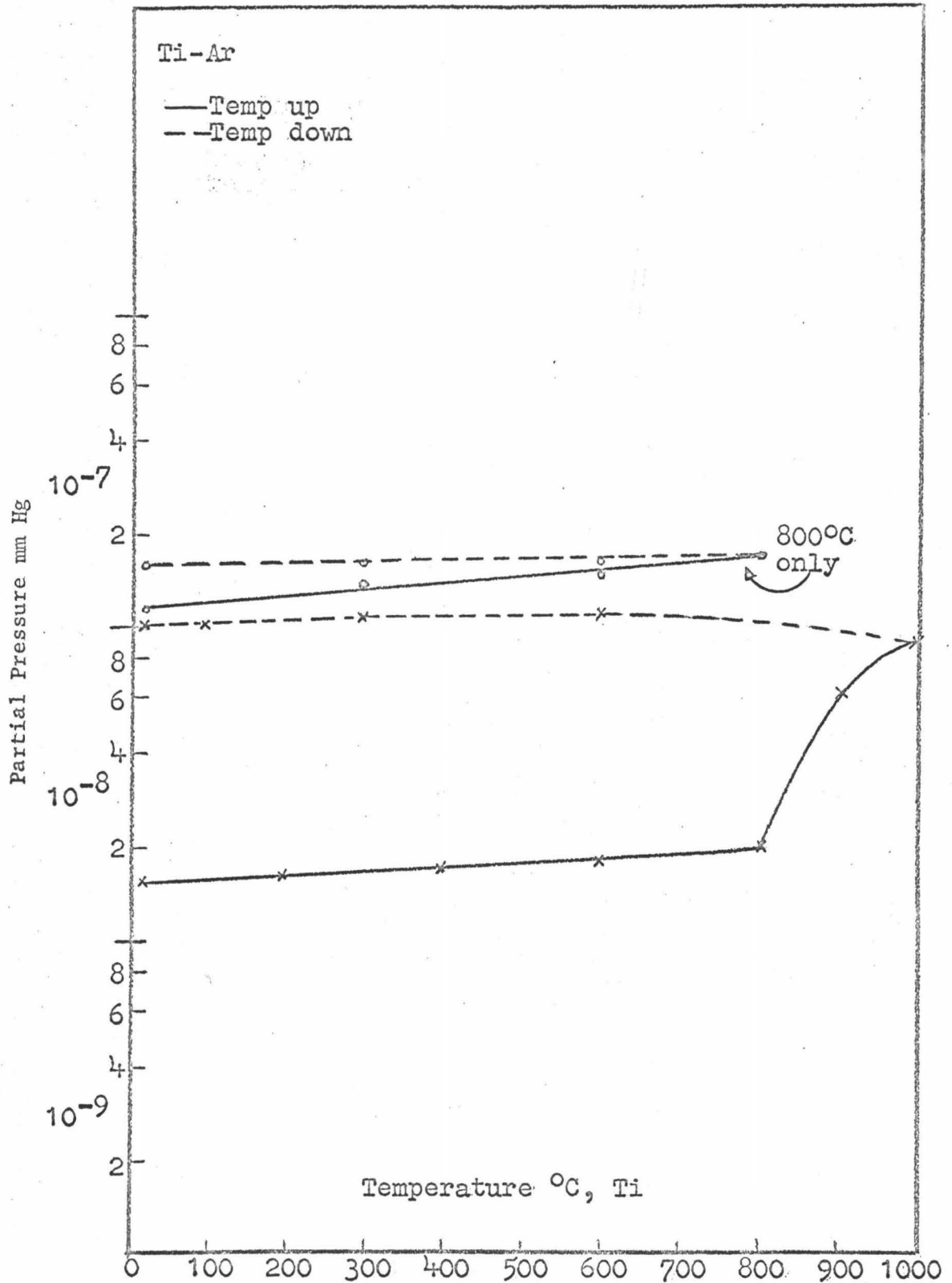


FIGURE 14 - Partial Pressure vs Temperature for Ti-Ar

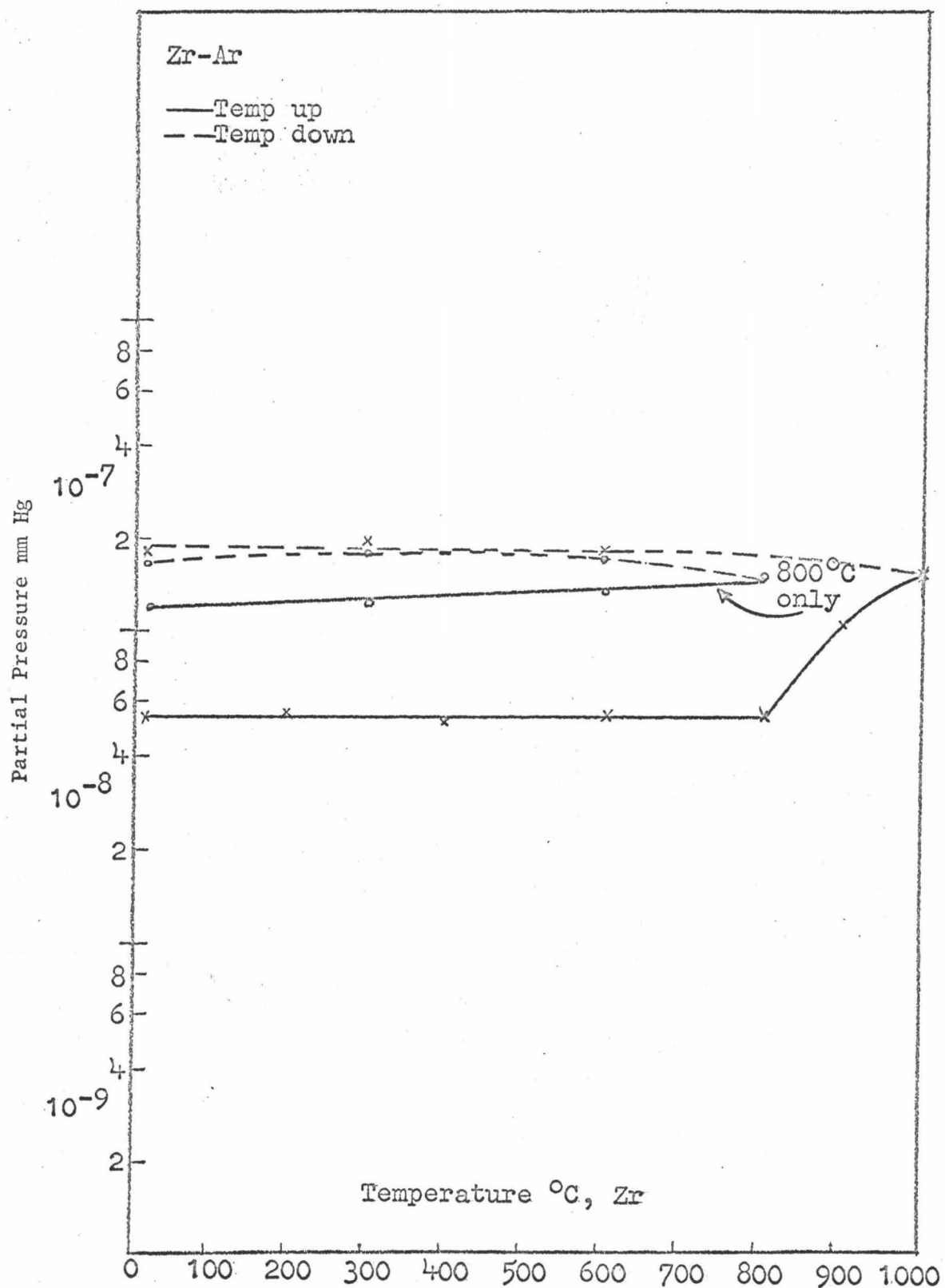


FIGURE 15 - Partial Pressure vs Temperature for Zr-Ar

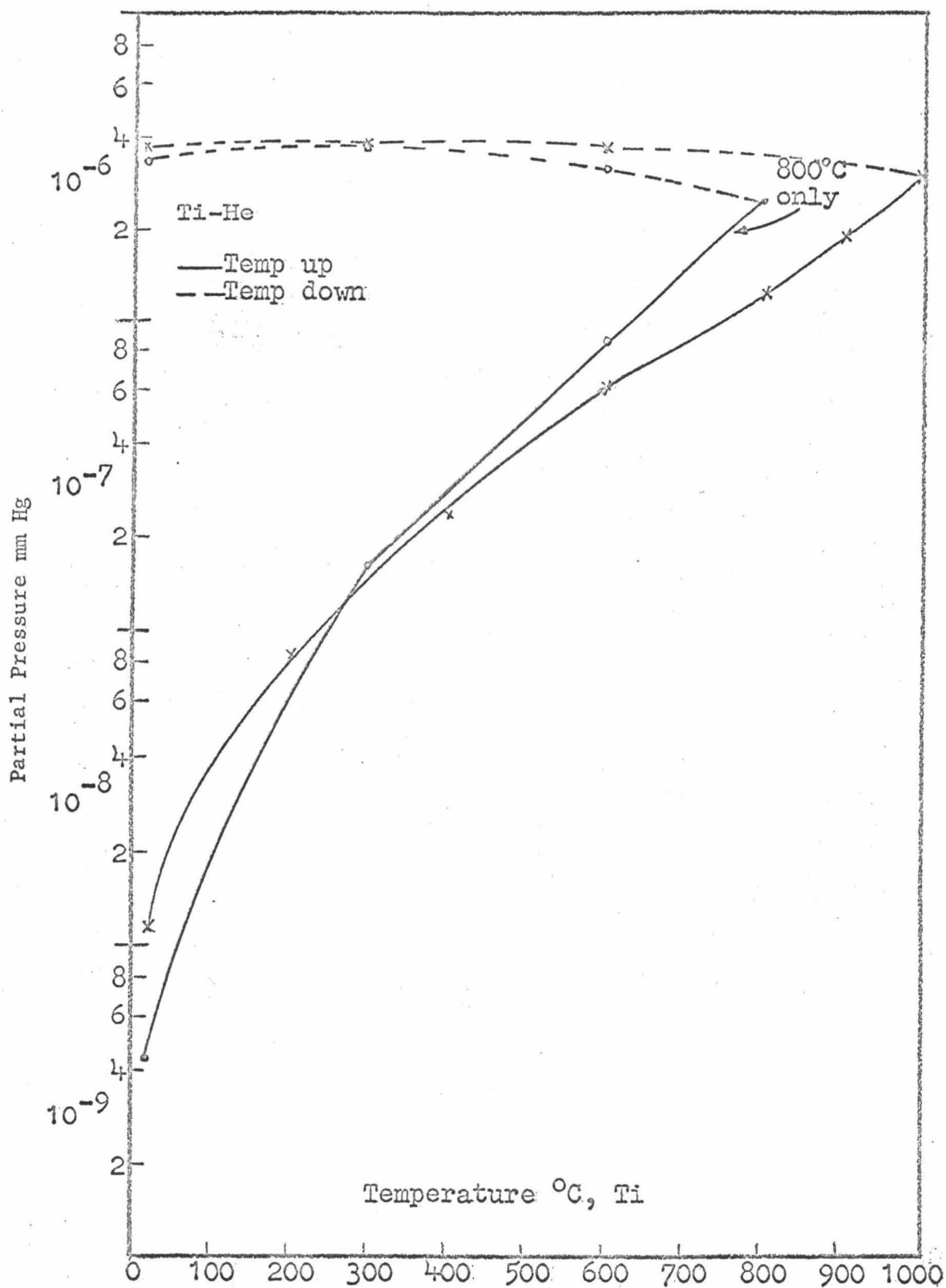


FIGURE 16 - Partial Pressure vs Temperature for Ti-He



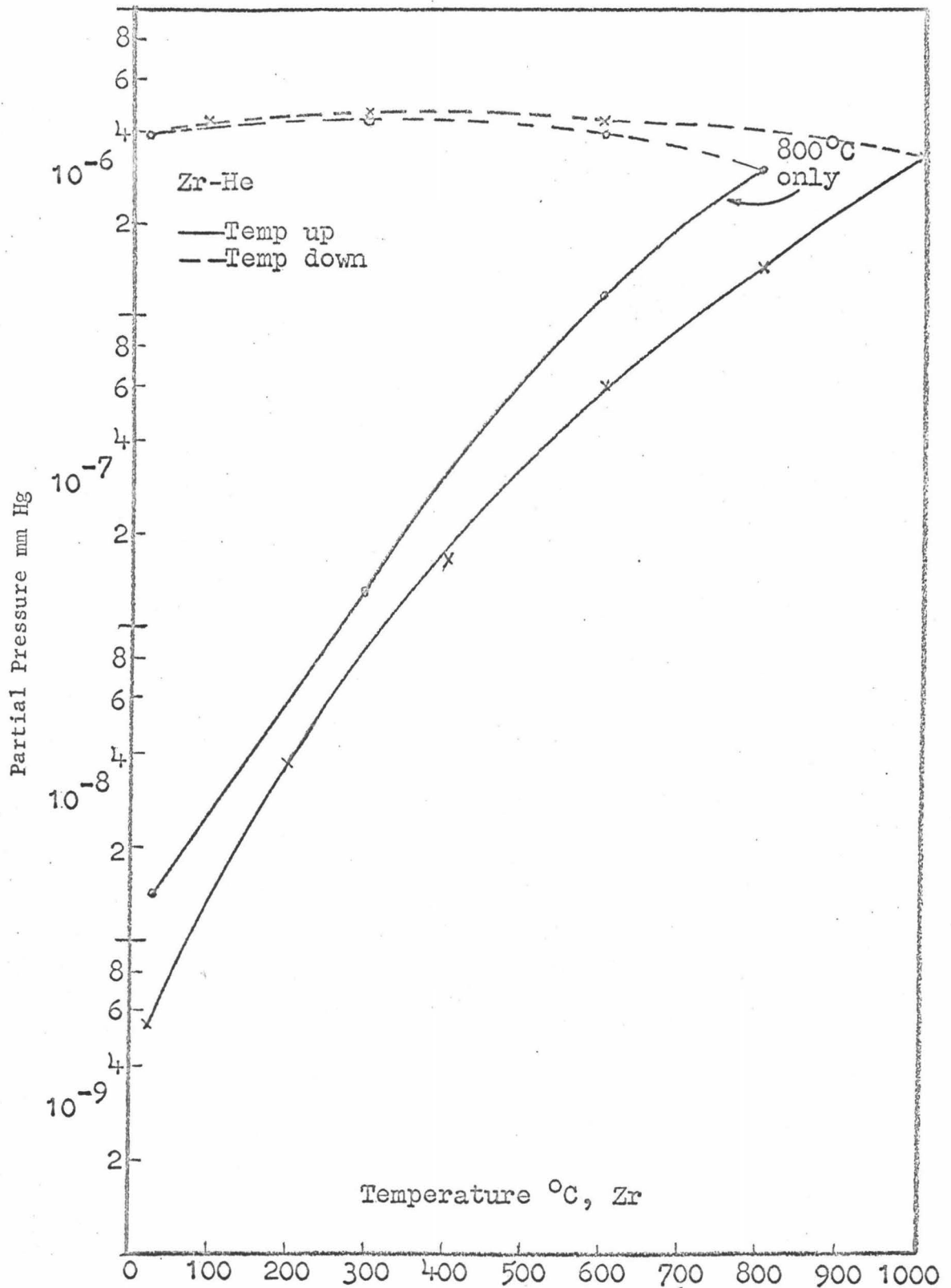
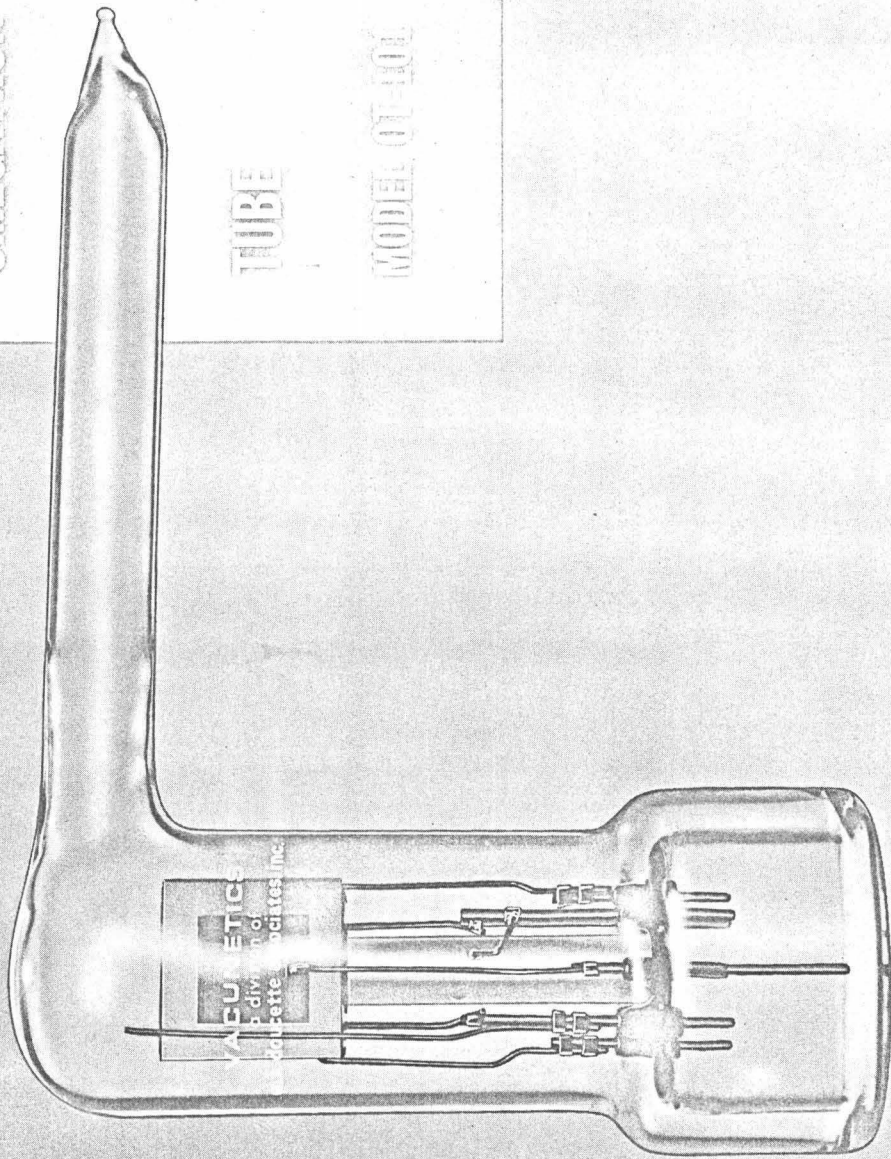


FIGURE 17 - Partial Pressure vs Temperature for Zr-He.

OMEGATRON

TUBE

MODEL OT-101



VACUUM ETICS  
a division of  
Sylvania Electric Products Inc.

### C. General Remarks

The results of the data obtained in this research and summarized in Table 7 show that Ti is superior to Zr as a getter for the gases studied with the exception of water vapor. It can also be implied from the data that the most probable reactions taking place between the various gases and the Cu/CuO getter were those involving the formation of H<sub>2</sub>O and CO<sub>2</sub>. As for Ti and Zr reactions, it is most probable that products formed were oxides, nitrides, carbides, and hydrides.

Data found in the literature indicate that Ti is a more efficient getter than Zr for CO<sub>2</sub>, CO, N<sub>2</sub>, and H<sub>2</sub>.<sup>56,57</sup> Zr seems to be slightly more efficient for oxygen sorption.<sup>58, 59</sup> No comparison of water vapor clean-up could be found except that both Zr and Ti serve to getter it.<sup>60,61</sup> With regard to the relative amounts of gases sorbed by Zr and Ti, Brennan<sup>62</sup> states that Ti absorbs nearly twice as much CO as does Zr. Results obtained in this research and tabulated in Table 7 show this to be true.

A reason that Ti is a better getter than Zr might be due to its smaller cell parameters (Ti:  $a = 2.95\text{\AA}$ ,  $c = 4.68\text{\AA}$ ; Zr:  $a = 3.23\text{\AA}$ ,  $c = 5.13\text{\AA}$ ), hence, the entrapped gas atom or ion could be held more tightly in Ti than in Zr. Another probable reason is that the diffusion rate of gas into Ti metal is greater than the diffusion rate of gas into Zr metal.

Titanium and zirconium form covalent bonds with the elements oxygen, nitrogen, and carbon in the conventional

manner. The hydrides of Ti or Zr might be thought of as interstitial solutions of the atoms or ions of the element hydrogen in a matrix of Ti or Zr metal atoms. The atoms or ions of carbon, oxygen, nitrogen, and hydrogen diffuse into the interior of the metal leaving the outer surface free to react with more of these atoms. An increase in temperature tends to increase the diffusion rate. With carbon, nitrogen, and oxygen dissolved in the lattice of the metal the absorbing capacity for hydrogen decreases.<sup>63,64</sup> The rate of diffusion for each gas into the metal is readily affected by temperature, pressure, surface films and impurities in the metal.<sup>65</sup> The carbides, nitrides, and oxides of Ti and Zr are all stable to 1500°C or more while the hydrides are stable at low temperatures (less than 400°C) and decompose at higher temperatures.<sup>66,67</sup>

Thus, for best gettering results this work shows that the getter, in conjunction with Cu/CuO at 400°C and a cold finger, should be heated to no more than 800°C and left there for a suitable reaction period and then allowed to cool to room temperature. To impede helium permeation and argon desorption it is suggested that a metal container be used to house the getter material in place of a quartz crucible and envelope. An RF heater might be used in place of the wire-wound resistance furnace to heat the getter. This should impede helium permeation and argon desorption as an RF heater should heat the getter without imparting an excess amount of heat to the quartz crucible.

#### IV. SUMMARY

An investigation has been made of the gettering properties of Zr and Ti along with the influence of a Cu/CuO getter and a cold finger on residual gases. It was found that Cu/CuO and a cold finger in use with Ti or Zr effectively reduced the amount of CO, water vapor, CH<sub>4</sub>, and H<sub>2</sub> in an ultra-high-vacuum system. The main disadvantage of these getter systems was that they increased the amount of CO<sub>2</sub> present. Ti was found to provide more effective clean-up than Zr for the gases CO<sub>2</sub>, CO, CH<sub>4</sub>, and H<sub>2</sub>; in the case of water vapor both worked about the same with Zr having a slight advantage. Results obtained agreed with those found in the literature.

The omegatrons used for detection in this study were effective as residual gas analyzers due to their high sensitivity, good resolution, small and simple construction, and low ionizing current. It is estimated that the minimum detectable partial pressure was approximately  $1.3 \times 10^{-9}$  mm Hg.

Table 3\*

The Getter Ti Sponge Metal Vs The Getters Ti Sponge Metal and Cu/CuO(at 400° C) + cold finger

Gas	Ti Temp of Max Sorption °C	System I	System II	<u>System II</u>
		Ti+Cu/CuO+cf	Ti	System I
		"Equilibrium" Partial P per gm Ti	"Equilibrium" Partial P per gm Ti	
CO <sub>2</sub>	600	1.92	0.75	0.39
	100	0.50	0.17	0.34
CO &/or N <sub>2</sub>	600	0.25	0.43	1.7
	100	0.08	0.25	3.1
H <sub>2</sub> O	400	0.41	1.67	4.1
	100	0.36	1.50	4.2
CH <sub>4</sub>	300	2.00	2.66	1.3
	100	0.10	0.33	3.6
H <sub>2</sub>	200	0.50	0.83	1.7
	100	0.33	0.65	1.9

\* In this Table and those that follow, it has been assumed for the purpose of calculation that equilibrium had been reached for the various reactions which took place in the vacuum system.

The total amount of Ti metal used as a getter was 12.0393 gm.

Table 4

The Getter Zr Sponge Metal Vs The Getters Zr Sponge Metal and Cu/CuO(at 400° C) + cold finger

Gas	Zr Temp of Max Sorption °C	System III	System IV	System IV
		Zr+Cu/CuO+cf	Zr	<u>System III</u>
		"Equilibrium" Partial P per gm Zr	"Equilibrium" Partial P per gm Zr	
CO <sub>2</sub>	600	2.83	0.73	0.26
	100	0.98	0.32	0.32
CO &/or N <sub>2</sub>	600	0.58	0.81	1.4
	100	0.23	0.40	1.7
H <sub>2</sub> O	400	0.33	1.41	4.3
	100	0.22	1.08	3.6
CH <sub>4</sub>	300	6.75	9.33	1.4
	100	1.79	2.92	1.6
H <sub>2</sub>	200	1.17	1.33	1.1
	100	0.80	1.21	1.5

The total amount of Zr metal used as a getter was 12.0096 gm.

Table 5

The Getter Ti Sponge Metal Vs The Getter Zr Sponge Metal

Gas	Ti or Zr Temp of Max Sorption °C	System II	System IV	System IV
		Ti	Zr	System III
		"Equilibrium" Partial P per gm Ti	"Equilibrium" Partial P per gm Zr	
CO <sub>2</sub>	600	0.75	0.73	0.98
	100	0.17	0.32	1.9
CO &/or N <sub>2</sub>	600	0.43	0.81	1.9
	100	0.25	0.40	1.6
H <sub>2</sub> O	400	1.67	1.41	0.85
	100	1.50	1.08	0.73
CH <sub>4</sub>	300	2.66	9.33	3.5
	100	0.33	2.92	8.8
H <sub>2</sub>	200	0.83	1.33	1.6
	100	0.65	1.21	1.9



Table 6

The Getters Ti Sponge Metal and Cu/CuO(at 400° C) + cold finger Vs  
 The Getters Zr Sponge Metal and Cu/CuO(at 400° C) + cold finger

Gas	Ti or Zr Temp of Max Sorption °C	System I	System III	<u>System III</u>
		Ti+Cu/CuO+cf	Zr+Cu/CuO+cf	System I
		"Equilibrium" Partial P per gm Ti	"Equilibrium" Partial P per gm Zr	
CO <sub>2</sub>	600	1.92	2.83	1.5
	100	0.50	0.98	2.0
CO &/or N <sub>2</sub>	600	0.25	0.58	2.3
	100	0.08	0.23	2.8
H <sub>2</sub> O	400	0.41	0.33	0.81
	100	0.36	0.22	0.61
CH <sub>4</sub>	300	2.00	6.75	3.4
	100	0.10	1.79	19
H <sub>2</sub>	200	0.50	1.17	2.3
	100	0.33	0.80	2.4

The total amount of Cu/CuO used as a getter was 19.9527 gm.

Table 7\*

## Relative Gettering Powers At Maximum Sorption

Gas	Ti vs Ti+Cu/CuO+cf		Zr vs Zr+Cu/CuO+cf	
	Best System	Factor	Best System	Factor
CO <sub>2</sub>	Ti	3	Zr	3
CO &/or N <sub>2</sub>	Ti+Cu/CuO+cf	3	Zr+Cu/CuO+cf	1.5
H <sub>2</sub> O	"	4	"	4
CH <sub>4</sub>	"	2.5	"	1.5
H <sub>2</sub>	"	2	"	1.3

Gas	Ti vs Zr		Ti+Cu/CuO+cf vs Zr+Cu/CuO+cf	
	Best System	Factor	Best System	Factor
CO <sub>2</sub>	Ti	1.5	Ti	2
CO &/or N <sub>2</sub>	Ti	2	Ti	2.5
H <sub>2</sub> O	Zr	1.3	Zr	1.3
CH <sub>4</sub>	Ti	6	Ti	10
H <sub>2</sub>	Ti	2	Ti	2

\*This Table is based on the data obtained from Figures 3 - 12 and Tables 3 - 6. The "factors" listed were determined in the following manner: By comparison of the partial pressure of CO<sub>2</sub> present in a system containing Ti as a getter and in a system containing Zr as a getter it was found that the partial pressure of CO<sub>2</sub> was approximately 1½ times less in the Ti system at the maximum sorption temperature; hence, a "factor" of 1.5 was assigned to the Ti system. The rest of the "factors" were determined in the same manner for the other gases and systems studied.

## V. APPENDIX - DIFFUSION STUDIES

After the completion of this research it was found that sufficient data was present for an approximate calculation of the diffusion coefficients of hydrogen and carbon monoxide in Ti and Zr metal. In this calculation the metals Ti and Zr were assumed to have spherical geometry, and a solution valid for a sphere was used and converted into an equation in terms of F, the fraction of hydrogen or carbon monoxide released in any time, t, from the metal Ti or Zr at various temperatures.

The equation given by Jost<sup>68</sup> and modified by Crank<sup>69</sup> is:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \frac{-n^2 \pi^2 Dt}{a^2}$$

where a is the radius of the sphere, n is the number of increments of gas obtained in the time period, t, and D is the diffusion coefficient.

Reichenberg<sup>70</sup> arrived at an approximation of the above equation. This equation is:

$$F = \frac{6}{\pi^{3/2}} \sqrt{Bt} - \frac{3}{\pi^2} Bt$$

where  $B = \frac{\pi^2 D}{a^2}$

Reichenberg gives a table of values of Bt for various values of F. These values of F may be used with certain other mathematical terms to calculate the diffusion constants of hydrogen and carbon monoxide into, and out of, Ti and Zr metal. The maximum partial pressure of hydrogen recorded in a complete temperature cycle (20-

1000°C) was taken as the total amount of hydrogen present. The ratio of the partial pressure of hydrogen recorded at each temperature to this maximum partial pressure recorded was taken as the F value for hydrogen. The F value for carbon monoxide was determined in a like manner.

From the Reichenberg tables a value of Bt is found for each value of F. B is related to the diffusion coefficient D by the following equations:

$$B = \pi^2 D/a^2$$

hence  $Bt = \pi^2 Dt/a^2$

and  $D/a^2 = Bt/\pi^2 t$

There is some uncertainty about the actual value of a, the effective radius of the particle; hence, values of  $D/a^2$  are usually used. In this study, values of  $\log D/a^2$  were calculated and plotted vs  $1000/T^\circ\text{K}$ . These graphs are shown in Figures 18, 19, 20, and 21.

The "energy of activation" for hydrogen and carbon monoxide diffusion in Ti or Zr can be obtained from the equation:

$$D = D_0 \exp \frac{-Q}{RT}$$

where Q is the activation energy.

The plot in Figures 18-21 is shown for temperatures at 600°C and above as Reichenberg values could not be obtained below 600°C. From an evaluation of the data shown in the hydrogen graphs, Figures 12 and 13, it is believed that a change in slope would result

below 400°C and that a lower energy of activation of hydrogen would exist for the Ti-hydrogen and Zr-hydrogen systems in this region.

The Ti-hydrogen and Ti-carbon monoxide systems possessed lower activation energies than the corresponding Zr-hydrogen and Zr-carbon monoxide systems. It can be postulated that Ti "getters" more effectively than Zr because of a greater diffusion of gas into Ti than into Zr at similar temperatures. See Table 10. In conclusion, this evidence as well as others obtained in this research leads to the strong belief that the rate of diffusion of gas into the metal Ti or Zr at a particular temperature was the controlling factor in the gettering process.

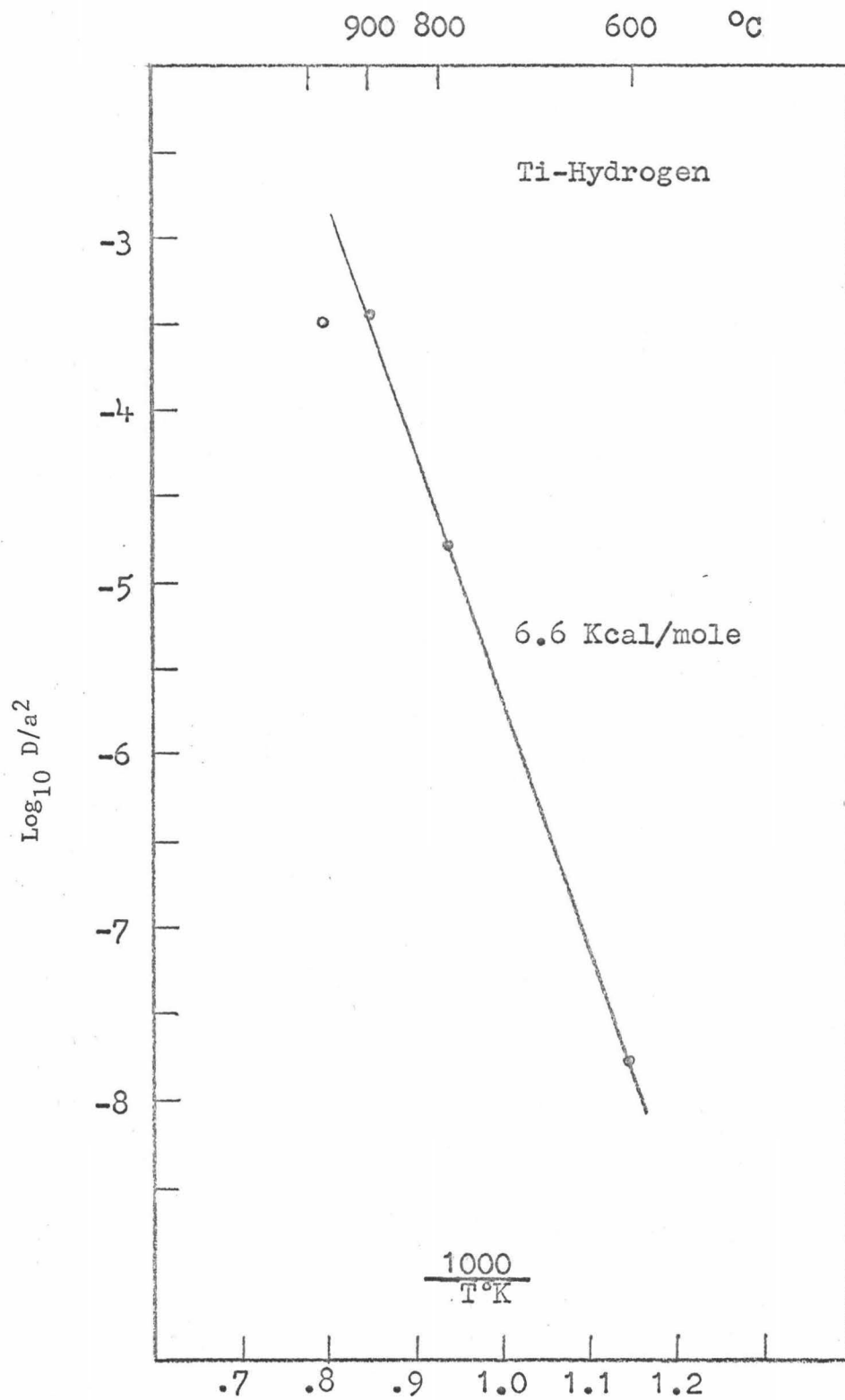


FIGURE 18 -  $\text{Log } D/a^2$  vs  $1000/T$  for Ti-Hydrogen

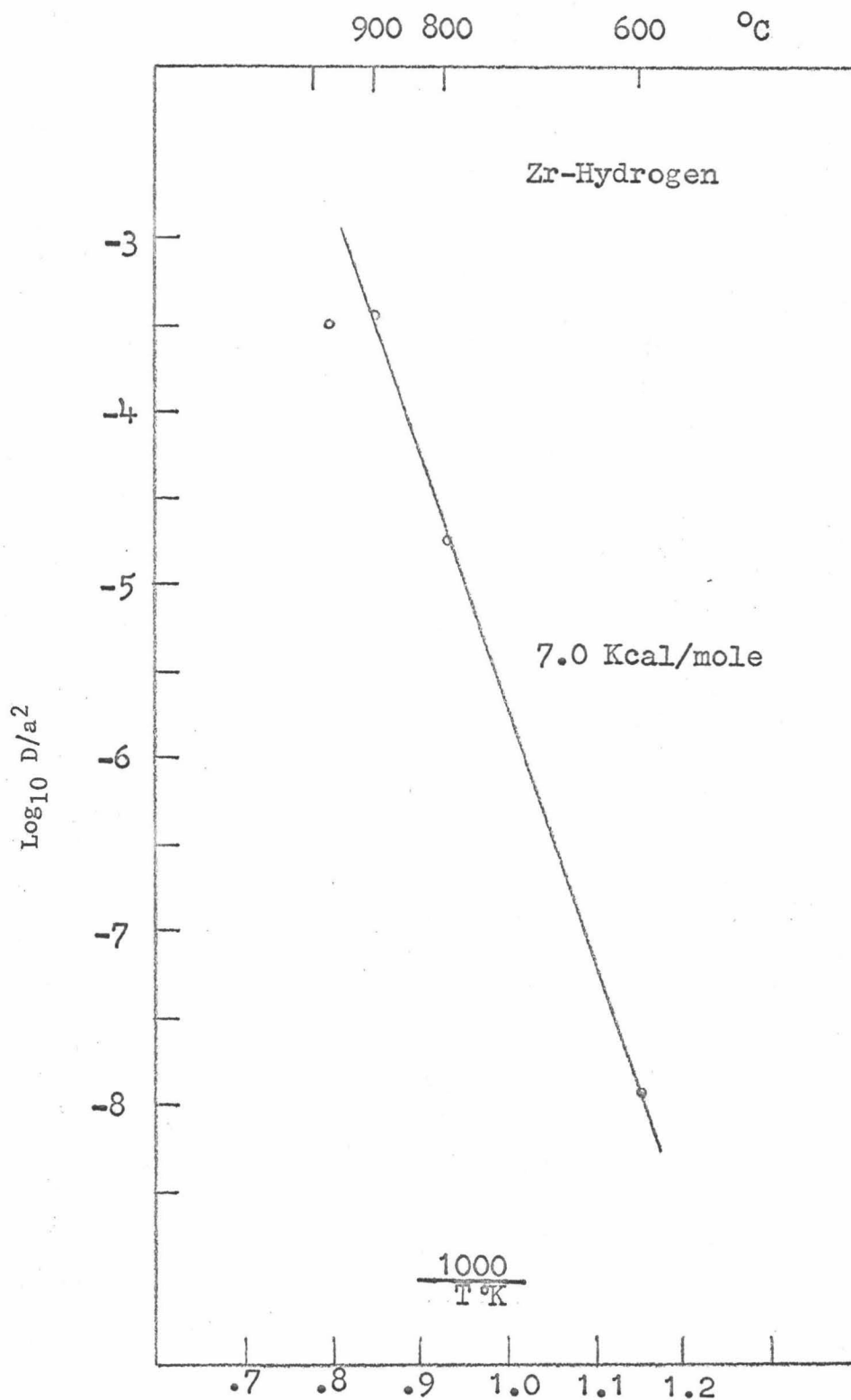
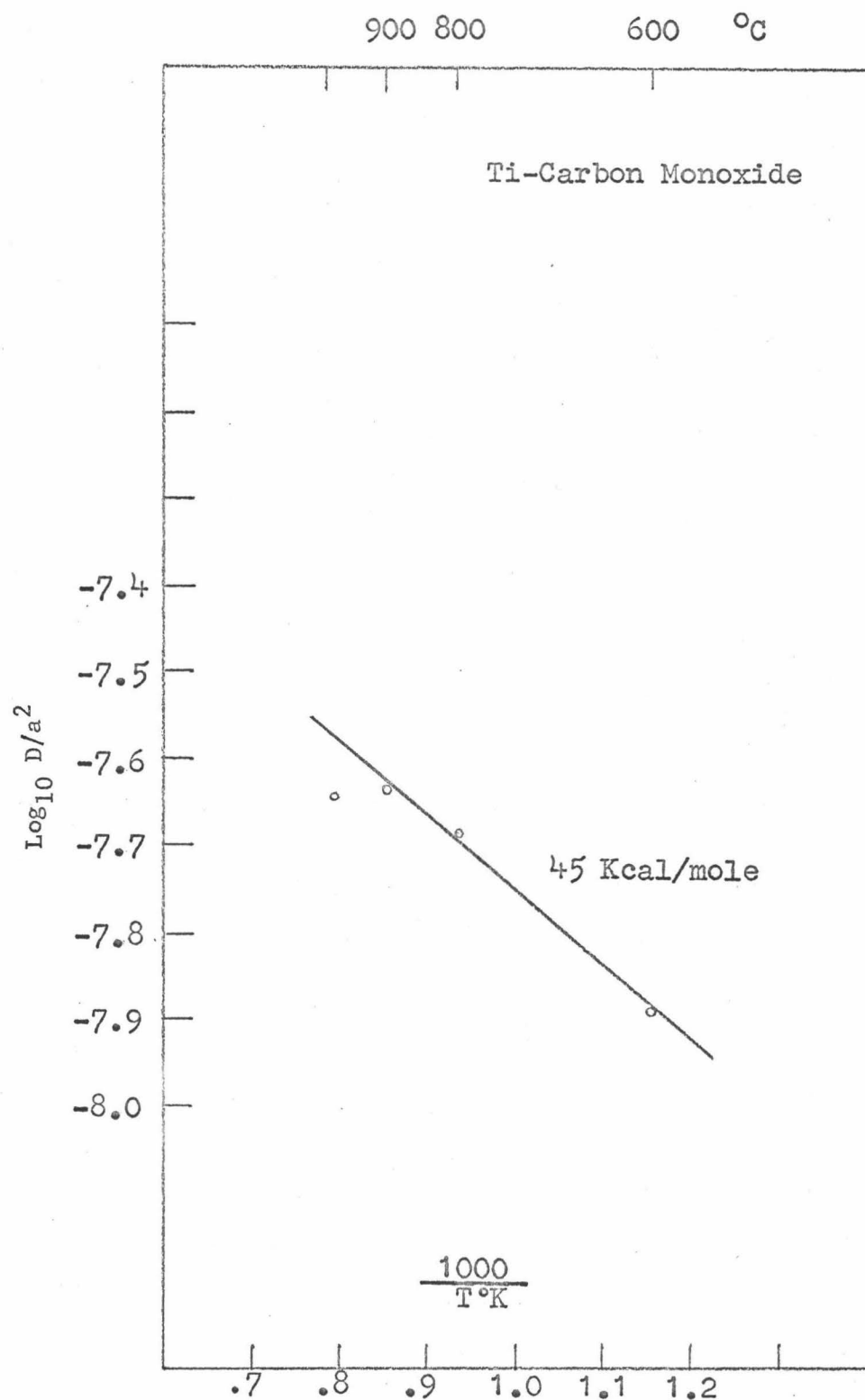


FIGURE 19 - Log D/a<sup>2</sup> vs 1000/T for Zr- Hydrogen

FIGURE 20 -  $\text{Log } D/a^2$  vs  $1000/T$  for Ti-Carbon Monoxide



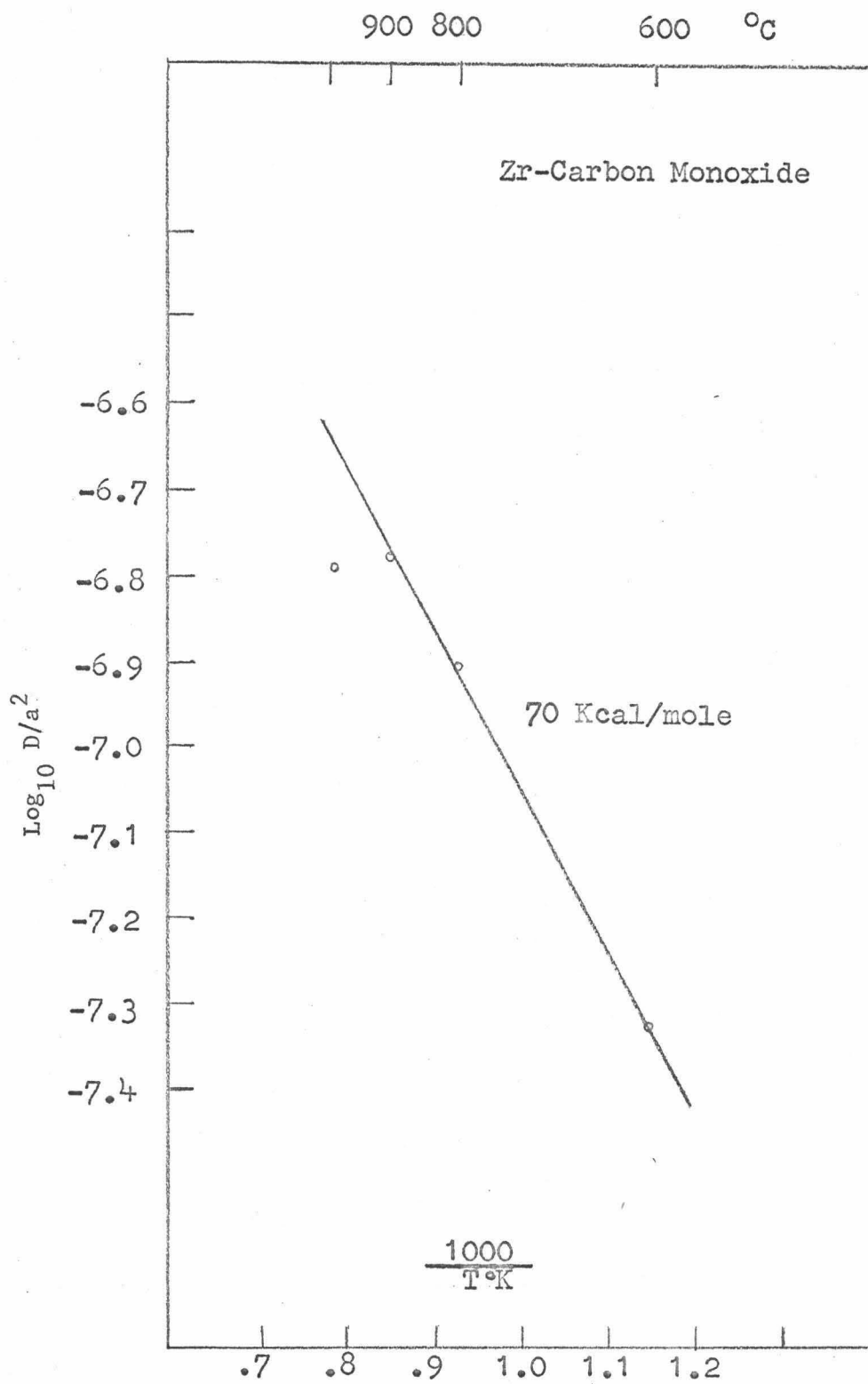
FIGURE 21 -  $\text{Log } D/a^2$  vs  $1000/T$  for Zr-Carbon Monoxide

Table 8

## Data for Hydrogen Diffusion Curves

Metal	Temp °C	1000 T°K	Hydrogen Released Partial P mmHg	Hydrogen Cumulative Total Partial P mmHg	F Fraction Released	Bt	D/a <sup>2</sup>	Log <sub>10</sub> D/a <sup>2</sup>
Ti	600	1.15	3x10 <sup>-7</sup>	2x10 <sup>-5</sup>	0.015	0.00021	1.77x10 <sup>-8</sup>	-7.751
	800	0.930	8x10 <sup>-6</sup>	2x10 <sup>-5</sup>	0.40	0.177	1.49x10 <sup>-5</sup>	-4.826
	900	0.851	2x10 <sup>-5</sup>	2x10 <sup>-5</sup>	0.99	4.11	3.47x10 <sup>-4</sup>	-3.460
	1000	0.758	1.5x10 <sup>-5</sup>	2x10 <sup>-5</sup>	0.75	0.905	7.36x10 <sup>-5</sup>	-4.118
Zr	600	1.15	6.4x10 <sup>-7</sup>	4x10 <sup>-5</sup>	0.0160	0.000133	1.12x10 <sup>-8</sup>	-7.950
	800	0.930	1.7x10 <sup>-5</sup>	4x10 <sup>-5</sup>	0.425	0.204	1.71x10 <sup>-5</sup>	-4.767
	900	0.851	4.0x10 <sup>-5</sup>	4x10 <sup>-5</sup>	0.999	4.11	3.47x10 <sup>-4</sup>	-3.460
	1000	0.785	3.3x10 <sup>-5</sup>	4x10 <sup>-5</sup>	0.814	1.19	1.01x10 <sup>-4</sup>	-3.997

Time = 1200 sec for all temperatures

Table 9

## Data for Carbon Monoxide Diffusion Curves

Metal	Temp °C	1000 T°K	Carbon Monoxide Released Partial P mmHg	Carbon Monoxide Cumulative Total Partial P mmHg	F Fraction Released	Bt	D/a <sup>2</sup>	Log <sub>10</sub> D/a <sup>2</sup>
Ti	600	1.15	5.0x10 <sup>-9</sup>	4x10 <sup>-7</sup>	0.0125	0.00015	1.27x10 <sup>-8</sup>	-7.894
	800	0.930	6.5x10 <sup>-9</sup>	4x10 <sup>-7</sup>	0.0162	0.00024	2.03x10 <sup>-8</sup>	-7.692
	900	0.851	7.0x10 <sup>-9</sup>	4x10 <sup>-7</sup>	0.0175	0.00027	2.28x10 <sup>-8</sup>	-7.642
	1000	0.785	6.8x10 <sup>-9</sup>	4x10 <sup>-7</sup>	0.0169	0.00026	2.19x10 <sup>-8</sup>	-7.660
Zr	600	1.15	1.00x10 <sup>-8</sup>	4x10 <sup>-7</sup>	0.0250	0.00056	4.73x10 <sup>-8</sup>	-7.325
	800	0.930	1.85x10 <sup>-8</sup>	4x10 <sup>-7</sup>	0.0462	0.00189	1.23x10 <sup>-7</sup>	-6.910
	900	0.851	1.75x10 <sup>-8</sup>	4x10 <sup>-7</sup>	0.0438	0.00161	1.65x10 <sup>-7</sup>	-6.782
	1000	0.785	1.70x10 <sup>-8</sup>	4x10 <sup>-7</sup>	0.0425	0.00159	1.62x10 <sup>-7</sup>	-6.791

Time = 1200 sec for all temperatures

Table 10  
Diffusion Coefficients

Metal	Gas	Temp °C	$\frac{D}{a^2}$ (cc/cm <sup>2</sup> /sec)
Ti	Hydrogen	600	$1.4 \times 10^{-6}$
		800	$2.9 \times 10^{-6}$
		900	$3.8 \times 10^{-6}$
Zr	Hydrogen	600	$1.1 \times 10^{-6}$
		800	$2.2 \times 10^{-6}$
		900	$3.0 \times 10^{-6}$
Ti	Carbon Monoxide	600	$1.0 \times 10^{-18}$
		800	$8.3 \times 10^{-17}$
		900	$7.4 \times 10^{-16}$
Zr	Carbon Monoxide	600	$9.5 \times 10^{-24}$
		800	$1.5 \times 10^{-20}$
		900	$7.4 \times 10^{-18}$

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