

In presenting the dissertation as a partial fulfillment of the requirements for an advanced degree from the Georgia Institute of Technology, I agree that the Library of the Institute shall make it available for inspection and circulation in accordance with its regulations governing materials of this type. I agree that permission to copy from, or to publish from, this dissertation may be granted by the professor under whose direction it was written, or, in his absence, by the Dean of the Graduate Division when such copying or publication is solely for scholarly purposes and does not involve potential financial gain. It is understood that any copying from, or publication of, this dissertation which involves potential financial gain will not be allowed without written permission.

^ ^ ^ ^
U

3/17/65
b

AN INVESTIGATION OF THERMAL TRANSPIRATION
IN POROUS MEDIA

A THESIS

Presented to
The Faculty of the Graduate Division

by

James Bruce Siberts, Jr.

In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Chemistry

Georgia Institute of Technology

July, 1967

AN INVESTIGATION OF THERMAL TRANSPIRATION
IN POROUS MEDIA

Approved:

L. A. D. W.

Chairman

L. A. D. W.

Date approved by Chairman: 7/20/67

ACKNOWLEDGMENTS

The author would like to thank Dr. G. A. Miller for the suggestion of this problem and for his invaluable assistance as his thesis advisor. He would also like to express his gratitude to Dr. R. A. Pierotti and Dr. S. L. Gordon for serving as members of the thesis committee.

The author is also indebted to Dr. W. M. Spicer, Director of the School of Chemistry, for a graduate teaching assistantship and to NASA which provided support for this study.

Also, the author wishes to thank Mr. D. E. Lilly for his assistance in constructing the special glass equipment.

TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS.	ii
LIST OF TABLES	iv
LIST OF ILLUSTRATIONS.	v
SUMMARY.	vi
Chapter	
I. INTRODUCTION.	1
Description of the Effect	1
Previous Studies of Thermal Transpiration	2
Purpose of this Work.	4
II. THEORY OF THERMAL TRANSPIRATION	6
III. INSTRUMENTATION AND EQUIPMENT	15
The Thermal Transpiration Cell.	15
The Vacuum and Gas System	17
The Thermocouple System	21
Procedure	22
IV. RESULTS	27
Results at Maximum.	27
The Low Pressure Limit.	29
Comparison with Theoretical Curve	30
The Eucken Factor	32
V. CONCLUSIONS	38
VI. RECOMMENDATIONS	40
BIBLIOGRAPHY	42

LIST OF TABLES

Table	Page
1. d and $(\Delta P)_{\sigma^2/\Delta T}^{\max}$ Obtained from Thermal Transpiration Data on 8 μ Alumina Powder.	28
2. d and $(\Delta P)_{\sigma^2/\Delta T}^{\max}$ Obtained from Thermal Transpiration Data on 10 μ Glass Beads.	29
3. Eucken Factor for $\Delta T = 70^\circ\text{C}$ in 8 μ Bed.	30

LIST OF ILLUSTRATIONS

Figure		Page
1.	Thermal Transpiration Cell.	16
2.	Transpiration System.	18
3.	High Pressure System Pressure Manometer	19
4.	Low Pressure System Pressure Manometer.	20
5.	Thermocouple Circuit.	20
6.	Correlation of $(\Delta P)_{\max} \sigma^2 / \Delta T$ with Critical Temperature in 8 μ Bed	31
7.	Correlation of $(\Delta P)_{\max} \sigma^2 / \Delta T$ with Critical Temperature in 10 μ Bed.	33
8.	Low Pressure Transpiration Limit for Argon in 8 μ Bed	34
9.	Low Pressure Transpiration Limit for Hydrogen in 8 μ Bed	35
10.	Low Pressure Transpiration Limit for Helium in 8 μ Bed	36
11.	Comparison of Experimental Data with Weber Prediction.	37

SUMMARY

This study concerns the application of the Weber equation for thermal transpiration to porous media. The predictions of the equation are compared to the experimental data in two regions. The first is the pressure region where the transpiration effect is greatest. This changes with the gas. The second is the pressure region below 5 mm. Hg.

Thermal transpiration in porous media offers several advantages over capillaries. It is difficult to obtain capillaries with bores small enough to attain transpiration effects large enough to be easily and accurately measured. A porous bed can be constructed whose average pore diameter is much smaller than the diameter of the smallest easily available capillary. Therefore, because of the larger transpiration effect, a U tube manometer can be employed which is accurate, very reliable, and easy to use. Also the use of the U tube manometer is not limited to non-condensable gases as is the McLeod gauge which is commonly used at lower pressures. Its use increases the number of substances that can be studied.

A transpiration cell was constructed and the properties of two beds of packed powders were investigated. One of these beds was constructed of 8 μ alumina particles. The other was constructed of 10 μ standardized glass beads. The maximum pressure differences for a number of common gases and vapors were observed with a temperature difference of about 100 degrees Centigrade across the bed. By evaluating the Weber equation at its maximum at a fixed temperature and temperature

difference, it was found that the parameter $(\Delta P)_{\max} \sigma^2 / \Delta T$ is a constant if the equation is obeyed. $(\Delta P)_{\max}$ is the maximum transpiration effect at a given temperature, ΔT is the temperature difference across the cell, and σ is the molecular diameter. Therefore, calculation of this parameter would test the agreement of the theory and the experimental data for each compound. Substantial changes were found to occur in the parameter and these changes were observed to correlate with the critical temperature of the various compounds. Because of the association of the critical temperature with intermolecular forces, it is possible that this correlation indicates an association of the size of the thermal transpiration effect and molecular forces.

The low pressure region was investigated using argon, helium, and hydrogen. Using the approximation to the Weber differential equation

$$\frac{dP}{dT} \left(\frac{2T}{P} \right) \approx \frac{\Delta P}{\Delta T} \left(\frac{2T}{P} \right) \approx \frac{(1-P_1/P_2)}{(1-(T_1/T_2))^{1/2}} \quad (1)$$

the factor $(1-P_1/P_2)/(1-(T_1/T_2))^{1/2}$ was calculated for each point as a function of the logarithm of the system pressure. It was found that, as the pressure approached zero, the factor approached unity as is required by the thermal effusion limit or the so-called Knudsen Limiting Law.

By matching the plots for the three gases with a plot from the Weber equation, the average pore diameter of the 8 μ alumina bed was determined to be about 6.2 μ . Using this value to construct a plot of the factor, the three curves were compared with a theoretical curve constructed from the Weber equation using generalized coefficients. The similarity of these curves shows that the Weber equation describes thermal

transpiration in porous media with only limited accuracy.

As a further application, aside from the Weber equation, of the maximum transpiration effect, the translational Eucken factor was calculated using Mason's "dusty gas" model for a number of gases.

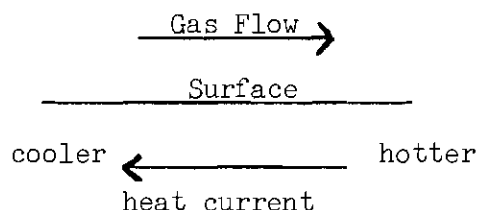
CHAPTER I

INTRODUCTION

Description of the Effect

This study is concerned with the gas transport phenomenon of thermal transpiration through porous media. This effect causes a gas to flow through a small capillary which is subjected to a temperature gradient parallel to its bore. This effect is not unique to capillaries, but occurs whenever a surface of any kind in contact with a gas is subjected to a temperature gradient.

If a temperature gradient is imposed on a surface in contact with a gas, the nonequilibrium condition at the gas surface interface causes a layer of gas about one mean free path thick to flow toward the high temperature region of the surface. The effect is illustrated diagrammatically below. This is what occurs in the capillary or pore if the



temperature gradient is applied longitudinally. If the capillary or pore is small enough or if the gas is rarefied enough, the thickness of the layer of gas flowing can be near the radius of the capillary. If this occurs a detectable pressure difference can result between the ends of the capillary.

Previous Studies of Thermal Transpiration

Thermal transpiration was discovered in 1878 by Osborn Reynolds, who observed the effect in porous plates made of stucco and meerschaum. He determined that at a given temperature gradient the magnitude of the effect was inversely proportional to the density at low pressures. The pressure ratio across the bed at low pressures obeyed the equation

$$\frac{P_2}{P_1} = \left(\frac{T_2}{T_1} \right)^{1/2} \quad (1)$$

He studied the effect using hydrogen, air, and carbon dioxide (1).

In 1879 James Clerk Maxwell published a theoretical interpretation of the effect. He pointed out that the phenomenon is basically different at low pressures than at high pressures. He defined the pressure ranges in terms of d/λ the ratio of the diameter of the capillary to the mean free path of the gas. What should properly be called thermal transpiration occurs in the high pressure range, where $d/\lambda > 10$. This effect is the consequence of momentum transfer between layers of gas near the surface. In the low pressure region, where $d/\lambda < 1$, the molecules act independently and the phenomenon is properly called thermal effusion. Maxwell's treatment was limited to the high pressure range. For a capillary he determined that the following equation should govern the effect

$$\frac{\text{Pressure Gradient}}{\text{Temperature Gradient}} = \frac{dP}{dT} = \left(\frac{c\eta}{\rho T} \right)^2 \left(\frac{1}{r^2 + 4 Gr} \right) \quad (2)$$

G is the coefficient of slip between the surface and the flowing gas, r

is the radius of the capillary, and ρ is the density of the gas (2).

Because the thermal transpiration effect is well defined only where $d/\lambda \gg 10$ and the thermal effusion effect $d/\lambda \ll 1$, the region $10 \gg d/\lambda \gg 1$ is a transition region in which the gas does not behave strictly in either manner. Sophus Weber attempted to formulate an equation which would predict this transition region. He introduced a slip coefficient containing semi-empirical constants based upon the low pressure flow measurements of Knudsen. He obtained the following equation where α , β , and μ' are semi-empirical constants and $y = d/\lambda$, where d is the capillary diameter and λ is the mean free path of the gas (3).

$$\frac{dP}{dT} = \left(\frac{P}{T}\right) \frac{1}{\alpha y^2 + \beta y + \mu'} \quad (3)$$

An approach has been developed by Mason et al. by applying classical kinetic theory diffusion equations. This method using what is known as the "dusty gas" model, assumes a binary mixture. One component is the transpiring gas and the other is the porous bed which is treated as if it were made of large molecules or dust particles which are held in place. This method predicts the phenomenon successfully. One value of this method is that it allows the calculation of the translational component of the gas's thermal conductivity which is related to its rotational relaxation time (4). Mason also extended this model to include transpiration in capillaries.

With the exception of the work of Reynolds, all experimental work reported in the literature deals with transpiration in capillaries.

Purpose of This Work

The purpose of this study was to compare the experimental data obtained from transpiration in porous media with predictions of the Weber equation. The two regions investigated were the region of the maximum effect and the low pressure region, below 5 mm. Hg. Because the pore size in the medium was much smaller than the bores of the smallest practical capillary, the transpiration effect was much larger. Consequently, it was possible to observe the pressure difference by means of a U-tube manometer which permitted the study of condensible vapors which was not possible using the standard low pressure McLeod gauge.

Since it was possible to relate the maximum transpiration effect to the molecular diameter, it was also the purpose of this study to determine if this relationship was rigorous or if deviations occurred. If deviations were observed, an attempt would be made to construct a correlation which could be used to calculate the molecular effect.

A second objective was to test the validity of the Knudsen limiting law, $P_2/P_1 = (T_2/T_1)^{1/2}$, for a porous bed at low pressures. This limit is important because some workers have observed deviations in capillaries for light gases (5,6). These deviations are believed to be the consequence of an increased number of elastic collisions occurring for these lighter gases (7). Because argon should behave ideally, by comparing the data from hydrogen and helium to that of argon, it can be determined if this deviation observed in capillaries is also seen in porous media.

Because of the ease in applying Mason's "dusty gas" model to the calculation of the translational Eucken factor, it was decided to calculate

the factor for a number of gases using the data from the maximum transpiration effect.

CHAPTER II

THEORY OF THERMAL TRANSPIRATION

The first and most detailed study of thermal transpiration was published by James Clerk Maxwell in 1879 as an appendix to a larger work on thermal stresses in gases. This study is the first application of modern kinetic theory to a nonequilibrium phenomenon (8).

Maxwell's study dealt in detail only with the high pressure case where $d/\lambda \gg 10$. In this region, the thermal transpiration effect depends upon the existence of an adsorbed and evaporated gas at the surface of the solid. This gas is the result of inelastic collisions at the surface during which the molecule may become temporarily attached. The effect at high pressures depends upon this type of collision known as a diffuse collision, in which the molecule accommodates with the surface and eventually rebounds in a random direction.

The low pressure phenomenon is of a different nature. It is more properly known as thermal effusion than thermal transpiration and occurs where $d/\lambda \ll 1$. In this region it is possible that a molecule can pass through the pore or capillary without colliding with another molecule. The steady state conditions, therefore, depend principally on the bulk gas temperature at either end of the capillary or pore. This effect obeys the equation formulated by Reynolds in 1878:

$$\frac{P_2}{P_1} = \left(\frac{T_2}{T_1} \right)^{1/2} \quad (1)$$

Maxwell knew that if a surface is perfectly reflecting it is impossible for the gas to exert a tangential force upon the surface. He assumed therefore that some collisions were inelastic, leading to the existence of a gas near the surface which is in thermal equilibrium with it. Consequently, near the surface a difference in temperature occurs between the bulk gas and the surface gas.

If we consider the surface again, we can assume that for a given area that some fraction, f , of all molecules approaching the surface are adsorbed and allowed to evaporate while $1-f$ of the molecules are reflected. Maxwell then wrote particle and momentum balances considering a single gas approaching the surface but a reflected and evaporated gas rebounding.

Maxwell now constructed a distribution function which would take into account the discontinuity in temperature which occurs in going from the bulk gas to a point near the surface. A Boltzmann distribution modified by a perturbation was used. Maxwell wrote

$$E = (1 + F(\dot{x}, \dot{y}, \dot{z})) h^{3/2} \Pi^{-3/2} e^{-h(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)} \quad (2)$$

where E is the perturbed Boltzmann distribution, $F(\dot{x}, \dot{y}, \dot{z})$ is the perturbation, h is $1/LT$ where T is the absolute temperature and L is a constant which depends on the gas being considered. Π has its usual mathematical meaning and \dot{x}, \dot{y} , and \dot{z} are the velocity components of the particle along the respective axes. The perturbation $F(\dot{x}, \dot{y}, \dot{z})$, which is small compared to unity, was expanded in half integral powers of h , introducing nineteen parameters. Systematically, each of these parameters was evaluated by normalization and from the dynamical and statistical relationships for the gas.

Maxwell then used the above results in conjunction with classical fluid mechanics to obtain the following equation for transpiration in a capillary:

$$\frac{Q}{\Pi \rho r^2} + \frac{1}{8\eta} (r^2 + 4 Gr) \frac{dp}{dz} - \frac{3}{4} \left(\frac{\eta}{\rho T} \right) \frac{dT}{dz} = 0 \quad (3)$$

In the above equation Q is defined as the flow rate at steady-state conditions, dp/dz is the pressure gradient and dT/dz is the temperature gradient both along the bore of the capillary, ρ is defined as the density of the gas, r as the radius of the capillary, η is the viscosity of the gas and T is defined as the absolute temperature at the point the differential equation is evaluated. The quantity G is the coefficient of slip which Maxwell determined to be equal to

$$1/2 \eta \left(\frac{2 \Pi}{\rho p} \right)^{1/2} \left(\frac{2}{f} - 1 \right) \quad (4)$$

where p is the pressure and f is the fraction of the molecules adsorbed per collision with the surface; ρ is defined as the density, and Π has its usual mathematical meaning. To calculate the steady-state situation Maxwell set the net flow equal to zero and obtained the following equation:

$$\frac{dP}{dT} = \frac{6\eta^2}{\rho T} \left(\frac{1}{r^2 + Gr} \right) = \frac{\text{pressure gradient}}{\text{temperature gradient}} \quad (5)$$

where the symbols have the same meaning as defined above. This was

Maxwell's final thermal transpiration equation for a capillary subjected to an axial temperature gradient (9).

Sophus Weber desired to extend the Maxwell equation for the high pressure region into the transition region. He joined the theoretical equation of Maxwell with low pressure flow data of Knudsen. Because it is possible to calculate the coefficient of slip from capillary flow data, Weber was able to use Knudsen's flow data to calculate an empirical coefficient of slip (10). He obtained an equation of the form:

$$G = k_2 \lambda \left(1 + q \frac{\lambda}{r} \right) \quad (6)$$

where λ is the mean free path and k_2 and q are empirical constants. If we set $Q = 0$ in equation (6) at steady-state conditions, introduce equation (8) as the expression for the slip coefficient, and insert another empirical constant k_1 before the thermal slip expression $3 \mu / 4 \rho T$, we obtain by arranging terms and applying the chain rule of calculus the following equation:

$$\frac{dp}{dT} = \left(\frac{6\eta^2}{\rho T} \right) \frac{1}{\frac{1}{k_1} r^2 + 4 \frac{k_2}{k_1} \lambda r + 4 q \frac{k_2}{k_1} \lambda^2} \quad (7)$$

Weber then substituted the mean free path into the equation using the following relationship:

$$\lambda \approx \eta \left(\frac{\Pi}{2p\rho} \right)^{1/2} \quad (8)$$

We rearrange the mean free path expression to obtain $\eta^2/\rho = 2P \lambda^2/\Pi$ and substituting $d = 2r$, we find that the transpiration equation becomes:

$$\frac{dP}{dT} = \frac{P}{2T} \frac{1}{\frac{\Pi}{96} \frac{1}{k_1} \left(\frac{d}{\lambda}\right)^2 + \frac{\Pi}{12} \frac{k_2}{k_1} \left(\frac{d}{\lambda}\right) + \frac{\Pi}{6} \frac{k_2}{k_1} q} \quad (9)$$

Experimentally, Weber found that generalized values could be calculated from the data of several gases. He determined that $k_1 \approx k_2 \approx 4/3$ and $\mu' = \Pi k_2 q/k_1 \approx 1.25$. The Weber equation with generalized coefficients can be written:

$$\frac{dP}{dT} = \frac{P}{2T} \frac{1}{\frac{\Pi}{128} y^2 + \frac{\Pi}{12} y + \mu'} = \frac{P}{2T} \frac{1}{\alpha y^2 + \beta y + \mu'} \quad (10)$$

where $y = d/\lambda$. It is this equation, developed for capillaries, which this work seeks to apply to porous media (11). This equation applies only to the region where $d/\lambda \gg 10$. At lower pressures μ' should approach unity, as required by the Knudsen limiting law, which in differential form is $dP/dT = P/2T$. Therefore in a later work Weber introduced the variable y into an expression for μ' so that $y \rightarrow 0$, $\mu' \rightarrow 1$ (12). Therefore he wrote:

$$\mu' = \frac{1 + gy}{1 + hy} \quad (11)$$

where $g/h = 1.25$ and $g-h+\beta = 1$ or $3/4$ so that as $y \rightarrow 0$, $\mu' \rightarrow 1$.

Miller in 1963 found that the Weber equation could be used to construct a generalized plot on which data from different gases and experiments could be compared (13). Starting with the Weber equation and using the generalized coefficients, he made the following finite difference approximation:

$$\frac{dP}{dT} \frac{2T}{P} \approx \frac{\Delta P}{\Delta T} \left(\frac{2T}{P} \right) \approx \frac{1}{\alpha y^2 + \beta y + \mu'} = \Pi \quad (12)$$

Miller then approximated the finite difference in the following manner:

$$\frac{\Delta P}{\Delta T} \frac{2T}{P} \approx \frac{(1 - P_1/P_2)}{(1 - (T_1/T_2)^{1/2})} \approx \Pi \quad (13)$$

If the factor $(1 - (P_1/P_2)) / (1 - (T_1/T_2)^{1/2})$ is plotted as a function of y for all gases the data will fall on a single generalized curve. This approximation obeys the thermal effusion limit in that it approaches unity as y or the system pressure approaches zero.

The application of kinetic theory diffusion equations offers an alternate theoretical approach. This is the method investigated by Mason in his "dusty gas" model. This method leads to a direct means of calculating the translational Eucken factor. The Eucken factor was introduced in an attempt to treat the thermal conductivity of a gas as a sum of the conductivity due to molecular motion and that due to energy carried internally by the molecule. Eucken separated the the thermal conductivity λ into two components (14). He wrote

$$\lambda = \lambda_i + \lambda_{tr} \quad (14)$$

where λ_i is the thermal conductivity due to energy carried internally and λ_{tr} that due to translational motion. In the general development of the transport properties in a gas from kinetic theory a constant appears when the thermal conductivity is related to the viscosity. This constant arises because of the correlation between the energies of molecules and their velocities. Thus the kinetic theory indicates

$$\lambda = f \eta \bar{C}_v \quad (15)$$

where f is the constant known as the Eucken factor, λ the total thermal conductivity, η the viscosity, and \bar{C}_v the heat capacity at constant volume. Eucken also separated \bar{C}_v into translational and internal components

$$\bar{C}_v = \bar{C}_{vtr} + \bar{C}_{vi} \quad (16)$$

where \bar{C}_{vtr} is the heat capacity component due to translational motion and \bar{C}_{vi} is the component due to excitation of internal energy levels.

The Eucken factor may be calculated for a monatomic gas by means of the Chapman-Enskog theory. This theory is a method of solving the Boltzmann transport equation by assuming that the solution is an infinite series and solving for each term by a method of successive approximations. If it is assumed that all collisions are classical and elastic, a value of $5/2$ is obtained for the Eucken factor. If the collisions in a gas are classical and elastic, the internal component of the heat capacity is zero. Because no energy may be carried in excited internal energy levels, the internal component of the thermal conductivity must also be zero. Therefore, the relationship between the thermal conductivity, the heat capacity, and the viscosity may be written

$$\lambda_{tr} = 5/2 \eta \bar{C}_{vtr}$$

The $5/2$ is now known as the translation Eucken factor, f_{tr} . Therefore, the equation becomes

$$\lambda_{tr} = f_{tr} \eta \bar{C}_{vtr}$$

where $f_{tr} = 5/2$ if the collisions in the gas are elastic and classical (14). It has been shown that the force exerted by a heat conducting gas on a body is proportional to λ_{tr} . Consequently, it is not surprising that λ_{tr} can be related to the transpiration effect. This relation is obtained from Mason's "dusty gas" model (15).

The importance of the translational Eucken factor lies in its dependence upon the nature of the collisions in the gas. Its value is 2.50 if all the collisions in a gas are elastic and classical. In many gases internal energy levels can be excited so that all collisions are not elastic. In these cases this effect is observed as a reduction in the value of the translational Eucken factor. Consequently, a knowledge of the factor gives insight into the nature of the collisions in the gas being studied.

Mason shows that this factor may be calculated for any gas by comparing its transpiration data at the maximum with that of a gas whose collisions are known to be classical. Argon is such a gas and consequently its translational Eucken factor is 2.50. Using this information, it is possible to construct a ratio containing only the quantities in the equation below.

$$F = (0.8743) \left(\frac{\eta_{AR}}{\eta} \right) \left(\frac{M}{M_{AR}} \right)^{1/2} \left(\frac{\Delta P_{AR}^{max}}{\Delta P_{AR}^{max}} \right) \quad (17)$$

We define M and M_{AR} as the molecular weights, η and η_{AR} as the viscosities, and ΔP^{max} and ΔP_{AR}^{max} as the maximum transpiration effects at a given system pressure and temperature difference for the gas being studied and argon, respectively. The quantity F is defined

$$F = f_{tr} \left(1 + (9 f_{tr}/808)^{1/2} \right)^{-2} \quad (18)$$

where

$$\delta = 3 \Pi / 16 \quad (19)$$

and f_{tr} is the translational Eucken Factor for the gas being studied. All of the above quantities are measured or calculated at the same conditions. If we substitute the Maxwell-Chapman expression based upon the same assumption of elastic solid and spherical particles (17)

$$\eta = 0.499 \frac{2 (M k T)^{1/2}}{\Pi^{3/2} \sigma_T^2} \quad (20)$$

where σ_T is the molecular diameter, M the weight of a single molecule, T the temperature, and k Boltzmann's constant, we obtain

$$F = (0.8743) \frac{(\sigma_T)^2}{(\sigma_T^{AR})} \frac{T_{AR}}{T}^{1/2} \left(\frac{\Delta P^{max}}{\Delta P_{AR}^{max}} \right) \quad (21)$$

σ_T and σ_T^{AR} are the molecular diameters and T and T_{AR} are the average temperatures of the gas being studied and argon, respectively.

CHAPTER III

INSTRUMENTATION AND EQUIPMENT

The Thermal Transpiration Cell

The first goal of this research was the construction of a cell containing a porous medium housed so that accurate measurements could be made of the temperatures, system pressure, and thermal transpiration pressure differences. Also the cell had to be heated so that a temperature gradient could be maintained and varied. The heat capacity of the cell had to be large compared to the gas contained in the cell and which flows through it as it reaches steady state. This prevented large temperature fluctuations as the gas was introduced and reduced the time between successive measurements. It was also required that the pores be large enough to allow a reasonable time to reach steady state.

The cell was constructed as shown in Figure 1. The porous medium in the form of a fine powder was packed between the two sintered glass discs. The lower disc was fused to the glass wall. The other was removable and was held in place by the weight of the brass plug. Both glass discs were penetrated by screws which held them to the brass plugs and served to secure two thermocouple wires. The thermocouples were welded chromel alumel which were placed on the surface of the glass discs next to the porous medium. The passage for the thermocouple wires through the brass plug was insulated by glass tubes. The thermocouple wires passed out of the cell through Apiezon black wax seals.

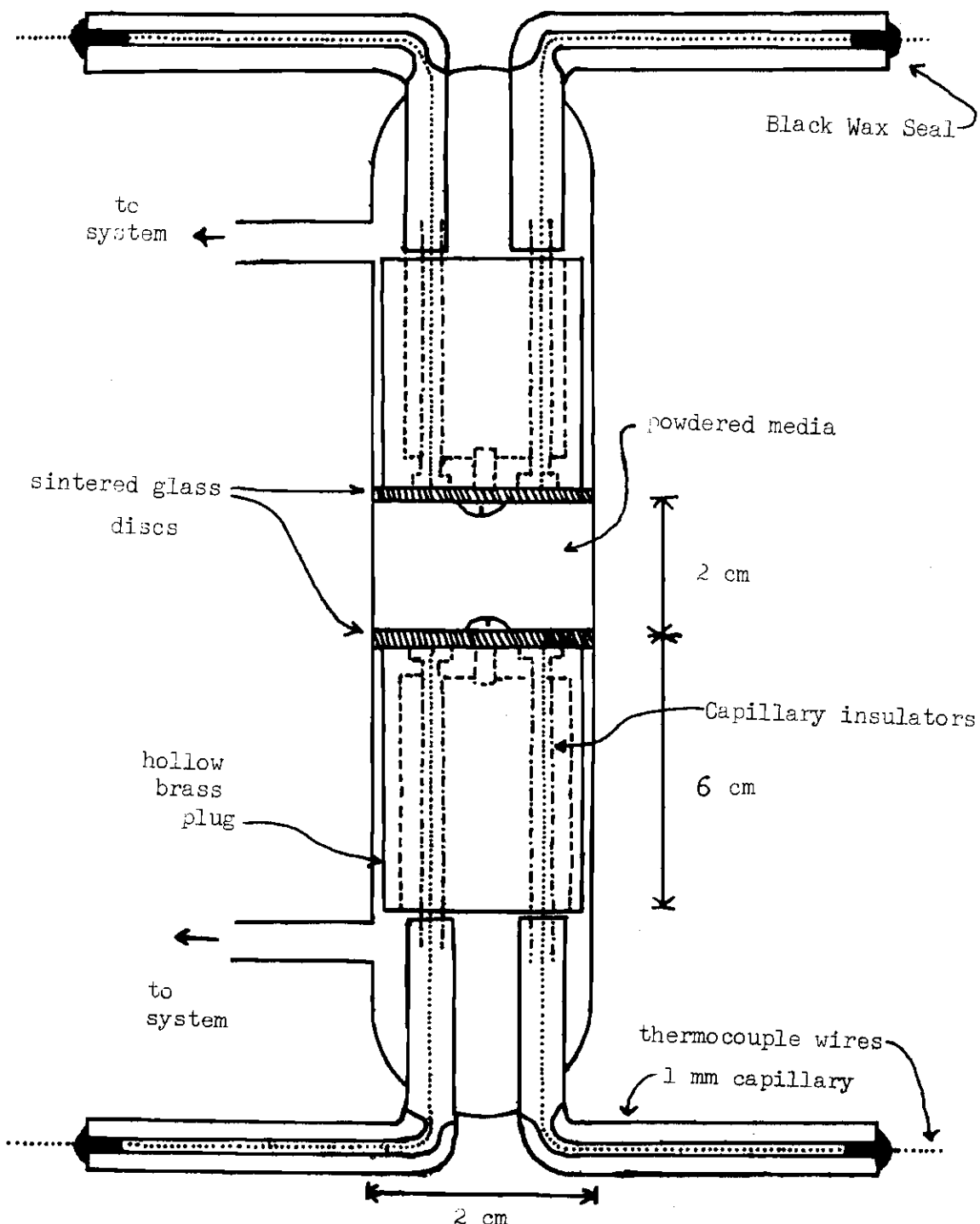


Figure 1. Thermal Transpiration Cell

The brass plugs were felt to be necessary to increase the heat capacity of the cell and to stabilize the temperature gradient when gas flowed through the cell. The face of each plug was cross-hatched to allow the gas to flow across the entire area of the sintered glass disc. The brass plugs were bored out to decrease their weight.

The temperature gradient was created and maintained by a small resistance heater which was controlled by a variac. The heater was wrapped in glass wool and surrounded by asbestos paper.

The Vacuum and Gas System

This study required that the cell be connected so that it was possible to observe the pressure difference across the cell which results from transpiration and the absolute system pressure on one side of the cell. Also, it was necessary to provide a means for evacuating the system and for controlling the introduction of the gas to be studied.

The system pressure and transpiration effect were measured by means of manometers which were connected together in a self-contained system which could be isolated from the rest of the system. This unit is shown in Figure 2. Since it was desired to observe the phenomenon at pressures from 760 mm. Hg to 1 mm. Hg, two manometers were used. One was mercury filled for use between 760 mm. Hg and 5 mm. Hg as shown in Figure 3. This manometer was read by means of a meter stick. The manometer for the measurement of pressures below 5 mm. Hg was oil filled and is shown in Figure 4. It was filled with Cenco HYVAC oil of density 0.8983 gm/ml at 25°C and was read by means of a Gaertner M 940 cathetometer. When the left side of the oil manometer was pumped out, it was

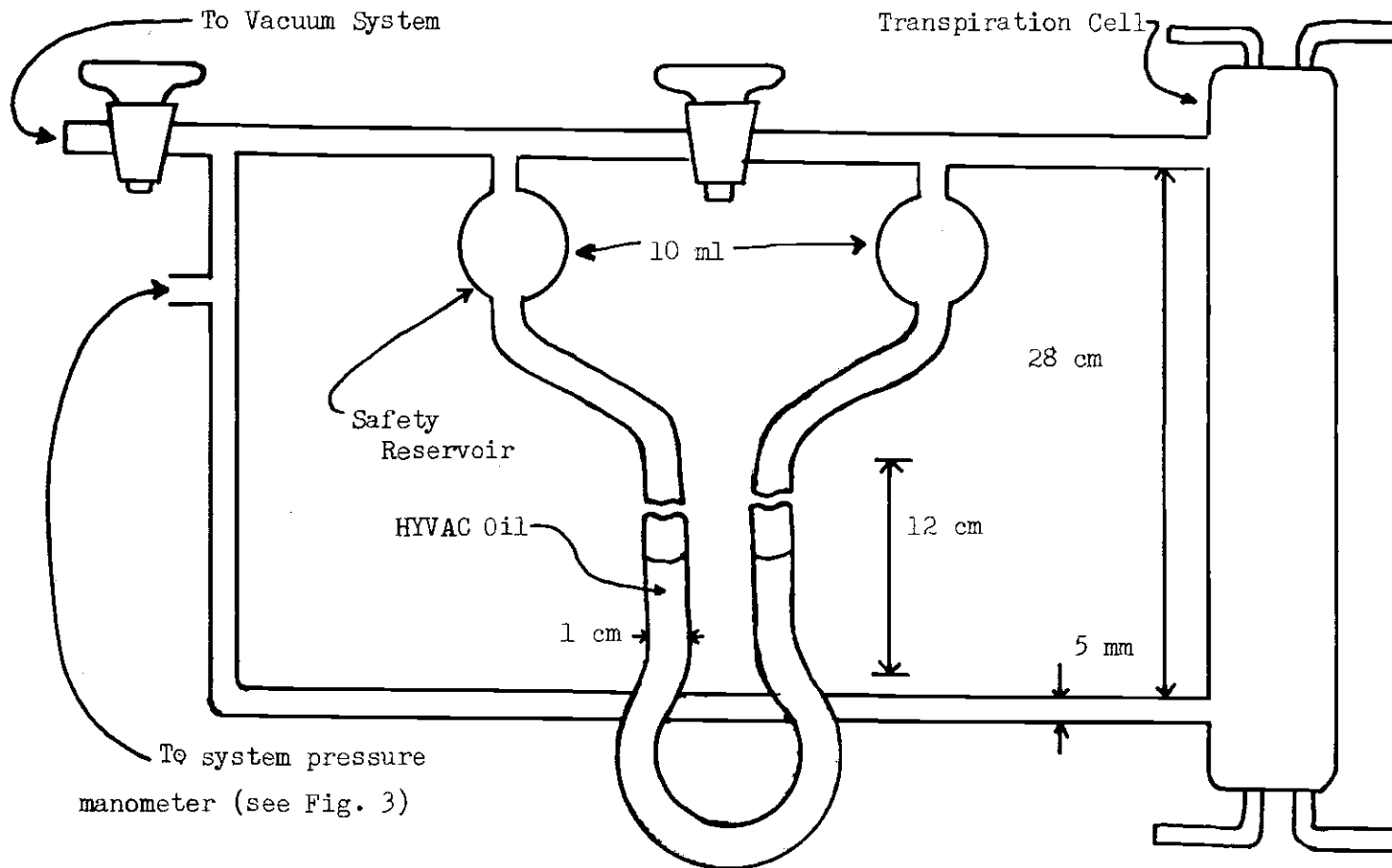


Figure 2. Transpiration System

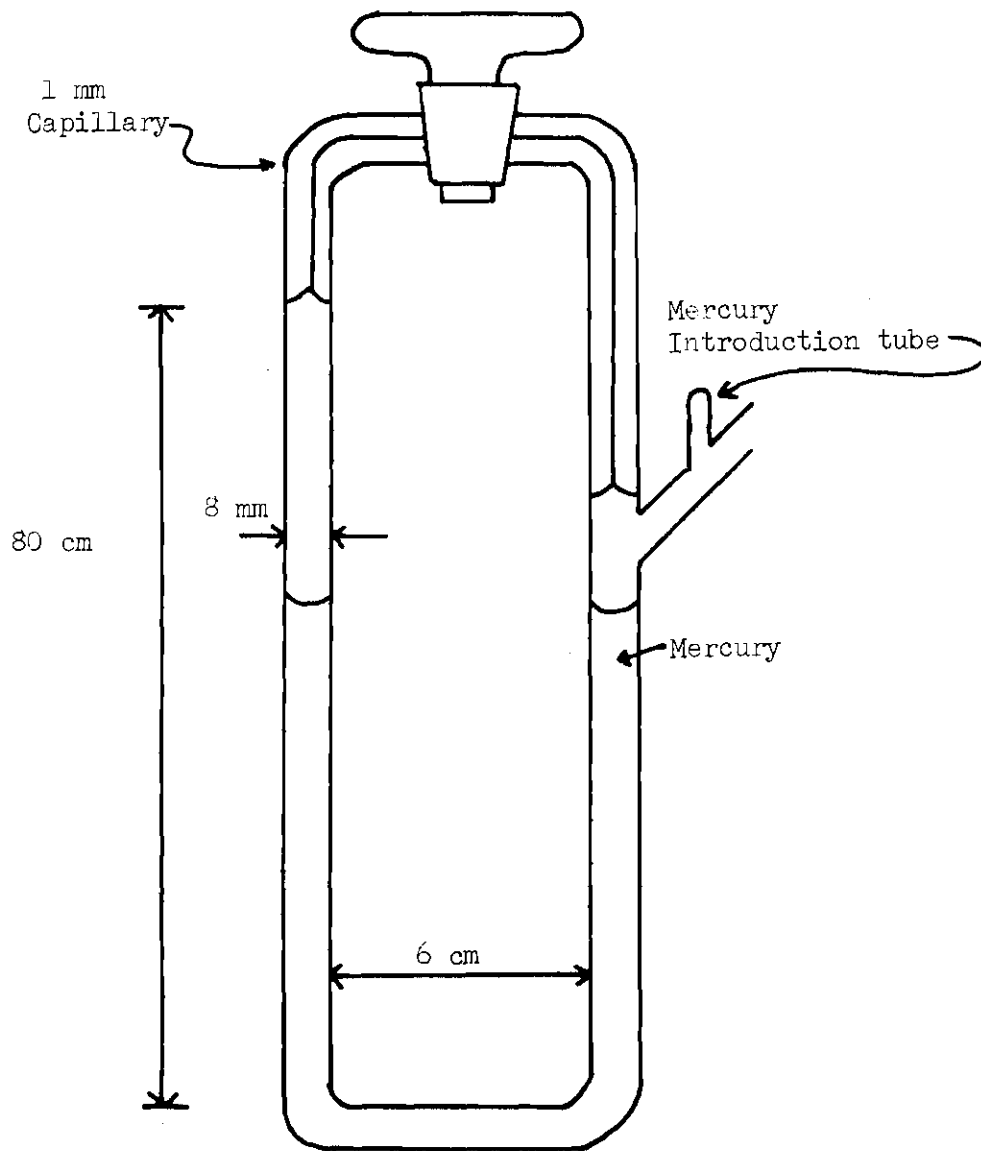


Figure 3. High Pressure System Pressure Manometer.

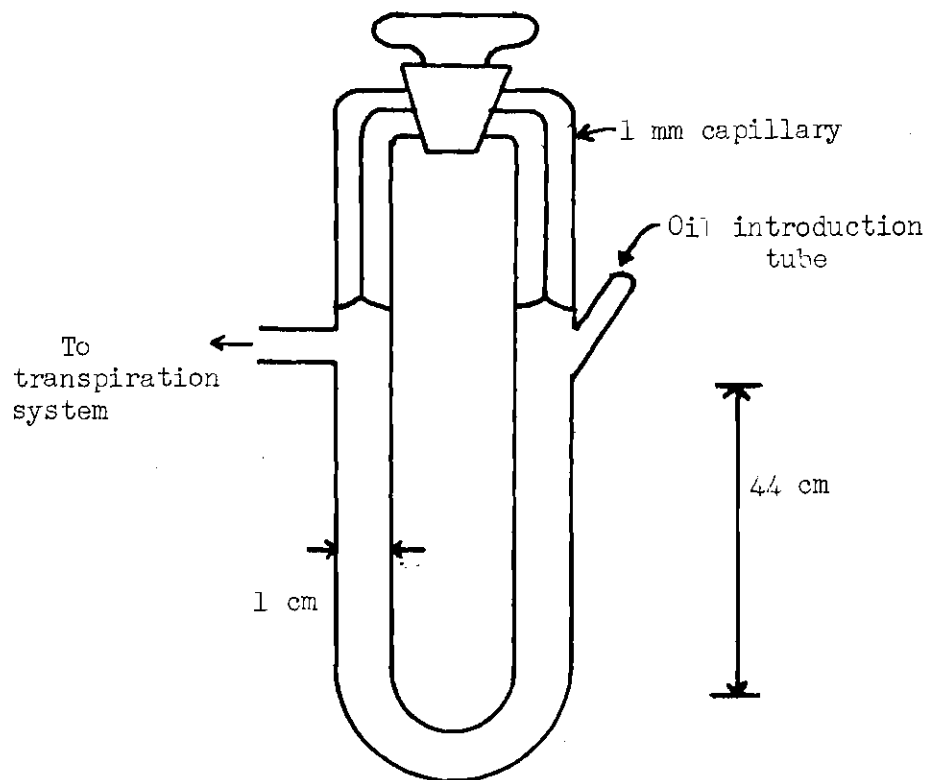


Figure 4. Low Pressure System Pressure Manometer.

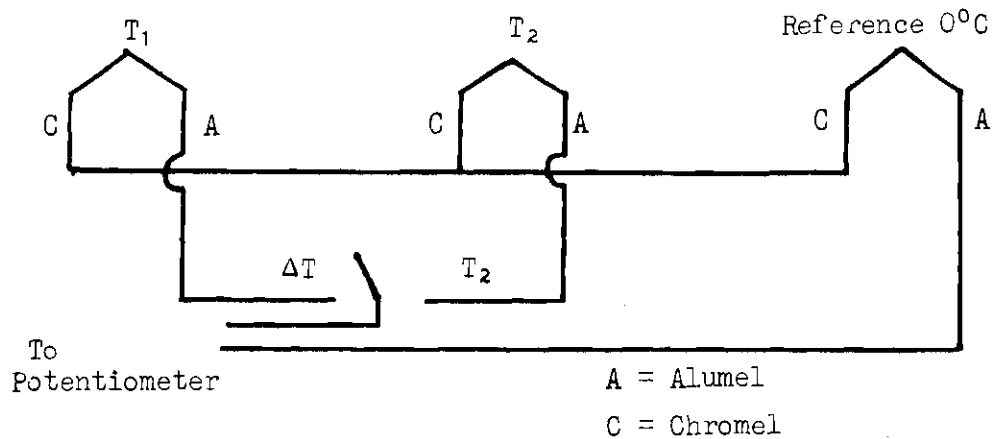


Figure 5. Thermocouple Circuit.

found that the oil was slightly permeable to the gases being studied. Therefore, after each measurement, both sides of the manometer were evacuated to prevent an accumulation of gas which would cause errors in the system pressure measurement.

The pressure difference across the medium was measured using the manometer shown in Figure 2. The stopcock between the U tube allowed the gas to be studied to be introduced into both sides of the tube quickly without blowing the oil from the manometer. The two bulbs on each side of the U were safety reservoirs which retained the oil in case of sudden changes in system pressure when the stopcock was closed. This manometer was filled with the same kind of oil as the system pressure manometer.

The introduction of the gas to be studied was accomplished by means of the pipette system. The gas was first introduced into a manifold from the cylinder or from a boiling liquid. It was then expanded into the large volume of the pipette from which smaller volumes were introduced into the system until the desired system pressure was reached.

The apparatus was equipped with a Cenco mechanical vacuum pump and a mercury diffusion pump for evacuation of the system. The system pressure at low pressures was determined by means of a thermocouple gauge.

The Thermocouple System

The two Chromel Alumel thermocouples were connected with a reference thermocouple which was held at 0°C by means of an ice-water bath in a Dewar flask. The circuit is shown in Figure 5. Using a potentiometer direct readings of the temperature difference across the cell and the

temperature of the cooler side of the cell could be made.

Procedure

The first objective of this study was to measure the maximum transpiration effect and to ascertain if there is a systematic deviation from what the Weber equation predicts. Therefore, it became necessary to put the equation in a form which will apply particularly to the maximum. Writing the equation, we have:

$$\frac{\Delta P}{\Delta T} \approx \frac{dp}{dT} = \frac{P}{2T} \frac{1}{\alpha y^2 + \beta y + \mu'} \quad (1)$$

where the α , β , and μ' are Weber's generalized coefficients. If we make a finite difference approximation, we obtain the following equation.

$$\Delta P \approx \frac{P\Delta T}{2T} \frac{1}{\alpha y^2 + \beta y + \mu'} \quad (2)$$

Now we wish to evaluate this equation at the maximum. Therefore we must take the derivative of the above equation with respect to the system pressure P and equate to zero. However, if μ' is considered a variable the algebra becomes very difficult. Because μ' varies only slightly with large changes in the system pressure, it may be considered a constant for the purposes of differentiation. Differentiating Equation (2), equating to zero, and collecting terms, we obtain the following equation.

$$y_{\max} = \sqrt{\frac{\mu'}{\alpha}} \quad (3)$$

(Because μ' is a function of y which is a variable in the resulting equation, the value of μ' consistent with the maximum of y can best be found by iteration until a value of y is found which calculates a value of μ' which is consistent with the value chosen to calculate the initial y .) If we choose $\mu' = 1.24$, we obtain a value for y of 7.1. This recalculates a value for μ' of 1.28. Now we write the equation at the maximum in the form:

$$(\Delta P)_{\max} = \frac{(P\Delta T)}{2 T} \frac{1}{\alpha y_{\max}^2 + \beta y_{\max} + \mu'} \quad (4)$$

If we write the expression for y substituting the kinetic theory expression for the mean free path, we obtain the equation:

$$y = \frac{d}{\lambda} = \frac{P_2 d \Pi 2^{1/2} \sigma^2}{k T} = \frac{P_2 d \sigma^2}{2.33 T} \times 10^3 \quad (5)$$

where the units of P are mm. Hg, σ^2 is the molecular diameter, in angstroms, d in millimeters, and T in degrees Kelvin. Using equation (5) to substitute for P/T in equation (4), we obtain equation (6).

$$(\Delta P)_{\max} \approx \frac{\Delta T y_{\max} (2.33)}{[2 d \sigma^2] \times 10^3} \left[\frac{1}{\alpha y_{\max}^2 + \beta y_{\max} + \mu'} \right] \quad (6)$$

Substituting the numerical values for the generalized coefficients, we obtain for the Weber equation evaluated at maximum,

$$(\Delta P)_{\max} \approx \frac{\Delta T}{d\sigma} \left[2 \times 10^{-3} \right] \quad (7)$$

Using the cell described in the equipment section, measurements were first made on a packed medium of standardized 10 μ glass beads. The maximum transpiration effect was measured at a temperature difference of 100°C for a number of gases. The gases observed were ethylene, ethane, nitrogen, argon, carbon dioxide, and helium. Using the equation developed at the maximum from the Weber equation, equation (6), the average effective pore diameter was calculated for each gas. The molecular diameter squared was obtained from the equation,

$$\sigma_T^2 = \sigma_w^2 \left(1 + \frac{C}{T} \right) \quad (8)$$

where σ_w and C are constants depending on the gas (18). The effect obtained from the 10 μ glass beads was smaller than anticipated.

Because of the small effect obtained from the 10 μ glass beads, the maximum effect for the larger molecules was too small to be observed accurately. Therefore, a powder of irregular 8 μ alumina was substituted. The average effective pore diameter was found to be smaller. The larger effect under similar temperature conditions enabled data to be obtained for larger molecules. Consequently, in addition to the gases whose effect was studied using the 10 μ bed, additional compounds were studied using the 8 μ alumina bed. A listing of the data obtained at the maximum is found under Results.

Because the transpiration curve is very flat near the maximum, in this part of the work only a precise determination of the transpiration effect was necessary. Therefore, a mercury manometer was used to observe the system pressure. The transpiration effect was read on the oil

manometer by means of a cathetometer which could read differences to 0.005 cm.

It was also desired to compare the transpiration data from the porous bed to the predication of the Weber equation for capillaries. This comparison was made for a number of gases by constructing plots of the logarithm of Miller's parameter Π as a function of the logarithm of y , the ratio of the mean free path of the gas to the pore diameter. These plots were then compared to a similar plot obtained from the Weber equation using the generalized coefficients. By means of the equation

$$\Pi = \frac{(1 - P_1/P_2)}{\left[1 - \left(\frac{T_1}{T_2}\right)^{1/2}\right]} = \frac{\frac{\Delta P}{P_2}}{\left[1 - \left(\frac{T_1}{T_2}\right)^{1/2}\right]} \quad (9)$$

where ΔP was the transpiration effect and P_2 was the pressure on the high pressure side of the cell, the parameter was easily calculated from the data. The calculation of y , however, was more complicated and required an estimate of the pore diameter in addition to the data. From the expression for y in terms of the kinetic theory mean free path, (19),

$$y = \frac{d}{\lambda} = \frac{P_2 d \sigma^2}{2.33 T} \times 10^3 \quad (10)$$

it was seen that the logarithm of y and the logarithm of the pressure P_2 were related to each other by the logarithm of the remaining variables and constants. Among these only d was not known. Therefore, by fitting

each curve to the theoretical curve, the value of the constant containing d was obtained. Using this value of d we calculated y for each data point and constructed the plots and observed the limiting values of Π .

CHAPTER IV

RESULTS

Results at Maximum

The first objective of this work was to measure the maximum transpiration effect of a number of substances and to test the altered Weber equation at that point. The form of the equation used is:

$$(\Delta P)_{\max} \approx \frac{(.002)\Delta T}{d \sigma^2} \quad (1)$$

Two quantities, d and the parameter $(\Delta P)_{\max} \sigma^2 / \Delta T$, were calculated from this equation. This parameter is a constant if the generalized Weber equation is obeyed at the maximum. This was done for a number of substances for both the 8 μ alumina bed and the 10 μ glass beads. The results are tabulated in Tables 1 and 2.

A definite pattern is observed. The parameter becomes smaller as the critical temperature becomes larger. This correlation can be seen in Figures 6 and 7. Consequently, helium and hydrogen see very small pores while to other gases the pores seem larger. The variations result from changes in the generalized coefficients which are multiplied into the factor .002. The basis of the Weber equation is the introduction of these semi-empirical constants into the Maxwellian slip coefficient and into the Maxwellian slip. Therefore, the use of the generalized α , β , and μ' preclude the possibility of individualized correction. However, Figures 6 and 7 show a definite relation between the factor and

Table 1. d and $(\Delta P)_{\max} \sigma^2 / T$ Obtained from Thermal Transpiration Data on 8μ Alumina Powder.

	d (Microns)	$(\Delta P)_{\max} \sigma^2 / \Delta T$	T_c ($^{\circ}K$) (Critical Temperature)
CH_3Br	13.9	0.144	----
CH_4	13.1	0.153	190.7
CH_3CH_3	13.8	0.147	305
Ar	12.8	0.156	151
CH_3Cl	15.3	0.131	416.4
He	7.1	0.282	----
$N-CH_3(CH_2)_4CH_3$	13.9	0.144	470
N_2	12.4	0.162	126
CH_2CH_2	13.8	0.145	283
CO_2	14.5	0.138	304
H_2	7.46	0.268	----
AR	11.8	0.171	151
CCl_4	12.6	0.159	455
Air	12.2	0.165	132
$N-C_6H_{14}$	14.4	0.139	508
C_6H_6	14.2	0.141	562
CH_3Cl	14.4	0.138	416.4

Table 2. d and $(\Delta P)_{\max} \sigma^2 / \Delta T$ Obtained from Thermal Transpiration Data on 10^{-4} μ Glass Beads.

	d (Microns)	$(\Delta P)_{\max} \sigma^2 / \Delta T$	T_c ($^{\circ}$ K) (Critical Temperature)
CO ₂	39.4	.0507	304
CH ₄	28.1	.071	191
AR	30.8	.065	151
He	11.6	.172	---
N ₂ ($\Delta T = 148^{\circ}$ C)	30.5	.0657	126
Air	30.1	.054	305
C ₂ H ₆	38.4	.052	283
N ₂ ($\Delta T = 98^{\circ}$ C)	32.6	.0614	126

the critical temperature. Because the critical temperature is associated with inter-molecular forces it may be possible that this variation is associated with the inter-molecular and surface-molecule forces.

It should be noted that the value of the parameter for carbon tetrachloride rose about 0.15 units above the typical value for compounds similar critical temperatures. This deviation may result because carbon tetrachloride possessing a higher degree of symmetry than the surrounding compounds behaves more as a hard sphere than N-pentane or benzene.

The Low Pressure Limit

The second part of this study involved the application of the Weber equation to the low pressure region. This is concerned with the behavior of the parameter $(1-P_1/P_2)/(1-(T_1/T_2))^{1/2}$ as the system pressure approaches zero. Using the oil manometer the parameter was calculated for argon, hydrogen, and helium. The results can be seen in Table 3

and in Figures 8, 9, and 10. As the system pressure approaches zero it can be seen that $(1-(P_1/P_2))/(1-(T_1/T_2)^{1/2})$ approaches one. Therefore, in the 1 mm. Hg. pressure range the transpiration effect has very nearly approached the free molecular region of thermal effusion where the parameter would be equal to unity.

Table 3. Eucken Factor for $\Delta T = 70^\circ\text{C}$ in 8μ Bed.

	$\sigma^2(\text{\AA})^2$	$\Delta P_{\text{max}}/\Delta P_{\text{AR}}$	F	f_{tr} (Eucken Factor)
AR	12.6	1.00	0.874	2.50
CO ₂	19.1	0.596	0.789	2.10
C ₂ H ₄	22.8	0.494	0.781	2.07
CH ₄	16.4	0.743	0.862	2.45
C ₂ H ₆	26.2	0.423	0.739	1.86
CH ₃ Br	30.7	0.378	0.802	2.17
CH ₃ Cl	25.4	0.397	0.695	1.71
C ₆ H ₆	50.6	0.199	0.697	1.71

Comparison with Theoretical Curve

From the generalized plot for $(1-P_1/P_2)/(1-(T_1/T_2)^{1/2})$ as a function of y , we calculate the average pore size by comparing the entire curve using both the data from the maximum region and from the low pressure range to construct the curve. For the 8μ alumina bed we obtained $d = 7.10 \mu$ for hydrogen, 6.62μ for argon, and 5.42μ for helium.

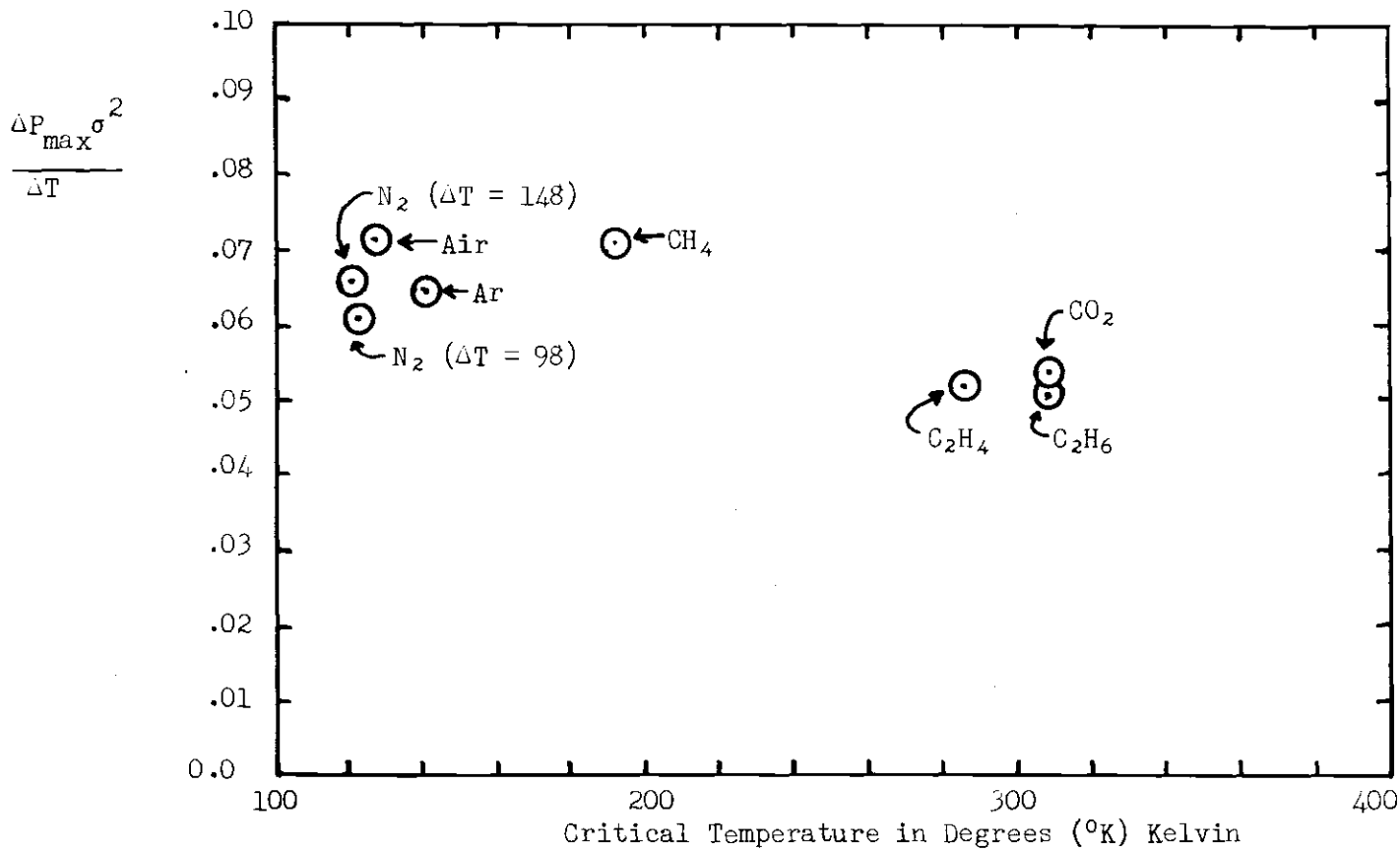


Figure 6. Correlation of $(\Delta P)_{\max} \sigma^2 / \Delta T$ with Critical Temperature in 8 μ Bed.

Choosing the value of $d = 6.20 \mu$ for the pore diameter, a generalized plot was constructed as shown in Figure 11. A value for d close to argon was used because it was mid-way between helium and hydrogen, and because argon should behave strictly as a classical hard sphere. The theoretical curve was constructed using the generalized α , β , and μ !. This curve shows that any theory must allow the coefficients to vary with the gas.

The Eucken Factor

Using the "dusty gas" model of Mason, the Eucken factor was calculated for gases for which data was obtained from the 8μ alumina bed. The results of the calculations are tabulated in Table 3.

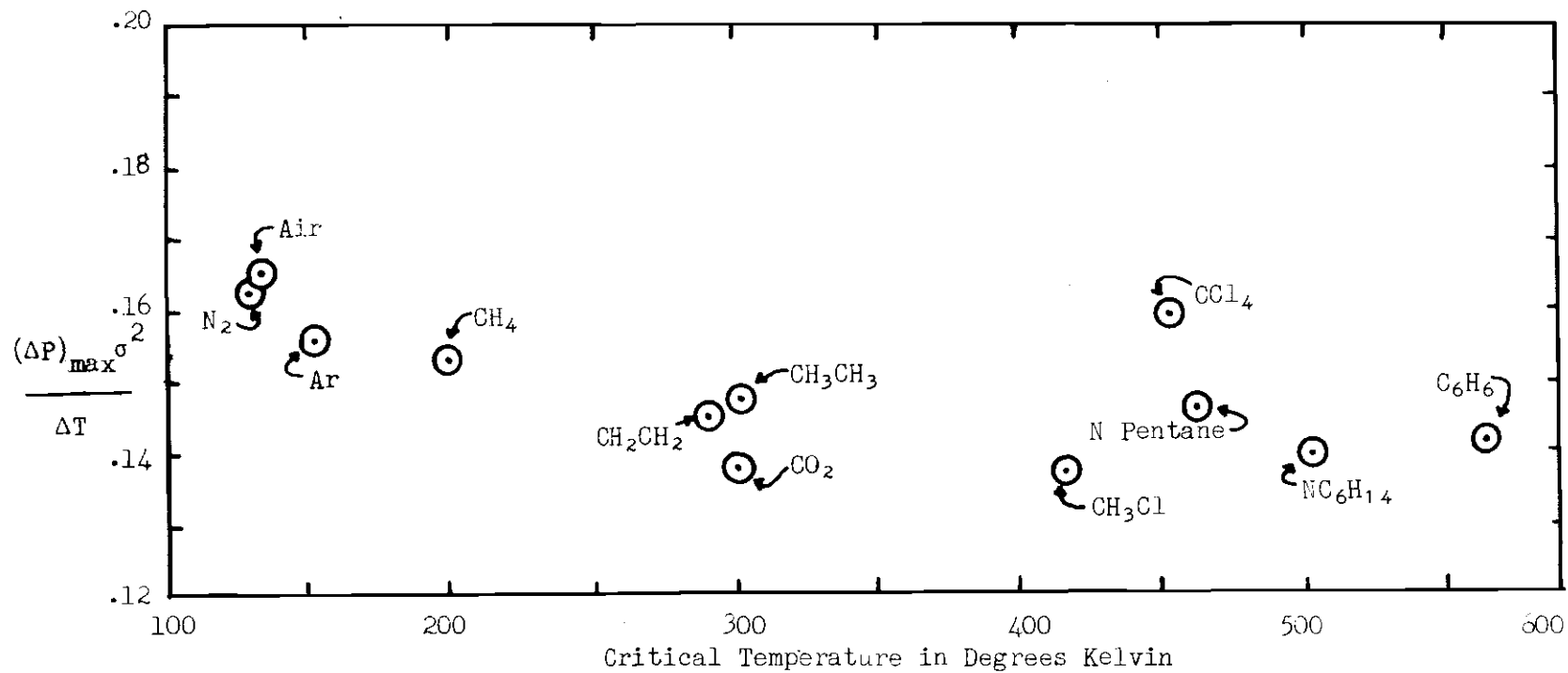


Figure 7. Correlation of $(\Delta P)_{\max} \sigma^2 / \Delta T$ with Critical Temperature in 10μ Bed.

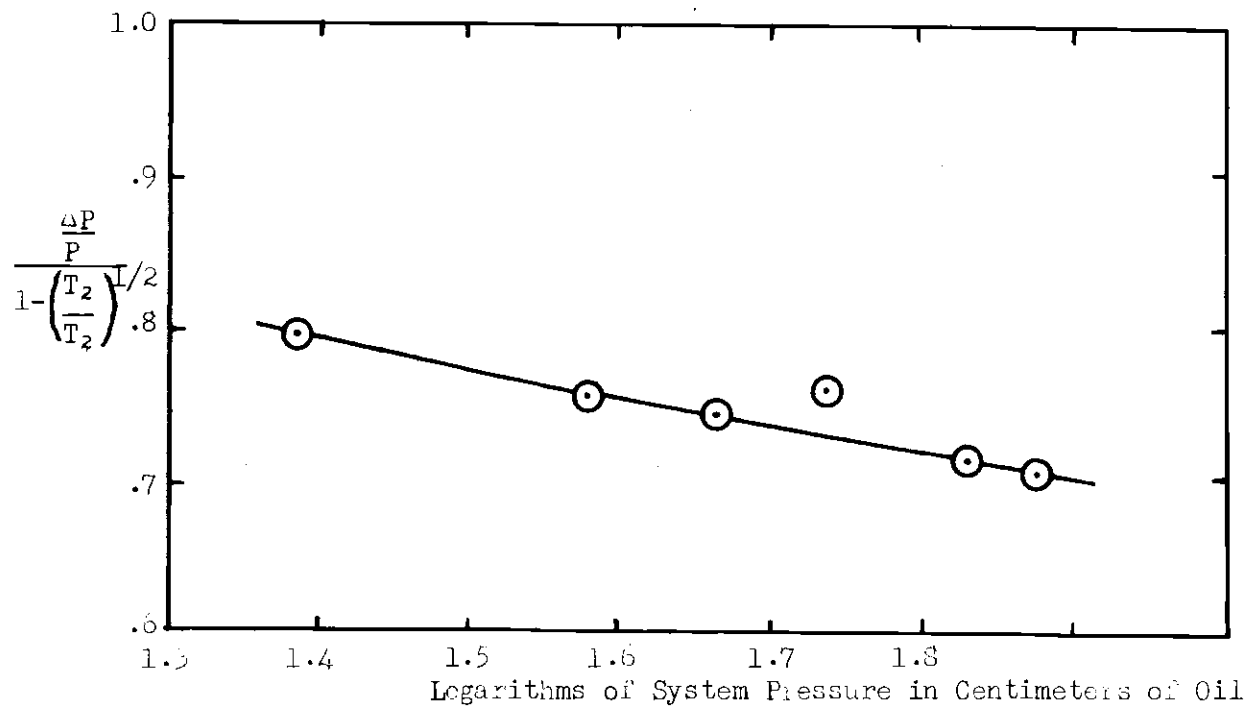


Figure 8. Low Pressure Transpiration Limit for Argon in 8 μ Bed.

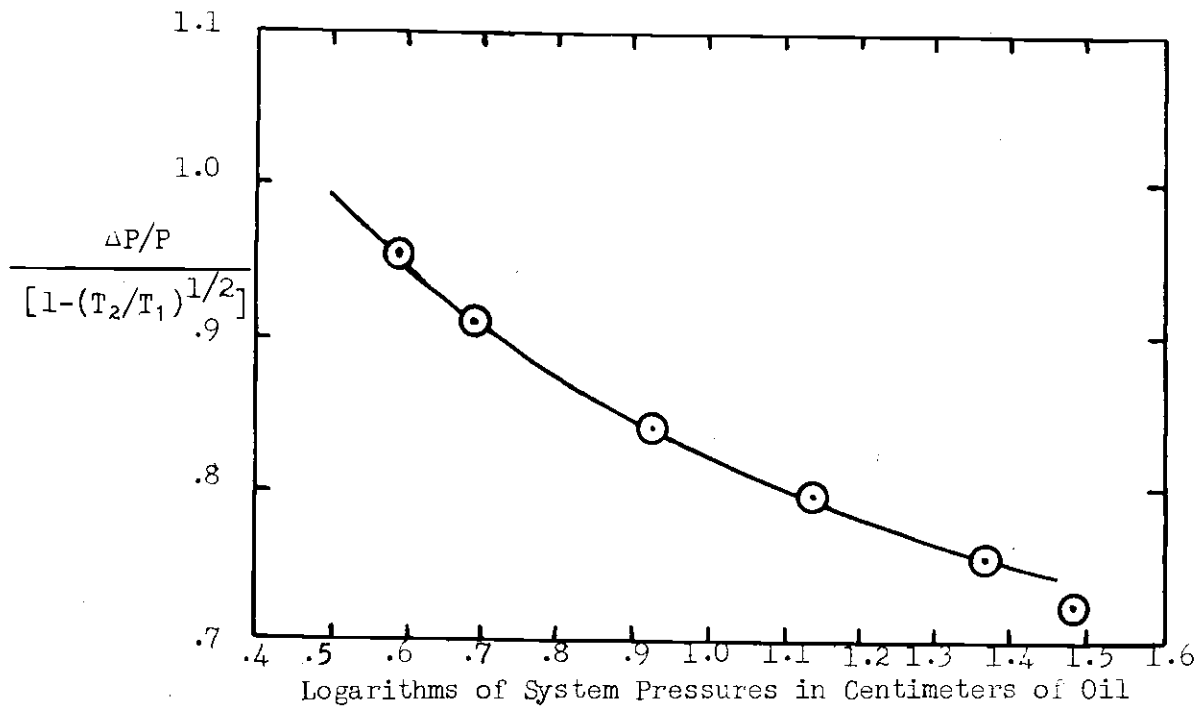


Figure 9. Low Pressure Transpiration Limit for Hydrogen in 8 μ Bed.

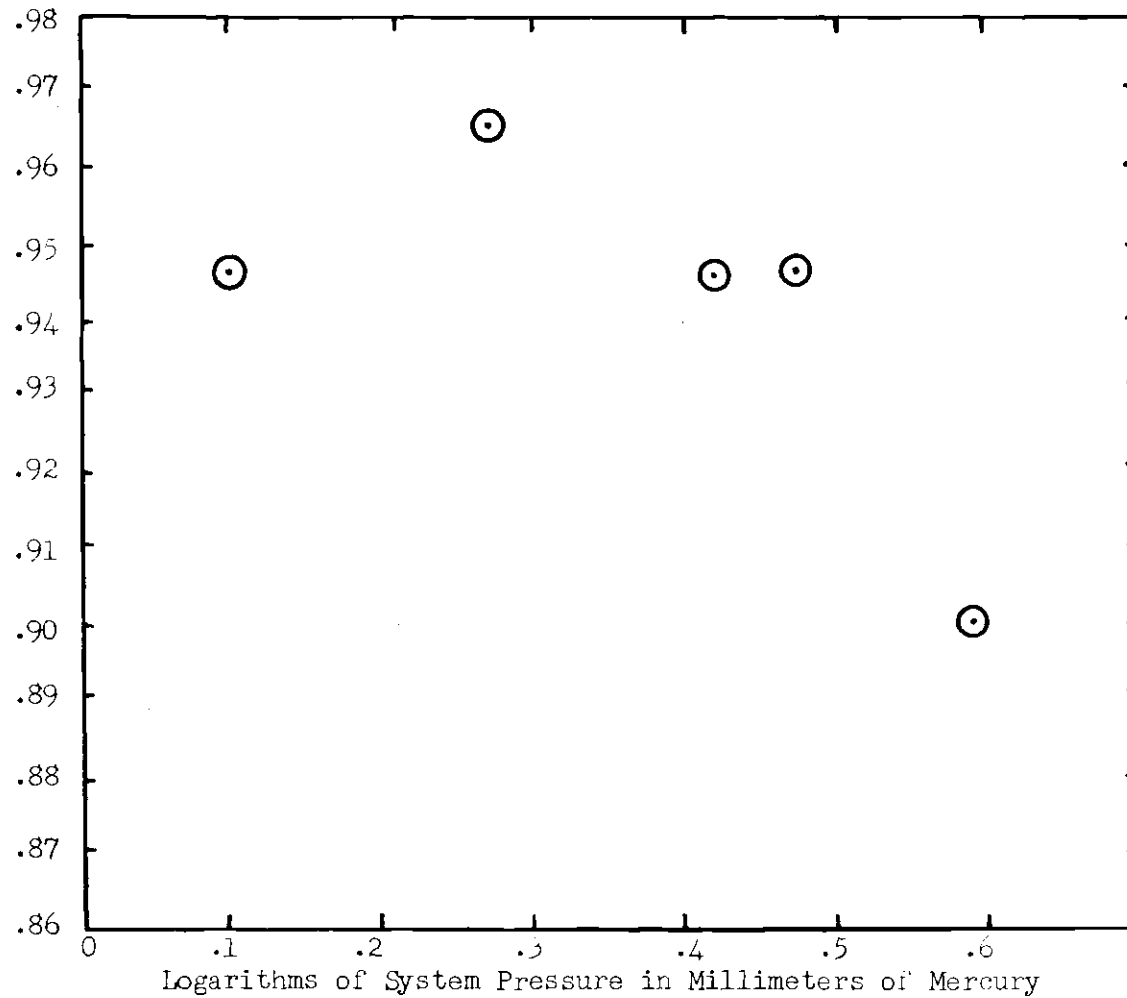


Figure 10. Low Pressure Transpiration Limit for Helium in 8 μ Bed.

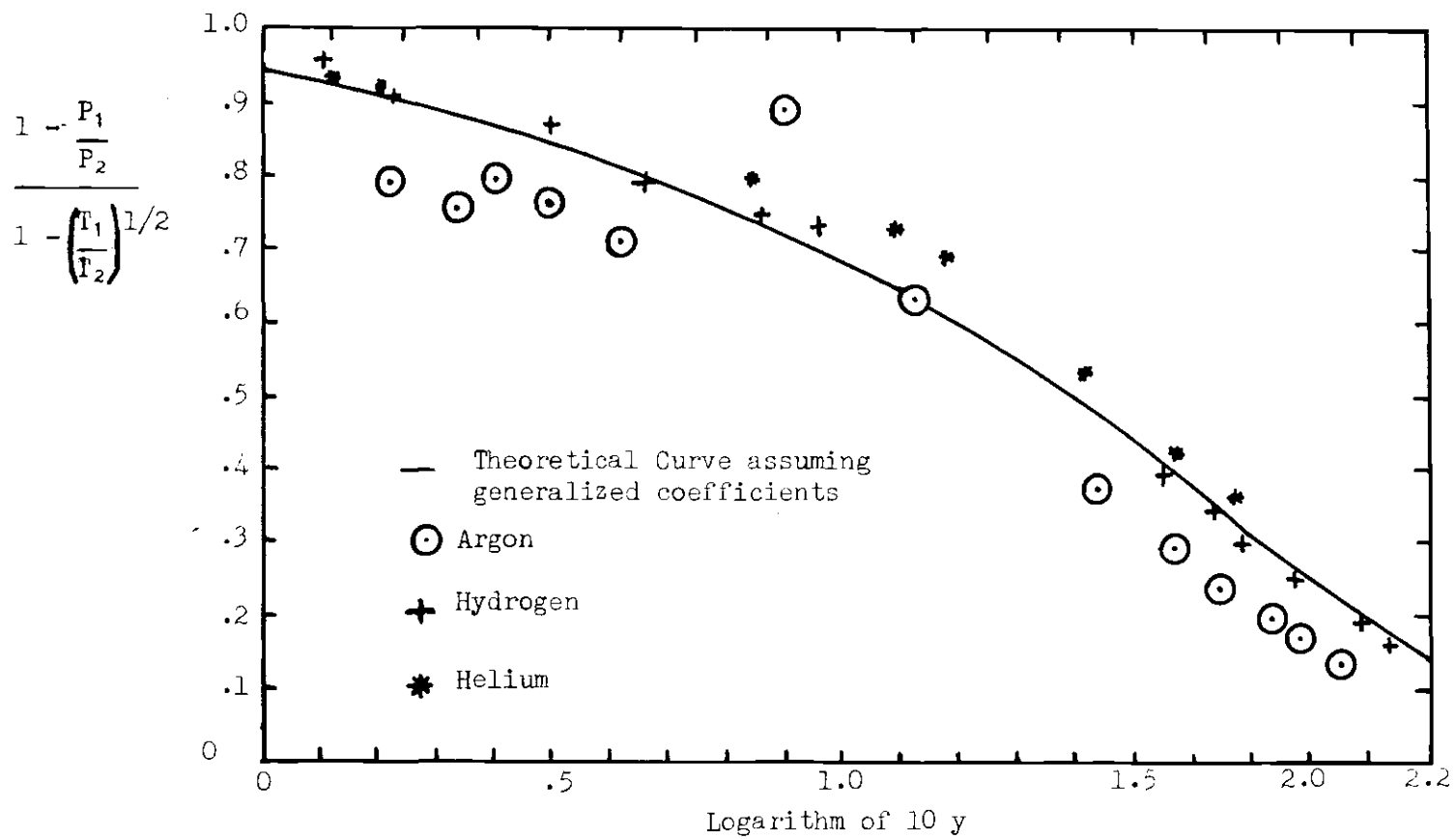


Figure 11. Comparison of Experimental Data with Weber Prediction.

CHAPTER V

CONCLUSIONS

This study of thermal transpiration in porous media shows that the Weber equation for thermal transpiration in capillaries can be applied with only limited accuracy to porous media. The application of this equation to the maximum has shown that the size of the molecule is not the only important molecular property which determines the thermal transpiration effect. The correlation of the critical temperature and the average pore size indicates that the strength of the inter-molecular forces may be significant in determining the magnitude of the effect.

The fact that the parameter $(1 - P_1/P_2)/(1 - (T_1/T_2)^{1/2})$ approaches one as the pressure approaches zero demonstrates that the hydrodynamic phenomenon of transpiration approaches the thermal effusion limit smoothly at a pressure of about 1 mm. Hg for the pore sizes used here.

The curve fitting of the data for hydrogen, helium, and argon shows that there is no substantial deviation from the Weber equation at low pressures for the gases observed, although deviations have been observed for transpiration in capillaries for hydrogen and helium. The deviations in the capillary data may be due to an increase in the number of specular collisions in these lighter gases over heavier gases. If this is the cause of the observed deviations, then it is not surprising that the effect is not seen in the porous medium. Because of the more tortuous path followed by a molecule when passing through a porous bed, it

would suffer more collisions with the wall than would a molecule passing through a capillary. The increased number of wall collisions would increase the probability that a diffuse collision would occur. Consequently, the increase in the number of diffuse collisions would cause the lighter gases to behave more like the heavier gases which have a higher probability of making a diffuse collision per wall collision.

The generalized plot and the data at the maximum show that the generalized constants fit the data. However, there is some spread in both situations indicating that the constants vary slightly with the gas.

CHAPTER VI

RECOMMENDATIONS

Because thermal transpiration is a molecular effect which in porous media with small pores can be measured with common instruments, it is of great potential usefulness in studying molecular transport phenomena with relatively simple equipment. This study has shown the correlation between the variations in the parameter $(\Delta P)_{\max} \sigma^2 / \Delta T$ and the critical temperature. If this correlation is the result of molecular forces, then thermal transpiration is a useful tool in studying their strength and properties. Maxwell developed his transpiration equation from kinetic theory. Consequently, his expression for the coefficient of slip and thermal slip contain no empirical factors. Weber's equation, however, introduces three empirical constants. A possible avenue of fitting is suggested in the form of Maxwell's coefficient of slipping. He reduces the coefficient G to the form:

$$G = \frac{2}{3} \left(\frac{2}{f} - 1 \right) \lambda \quad (1)$$

where f is the fraction of incident molecules adsorbed per unit surface area. Therefore by fitting f , data about the surface - molecule interaction might be obtained.

Returning to the Weber equation, because of the systematic variation $(\Delta P)_{\max} \sigma^2 / \Delta T$, it seems possible that by making α , β , and μ' functions of the critical temperature that a form of the Weber equation with

generalized coefficients might be obtained which would allow the theoretical curve to fit individual gases.

Mason et al., have applied thermal transpiration to the investigation of molecular excitations (20). This application is based upon the discovery by Einstein in 1924 that the force on a body in a heat conducting gas is directly proportional to the translational component of the thermal conductivity. This quantity can be used to calculate the rotational relaxation times and the mean number of collisions necessary to transfer a quantum of rotational energy. Because the theory is well developed and because of the importance of the translational component of the thermal conductivity in other phenomena such as the radioscope, this area could yield significant results. Therefore, by curve fitting transpiration data to determine the effective value of G , a determination of f , the fraction of the molecules adhering to the medium surface per collision, might be possible.

The plot of the transpiration data for the gases studied indicate that variables other than the molecular influence the magnitude transpiration effect. Consequently, because of the variation of $(\Delta P)_{\max} \sigma^2 / \Delta T$ with the critical temperature, it seems possible that by making α , β , and μ' functions of the critical temperature that a form of the Weber equation with variable coefficients might be obtained which would fit the transpiration data for porous beds more accurately.

BIBLIOGRAPHY*

- (1) Osborn Reynolds, Scientific Papers, Cambridge University Press 1900, Vol. 1, pp. 264-290.
- (2) James Clerk Maxwell, Scientific Papers, Dover Publications 1952, Vol. 11, pp. 703-712.
- (3) S. Weber, Leiden Comm. Supple., No. 71b, 1931.
- (4) E. A. Mason, R. B. Evans, and G. M. Watson, J. Chem. Phys., 38, 1808-1826 (1963).
- (5) H. H. Podgurski and F. N. Davis, J. Phys. Chem., 62, 457 (1961).
- (6) T. Edmonds and J. P. Hobson, J. Vacuum Sci. Technology 2, 182 (1965).
- (7) G. A. Miller and R. L. Buice, J. Phys. Chem., 70, 387 (1966).
- (8) James Clerk Maxwell, op. cit.
- (9) James Clerk Maxwell, op. cit.
- (10) L. B. Loeb, The Kinetic Theory of Gases, McGraw-Hill Book Company, Inc., New York, N. Y., 1934, pp. 281-284.
- (11) S. Weber, op. cit.
- (12) S. Weber and G. Schmidt, Leiden Comm. Supple., No. 246 C, 1936.
- (13) G. A. Miller, J. Phys. Chem., 67, 1359 (1964).
- (14) S. Chapman and T. G. Cowling, The Mathematical Theory of Non-Uniform gases, Cambridge Press, 1939, pp. 103-107.
- (15) E. A. Mason, J. Chem. Phys., 39, 522-526 (1963).

* Abbreviations used herein follow the form given in List of Periodicals abstracted by Chemical Abstracts Series, Ohio State University, Columbus, Ohio, 1956.

- (16) E. A. Mason, ibid.
- (17) Landolt-Bornstein, Zahlenwerte und Funktionen, Sections 13241 and 13242, Springer-Verlog, Berlin 1950-1951.
- (18) Landolt-Bornstein, ibid.
- (19) G. A. Miller, op. cit.
- (20) E. A. Mason, R. B. Evans, and G. M. Watson, op. cit.