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ISOTHERMAL TRANSPORT OF SORBABLE GASES IN
GRAPHITISED CARBON MEMBRANES: THE EFFECT
OF TEMPERATURE

by

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MEMBRANES: THE EFFECT OF TEMPERATURE -- David E.G. Whiting.

ABSTRACT

The isothermal steady-state flow of twelve gases through a Sterling S graphitised carbon membrane of porosity, $\epsilon = 0.524$ has been investigated and a complimentary study of the flow of helium and carbon dioxide through a second, more highly compressed, Sterling S membrane ($\epsilon = 0.321$) undertaken. For the first membrane the flow has been studied over the wide temperature range of 198K to 473K; for the second membrane temperatures between 273K and 473K have been considered.

The integral permeabilities, $\tilde{K}_0$, divided by the square root of the membrane temperature show a marked temperature dependence of the transport through both membranes. The quotient ($\tilde{K}_0/T^{1/2}$) either decreases with decreasing temperature, increases with decreasing temperature, or shows a temperature minimum. Even for helium the value is not independent of temperature, which is in sharp contrast to predictions from classical theory for flow through single capillaries and porous media and to much previous experimental findings. The experimental results have been used to test various theoretical equations, and have been compared with predictions from theoretical treatments. The nature of the results is attributed primarily to the forces of interaction between the pore walls and the flowing gas molecules.

The pressure dependence of the integral permeabilities was small for all the gases except (at low temperatures) for the most strongly adsorbed species, where the pressure dependence showed a number of interesting features.

DEDICATION

This thesis is dedicated to my parents, sister
and brother for all their love and patience.

ACKNOWLEDGEMENTS.

I am particularly indebted to my supervisor, Mr. R. Ash, for his advice, encouragement and friendship throughout the duration of this research project. I would also like to thank Professor R.M. Barrer F.R.S. for his interest and many helpful comments and Dr. D. Nicholson for providing typed manuscripts of some of his papers prior to publication. Finally I would like to express appreciation to Dr. A.D. Hamilton, Mr. J.N. Michaels, Mr. A. Rizvi and other friends from the Diffusion Research Group for many interesting discussions.

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LIST OF SYMBOLS

The more important symbols used in this work are listed below. Where it is useful, the number of the equation in which the symbol is introduced is given in brackets.

A	surface area per unit volume of porous media.
A	geometry constant used in equation 2.69.
A	parameter used in equation 2.75 characterizing the repulsive term of the molecule-molecule interaction potential.
A'	parameter used in equation 5.17.
A _c	cross-sectional area of the membrane.
A _{B.E.T.}	B.E.T. surface area.
a _m	average area occupied by an adsorbate molecule.
B	constant used in equation 2.69.
B	parameter used in equation 2.75 characterizing the dispersive term of the molecule-molecule interaction potential (Dispersion energy constant).
B'	parameter used in equation 5.17.
b	width of slit.
C	total concentration of diffusant.
C	constant used in B.E.T. equation (2.110).
C ₀	total concentration of diffusant at ingoing face of membrane (2.1.(a))
C ₁	total concentration of diffusant at outgoing face of membrane (2.1.(c))
C _s	Gibbs surface excess.
C _g	gas phase concentration.
C _{n,m}	constant used in equation 2.76.
C _s	surface excess per unit surface area (2.5).
C _g	gas phase concentration per unit pore volume (2.6).
c	speed of light in vacuum.
$\bar{c}$	mean molecular speed.
D	diffusion coefficient (2.2).
D _K	Knudsen diffusion coefficient (2.31).

List of symbols (continued)

D_{gs}	diffusion coefficient for gas phase flow, defined for steady state.
D_{ss}	diffusion coefficient for extra flow, defined for steady state.
d	half width of a slit.
d_{He}	helium density
E	energy of interaction between two molecules.
E_p	energy of interaction between a single gas molecule and a plane.
E_s	energy of interaction between a single gas molecule and a solid.
E_{zp}	zero point energy.
E_{ss}	activation energy for "surface" diffusion (5.6).
E^*	minimum potential energy for an adsorbed molecule.
$E^\ddagger$	height of a potential energy barrier.
ΔE	energy of adsorption (2.109)
$\Delta E'$	energy of adsorption used in equation 5.9.
e	protonic charge.
F	fraction of molecules engaged in wall to wall paths and which do not collide with other molecules (2.38).
f	fraction of molecules randomly scattered after collision with wall (2.28).
G	total transport in pressure-volume units per unit time.
h	Plank's constant.
I	integral defined by equation 2.24.
I	ionization energy.
J	flux
J_∞	steady-state flux.
J_g	gas phase flux (2.62)
J_s	flux associated with extra flow (2.62).
K	differential permeability (2.7).
K_K	Knudsen permeability (2.29).
K_g	differential gas phase permeability.
K_s	differential permeability associated with extra flow.
K_0	differential permeability corresponding to zero pressure.

List of symbols (continued)

K_{eq}	gas-solid equilibrium partition function (2.79).
K^{cyl}	permeability of a gas flowing through a capillary (2.41).
$\tilde{K}$	integral permeability (2.10).
$\tilde{K}_g$	integral gas phase permeability.
$\tilde{K}_B$	integral permeability associated with extra flow.
$\tilde{K}_0$	integral permeability corresponding to zero pressure.
$\tilde{K}_T$	$\tilde{K}(M/T)^{\frac{1}{2}}$.
k	Boltzmann constant.
k	Kozeny constant (2.46).
k_g	Henry law constant used in equation 2.73, corresponding to molecules with sufficient energy to cross the adsorption barrier.
k_s	Henry law constant (5.9).
k_0	shape factor (2.41).
k_1	shape factor (2.41).
k_2	geometrical constant (2.74).
k_3	geometrical constant (2.74).
k_t	tortuosity (2.48).
k'	shape factor (2.46).
k_s^+	Henry law constant used in equation 2.73, corresponding to molecules with insufficient energy to cross the adsorption barrier.
L_1^a	adsorption time-lag at outgoing face of membrane.
L_0^a	adsorption time-lag at ingoing face of membrane.
L_1^d	desorption time-lag at outgoing face of membrane.
L_0^d	desorption time-lag at ingoing face of membrane.
l	length of membrane
M	molar mass.
m	mass of a diffusing molecule.
m	electronic mass.
m	index of dispersive component of interaction potential (2.75).

List of symbols (continued)

N_A	Avogadro's constant.
n	index of repulsive component of interaction potential (2.75).
n_g	number of molecule-molecule collisions.
n_w	number of molecule-wall collisions.
$\bar{n}$	number of density of solid atoms per unit volume.
P_0	saturated vapour pressure.
P_T	permeability as used by Carman and Malherbe (1950) (2.18).
p	gas pressure.
P_0	gas pressure at ingoing side of membrane.
p_l	gas pressure at outgoing side of membrane.
p_i	component of momentum in direction of i .
$\bar{p}$	mean pressure
Q	quantity of gas.
Q	permeability as used by Hwang and Kammermeyer (1966 (a)) (2.19).
q_{st}	isosteric heat of adsorption.
q_{st}^0	isosteric heat of adsorption corresponding to zero uptake.
R	gas constant.
r	radius of capillary or tube.
r_h	hydraulic radius (2.40).
r_0	separation distance corresponding to zero potential energy.
r^*	equilibrium distance between two interacting molecules or atoms.
$S_{n,m}$	generalised Sutherland constant used in equation 2.76.
s	circumference of capillary tube.
T	membrane temperature
T_R	room temperature.
T_{min}	temperature corresponding to minimum of plot of $K_0 M^{\frac{1}{2}} T^{-\frac{1}{2}}$ versus T .
T_{OG}	Outgassing temperature.
t	time.

List of symbols (continued)

u	corrected flow velocity of diffusing gas molecules (2.26).
$\bar{u}$	average flow velocity of diffusing gas molecules.
V	volume.
v	volume of gas adsorbed.
v_m	volume of gas required to cover the surface with a complete monolayer.
v_i	componant of velocity whose direction is i .
w	dimensionless transport parameter defined by equation 5.26.
w_0	limit of w at vanishing pressure.
x	distance in x direction
z	distance in z direction
z	perpendicular distance between the gas molecule and the solid surface.
z_0	perpendicular distance corresponding to zero energy.
z^*	perpendicular distance at which the interaction energy is at a minimum.
α	polarizability.
Δ	energy term defined by equation 2.70.
Δ'	parameter used in equation 5.17.
δ	pressure dependent parameter (2.41).
ϵ	porosity
ϵ_0	permittivity of a vacuum.
ϵ^*	depth of potential energy minimum ($\epsilon^* = -E(r^*)$).
η	gas viscosity.
η_{AB}	enrichment (or separation) factor for componant A in a binary gas mixture A and B (5.39)
θ	angle used in equation 2.24.
χ	structure factor
χ_g	structure factor for gas phase flow defined for transient state.
χ_s	structure factor for extra flow defined for transient state.
χ_{gs}	structure factor for gas phase flow defined for steady-state.

List of symbols (continued).

X_{ss}	structure factor for extra flow defined for steady-state.
X_p	structure factor defined for Poiseuille flow regime.
X_c	structure factor defined for conduction flow regime.
X_k	structure factor defined for Knudsen flow regime.
λ	mean free path of flowing gas.
ν	frequency of vibration.
ρ	chord of cross-section used in equation 2.24.
σ	standard deviation.
τ	tortuosity factor.
ϕ	$10^{-3} \text{ kg g}^{-1}$
φ	flux ratio (2.73).
χ	diamagnetic susceptibility
$\Omega_{1d}^{(1.1)*}$	reduced collision integral for diffusion (2.61).

CHAPTER 1

INTRODUCTION

The transport of fluids through porous media is important in a number of fields of which heterogeneous catalysis, the recovery of oil and natural gas from porous strata, separational science and membrane technology are typical examples. Several reviews have appeared in recent years dealing with various aspects of the subject (for example Barrer, 1967; Hwang and Kammermeyer, 1975; Massignon, 1979; Nicholson and Sing, 1979).

Graham (1846) formulated the empirical law that the "diffusive velocities of different gases vary inversely as the square root of their densities". The law was later shown to hold only when the mean free path of the gas molecules was much greater than the dimensions of the pores or the radius of the capillary through which the gas molecules were flowing (Knudsen, 1909). Knudsen derived a theoretical equation for gases flowing under such conditions (free-molecular flow), and obtained a semi-empirical equation to describe the flow of gases of higher pressures. Knudsen's equations were derived for the flow of gases through long capillaries. The term "long capillary" refers to a capillary that has a length that is very much greater than its radius. Further expressions have been obtained governing the free-molecular flow of gases through short capillaries or tubes (for example Dushman, 1931; Clausing 1932) and through capillaries with non-circular cross-sections (for example Smoluchowski, 1910; Steckelmacher, 1978). Equations derived for single capillaries can readily be applied to a system of parallel capillaries. A model which has been frequently employed to describe porous media, despite its lack of realism (Barrer, 1963).

There has been much interest in obtaining an equation to explain the flow of gases through capillaries and porous media over a wide range of pressures. Weber (1954) obtained a three term equation: one term due to viscous flow (also known as Poiseuille or streamline flow), a second arising from slip of

the gas layer at the channel wall (conduction flow), and a third known as Knudsen flow, free-molecular flow or molecular streaming resulting from self-diffusion in a pressure gradient. This equation has been adapted for use with porous media (Ash, Barrer and Coughlan, 1972).

Various improvements have been made to the simple parallel cylindrical capillary model used to represent a porous medium. Hiby and Pahl (1956) considered the free-molecular flow of gases through repeatedly bent tubes. Other workers notably Nicholson and Petropoulos (for example 1968, 1971, 1973(a)) have looked at the effect of various radius distributions in a serial model and a model in which the capillaries are interconnected in three dimensions to form a network.

An alternative approach is to consider the porous medium as being composed of spheres distributed randomly in space (Deryagin and Bakanov, 1957). The diffusion of a gas through a porous medium can be regarded as the mutual diffusion of two gases with the molecules of one gas having an infinitely greater mass than the molecules of the other gas. This is known as the "dusty gas" model and has been further developed by Mason and coworkers (for example, Evans, Watson and Mason, 1961).

The models discussed were formulated for situations where the wall forces are infinitely repulsive and flow is purely in the gas phase. There is, however, an additional flow contributing to the total flow attributed to the existence of mobile adsorbed films in the presence of a concentration gradient (Barrer and Gabor, 1960). At sub-monolayer coverage the mechanism of the extra flow is thought to be that of a diffusive random walk mechanism (Ash, Barrer and Pope, 1963(a); Barrer, 1963; Aylmore and Barrer, 1966). Whereas at greater than monolayer coverage a hydrodynamic flow mechanism is more important (Babbitt, 1950; Gilliland, Baddour and Russell, 1958).

There have been cases even when adsorption is too small to be considered measurable (for example Lund and Berman, 1958, 1966(a)) where the flow of different gases differs

from the behaviour predicted by simple kinetic theory. Nicholson and Petropoulos (1975(b)) have developed an approach which takes into account the fact that all molecules travel in a potential field due to the adsorbent. This approach has been used to explain in terms of pore size contradictions between the results of various experimentalists (Hwang and Kammermeyer, 1966(a); Ash, Barrer and Lowson, 1970).

In the past twenty five years there have been a number of experimental investigations of the flow of gases through porous media and more particularly through carbon membranes. In these laboratories several carbons have been used to fabricate membranes: Carbolac, Black Pearls and Graphon. Black Pearls and Graphon are both graphitised carbon blacks, Graphon having a lower surface area than Black Pearls. The flow of gases through Graphon membranes has been studied in great detail (Ash, Baker and Barrer, 1967, 1968; Ash Barrer and Lowson, 1970, Ash, Barrer, Clint, Dolphin and Murray, 1973; Ash, Barrer and Edge, 1976, Ash Barrer, Chio and Edge, 1979; Ash and Hamilton, to be published), the flow through Black Pearls has been less well studied (Ash, Barrer and Baker, 1967, 1968; Ash and Hamilton, to be published; Ash and Michaels, to be published). The indications are that with decreasing surface area and increasing energetic homogeneity the effect of surface interaction becomes more important when considering gas flow (Ash, Barrer and Baker, 1967). With this result in mind this work is concerned with the isothermal flow of gases through porous membranes formed by compaction of Sterling S. This material is a graphitised carbon powder with a lower surface area than Graphon and has hitherto not been employed in flow studies.

CHAPTER 2.REVIEW AND THEORETICAL BACKGROUND2. 1. EXPERIMENTAL STUDIES.

There have been a number of studies in recent years concerned with the flow of gases through carbon membranes, and other porous materials such as porous glass, ceramics and catalyst pellets. There are several experimental approaches to the study of flow through porous media and various techniques have been reviewed in articles by Grove (1967) and Barrer (1967). Broadly speaking experimental studies of the isothermal transport of single gases through porous media fall into five main categories.

- (a) Steady-state flow experiments (Ash, Barrer and Pope 1962 (a), (b); Ash, Baker and Barrer 1967; Carman, 1950; Gilliland, Baddour and Russell, 1958).
- (b) Time-lag studies (Ash, Baker and Barrer, 1968; Ash, Barrer, Clint, Dolphin and Murray, 1973; Ash, Barrer, Chio and Edge, 1979; Roussis and Petropoulos, 1976, 1977).
- (c) Pressure decay or quasi steady-state measurements (Ash, Barrer and Sharma, 1975; Ash and Hamilton, to be published; Horiguchi, Hudgins and Silveston, 1971; Wright, Berman and Prager, 1978)
- (d) Early-time procedures (Ash, Barrer and Edge, 1976; Ash and Michaels, to be published).
- (e) Kinetics of sorption (Haul and Hübner, 1974, 1975; Haul, Heintz and Stremming, 1980).

Ash and Barrer and their co-workers have used the method of incremental compaction of powder in stainless steel tubes to produce their porous membranes. The technique has been used with materials such as alumina-silica cracking catalyst (Barrer and Gabor, 1959, 1960) and carbons. Four carbons have been used by the school of Ash and Barrer. In order of decreasing surface area and increasing energetic homogeneity

these carbons are Carbolac, Black Pearls, Graphon and Sterling S. In other cases consolidated membranes may be used (porous ceramic and Vycor porous glass are frequently used examples).

For steady-state flow experiments the membrane is made to separate a reservoir of fluid or gas from a receiving volume. It is bounded by planes $x=0$ and $x=1$, flow occurring in the direction of increasing x . The boundary conditions are

$$C(0, t) = C_0, \quad t > 0 \quad (2.1(a))$$

$$C(x, 0) = C_1(x), \quad 0 < x < 1 \quad (2.1(b))$$

$$C(1, t) = C_1, \quad t > 0 \quad (2.1(c))$$

C denotes the total concentration of diffusant in both the absorbed and the gas phase and t is time. In the steady-state studies of Carman (1950); Gilliland, Baddour and Russell (1958); Hwang and Kammermeyer (1966 (a), (b); 1967) C_1 is held constant as indicated above, whereas in the experiments of the group of Ash and Barrer conditions 2.1 (b) and 2.1 (c) are replaced by

$$C(x, 0) = 0, \quad 0 < x < 1, \quad (2.1(d))$$

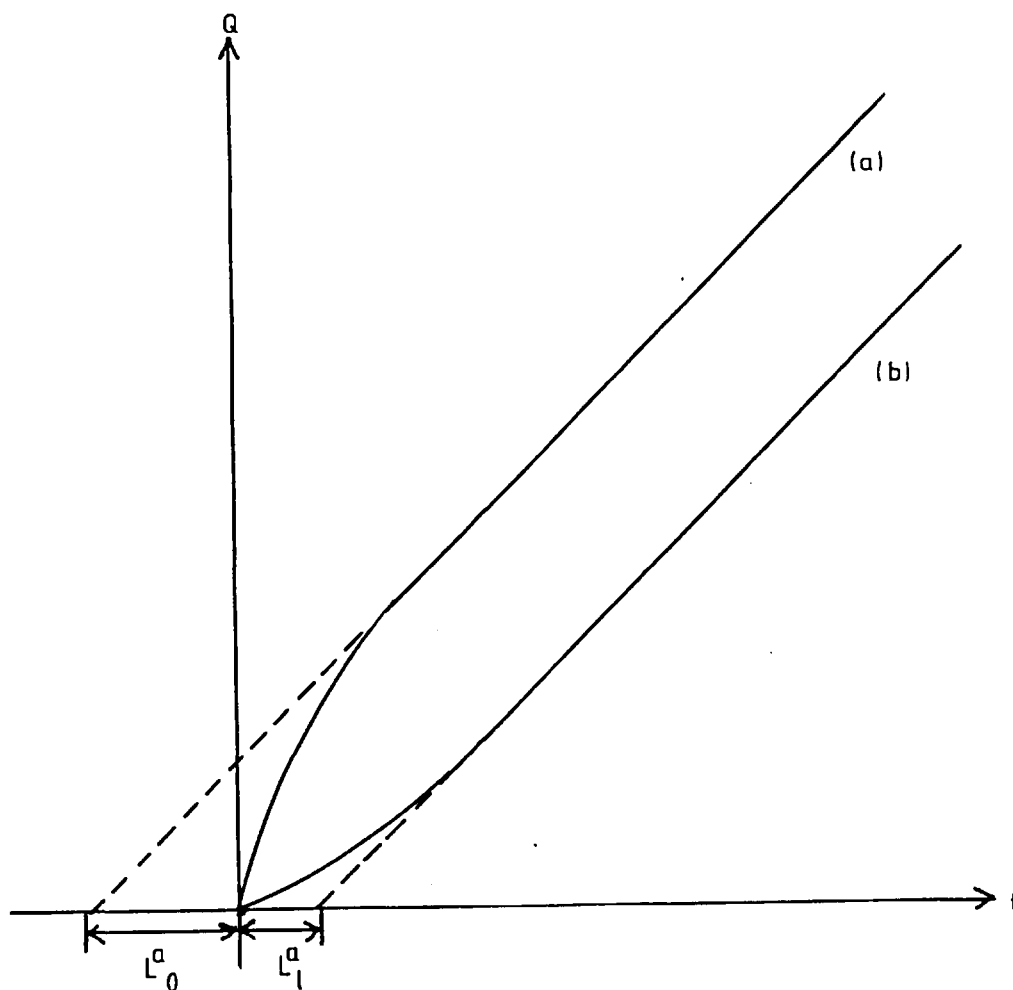
$$C(1, t) = C_1(t) \quad C_0, \quad t > 0 \quad (2.1(e))$$

Under such conditions it is possible to define two adsorption time-lags, L_1^a and L_0^a (Barrer, 1970). A plot of the increase of the quantity of gas, Q , or the pressure in the outgoing side ($x=1$) against time approaches asymptotically to a straight line (see figure 2.1). The intercept this asymptote makes with the time axis is time-lag L_1^a . A similar plot of the decrease of the quantity of gas on the ingoing side ($x=0$) against time approaches asymptotically a line parallel to the asymptote obtained from the outgoing plot. The intercept of this asymptote with the time axis give L_0^a . From the gradient of the asymptote the permeability can be obtained (see section 2.2). Early time studies have been performed using the same set of boundary conditions (Ash, Barrer and Edge, 1976).

Another alternative condition 2.1(b) is

$$C(x, 0) = C_0, \quad 0 < x < 1. \quad (2.1(f))$$

Steady state is now approached by desorption and desorption

Figure 2.1. Adsorption Time-Lags.

For curve (a) Q denotes the decrease in the quantity of gas at the ingoing side of the membrane.

For curve (b) Q denotes the increase in the quantity of gas at the outgoing side of the membrane.

time-lags at $x = 1$ and $x = 0$ designated L_1^d and L_0^d , respectively can be obtained in an analogous manner to the adsorption time-lags (Barrer, 1970).

This study is concerned with flow in the steady-state and the boundary conditions used correspond to 2.1 (a), (d) and (e).

2.2. DEFINITION OF PERMEABILITY AND NOTATION

Fick's equation for flow in one dimension is

$$\frac{J}{A_c} = -D \frac{\partial C}{\partial x}(x, t) \quad (2.2)$$

where J is the flux, A_c is the cross sectional area presented to flow and D is a diffusion coefficient and C is the concentration of the diffusing species. If the steady state flux J_{∞} is considered the partial derivative in equation 2.2 becomes a total derivative.

$$\frac{J_{\infty}}{A_c} = -D \frac{dC}{dx}(x) \quad (2.3)$$

For a sorbable gas diffusing in a porous medium C can be divided into two components

$$C = C_s + C_g \quad (2.4)$$

where C_s is the Gibbs surface excess and C_g is the gas phase concentration. All concentrations being expressed in moles per unit and volume of porous media. C_s and C_g are related to more convenient experimentally measurable quantities C'_s (surface excess in moles per unit surface area) and C'_g (the gas phase concentration in moles per unit pore volume).

$$C_g = \epsilon C'_g \quad (2.5)$$

$$C_s = A C'_s \quad (2.6)$$

ϵ is the porosity and A is the surface area per unit volume of porous media. By analogy with equation 2.3 a differential permeability K may be defined

$$\frac{J_{\infty}}{A_c} = -K \frac{dC'}{dx} \quad (2.7)$$

Hence K is related to the overall diffusion coefficient by

equation 2.8

$$K = D \left(\frac{\partial C}{\partial C'_g} \right)_T \quad (2.8)$$

Using equations 2.3 and 2.5

$$K = D \left[A \left(\frac{\partial C'_s}{\partial C'_g} \right) + \epsilon \right] \quad (2.9)$$

Under the conditions used in this work it is more convenient to define an integral permeability $\tilde{K}$ (Hamilton, 1980)

$$\frac{J_\infty}{A_c} = \frac{\tilde{K} \Delta C'_g}{1} \quad (2.10)$$

This integral permeability can be related to the differential permeability by integrating equation 2.7.

$$\frac{J_\infty}{A_c} = \frac{1}{1} \int_{C'_{g1}}^{C'_{g0}} K d C'_g \quad (2.11)$$

where C'_{g0} and C'_{g1} are the gas phase concentrations at the $x=0$ and $x=1$ respectively. Combining equations 2.10 and 2.11.

$$\tilde{K} \Delta C'_g = \int_{C'_{g1}}^{C'_{g0}} K d C'_g \quad (2.12)$$

Under the experimental conditions used in this study $C'_{g0} \gg C'_{g1}$

$$\Delta C'_g \approx C'_{g0} \quad (2.13)$$

Equation 2.12 becomes

$$\tilde{K} C'_{g0} = \int_0^{C'_{g0}} K d C_g \quad (2.14)$$

or in a differential form

$$\tilde{K} (C'_{g0}) + C'_{g0} \left(\frac{\partial \tilde{K}}{\partial C'_{g0}} \right)_T = K (C'_{g0}) \quad (2.15)$$

Hence $\tilde{K}$ and K will only be numerically equal if $(\partial K / \partial C'_{g0})_T$ is zero.

If ideal behaviour is assumed C'_g can be related to the pressure, p

$$C'_g = \frac{p}{RT} \quad (2.16)$$

R is the gas constant and T is the temperature of the porous

membrane. Recalling equation 2.11 the permeability was experimentally calculated by the relationship

$$\frac{J_{\infty}}{A_c} = \frac{\tilde{K}}{RT} \frac{p_0}{1} \quad (2.17)$$

where p_0 is the pressure on the ingoing side of the membrane.

Other workers (for example Carman and Malherbe, 1950; Gilliland, Baddour and Russell, 1958; Kammermeyer, 1959; Hwang and Kammermeyer, 1966 (a)) define the permeability in terms of a pressure difference. The permeability P_T used by Gilliland, Baddour and Russell (1958) and Carman and Malherbe (1950) is simply related to $\tilde{K}$ by the equation

$$P_T = \frac{\tilde{K}}{RT} \quad (2.18)$$

On the other hand the permeability, Q , used by Hwang and Kammermeyer (1966 (a)) and others is more directly related to K

$$Q = \frac{K}{RT} \quad (2.19)$$

2.3 FLOW IN A SINGLE CAPILLARY.

Knudsen (1909) derived an equation for the flow of gas through a tube of infinite length and of arbitrary cross-section. The equation being derived in circumstances when the mean-free path, λ , of the flowing gas was much greater than the dimensions of the tube cross-section. In other words the number of molecule-wall collisions is much greater than the number of molecule-molecule collisions. Knudsen's equation is

$$J_{\infty} = \frac{4}{3} \frac{\bar{c}}{s} \frac{A_c^2}{s} \frac{\Delta C'_g}{1} \quad (2.20)$$

where s is the circumference of the tube and $\bar{c}$ is the mean molecular speed

$$\bar{c} = \left(\frac{8RT}{\pi M \phi} \right)^{\frac{1}{2}} \quad (2.21)$$

where M (g mol^{-1}) is the molar mass and ϕ is defined by $\phi = 10^{-3} \text{ kg } \text{g}^{-1}$. For a circular cross-section of radius, r ,

Knudsen's equation becomes

$$J_{\infty} = \frac{2}{3} \pi r^3 \bar{c} \frac{\Delta C'_E}{1} \quad (2.22)$$

For perfectly diffuse reflection von Smoluchowski (1910) derived an alternative equation to 2.20 (see Clausing, 1932)

$$J_{\infty} = \frac{1}{8} \bar{c} I \frac{\Delta C'_E}{1} \quad (2.23)$$

where

$$I = \int_s \int_{-\pi/2}^{\pi/2} \frac{1}{2} e^2 \cos \theta d\theta ds \quad (2.24)$$

where θ represents a chord of the cross-section forming an angle θ with the normal at ds , an element of circumference. For a circular cross-section.

$$I = \frac{16}{3} \pi r^3 \quad (2.25)$$

Substituting 2.25 into 2.23 gives equation 2.22. Clausing (1932) points out that it is probably accidental that Knudsen's equation and von Smoluchowski's equation are in agreement for a circular cross-section and indeed the two expressions lead to different values for non-circular cross-sections. There are a number of criticisms of Knudsen's derivation (eg. Steckelmacher, 1978). Knudsen considered the momentum transfer to the wall of the tube. In the calculation a quantity $\bar{u}$, the average flow velocity of the gas molecules along the tube, is used which is assumed not to vary with distance from the axis. Knudsen corrected $\bar{u}$ for the Maxwell velocity distribution by putting

$$\bar{u} = \frac{3\pi u}{8} \quad (2.26)$$

u was used in place of $\bar{u}$ in the calculation of the momentum transferred to the wall. Pollard and Present (1948) suggest that this correction is invalid, in which case Knudsen's equation for a circular tube becomes

$$J_{\infty} = \frac{\pi^2}{4} r^3 \bar{c} \frac{\Delta C'_E}{1} \quad (2.27)$$

The assumption that $\bar{u}$ is independent of the distance from the axis has been shown to be incorrect (Pollard and Present, 1948; Weber, 1954).

The method used by von Smoluchowski is a molecular path tracing (M.P.T.) method, which is based on the molecular impact taking into account the individual contributions to the flux from all elements of surface on the wall. The method has been clearly presented for a tube of circular cross-section by Present (1958).

Von Smoluchowski also made a further refinement to take account of the fact that only a fraction of the molecules, f , are randomly scattered.

$$J_{\infty} = \frac{2}{3} \pi r^3 \bar{c} \frac{\Delta C'_g}{1} \frac{(2-f)}{f} \quad (2.28)$$

This equation for a circular capillary has been derived by De Marcus (1961) using an integral method arising from Clausing (1932). When $f = 1$ equation 2.22 is obtained. A Knudsen permeability K_K can be defined for a circular capillary.

$$K_K = \frac{J_{\infty} l}{r^2 \Delta C'_g} = \frac{2}{3} r \bar{c} \frac{(2-f)}{f} \quad (2.29)$$

Substituting for $\bar{c}$ using equation 2.21

$$K_K = \frac{4}{3} r \left(\frac{2RT}{\pi M \phi} \right)^{\frac{1}{2}} \frac{(2-f)}{f} \quad (2.30)$$

Under the conditions for which equation 2.23 was derived $\Delta C'_g/l$ can be equated with $-(dC/dx)$. Using Fick's equation (equation 2.3) a Knudsen diffusion coefficient, D_K can be obtained.

$$K_K = D_K \quad (2.31)$$

Providing f is independent of the gas and that molecule-wall collisions are dominant the permeability of gas species 1 (K_1) through a capillary can be related to the permeability of gas species 2 (K_2) by the relation:

$$K_1 \left(\frac{M_1}{T_1} \right)^{\frac{1}{2}} = K_2 \left(\frac{M_2}{T_2} \right)^{\frac{1}{2}} \quad (2.32)$$

This equation is valid irrespective of the cross-sectional

shape of the capillary and is frequently used in flow studies with porous media when free molecular flow (also known as Knudsen flow or molecular streaming) becomes the predominate flow mechanism.

At higher pressures the mean free path of the diffusing gas becomes less than the dimensions of the capillary cross-section and the flow becomes dependent on the gas viscosity (for example Grove, 1967). Such a flow regime is known as viscous or Poiseuille flow. The transition from Knudsen flow to Poiseuille flow is accompanied by a minimum in the plot of permeability against mean pressure (for example Knudsen, 1909; Adzumi, 1937 (a)). Such minima have also been observed for long slit shaped capillaries (Gaede, 1913) and porous media (Grove and Ford, 1958; Ash, Barrer and Coughlan, 1972). At zero pressure the entire transport comes from Knudsen diffusion. As the pressure is increased the flow is on one hand decreased because of the obstruction of the long diffusion paths due to the added molecules, and on the other hand it is increased through the development of a drift transport due to collisions so a minimum in the permeability can result (Pollard and Present, 1948). Weber (1954) has considered the transition in terms of three components of flow. For a cylindrical capillary these are as follows

- 1). A Poiseuille term

$$J_p = - \left(\frac{3\pi r}{64 \lambda} \right) \pi r^2 K_K \frac{dc'_g}{dx} \quad (2.33)$$

- 2). A conduction term arising from a non-zero velocity (or slip) of the gas layer adjacent to the capillary wall

$$J_c = - \pi \left(\frac{2r/\lambda}{4 (1+2r/\lambda)} \right) \pi r^2 K_K \frac{dc'_g}{dx} \quad (2.34)$$

The factor $\pi/4$ corresponds to Weber's choice of the most probable experimental value. It is not theoretically derived. $(2r/\lambda) / (1+2r/\lambda)$ is equal to $n_g/(n_w+n_g)$ where n_w is the number of molecule-wall

collisions and n_g is the number of molecule-molecule collisions (Barrer, 1967).

- 3.) A term arising from self diffusions is a pressure gradient, this is the Knudsen term

$$J_k = - \left(\frac{1}{1+2r/\lambda} \right) \pi r^2 K_K \frac{dC'_g}{dx} \quad (2.35)$$

The factor $1/(1+2r/\lambda)$ is equal to $n_w/(n_w + n_g)$.

The total flux is the sum of the three terms (2.36)

$$J_\infty = - \left(\frac{3\pi}{64} \frac{r}{\lambda} + \frac{\pi}{4} \frac{2r/\lambda}{(1+2r/\lambda)} + \frac{1}{(1+2r/\lambda)} \right) \pi r^2 K_K \frac{dC'_g}{dx}$$

The equation applies for small pressure differences (ie. $\Delta p \ll \bar{p}$) in which case λ is the mean free path corresponding to the mean pressure. This compares with a semi-empirical equation obtained by Knudsen (1909) and quoted by Weber (1954). (2.37)

$$J_\infty = - \left(\frac{3\pi}{64} \frac{r}{\lambda} + \left(\frac{\pi}{2} \right)^{\frac{1}{2}} \frac{2r/\lambda}{(1+3.096r/\lambda)} + \frac{1}{(1+3.096r/\lambda)} \right) \pi r^2 K_K \frac{dC'_g}{dx}$$

Both equations give the same limits

$$\frac{r}{\lambda} \rightarrow \infty; J_\infty \rightarrow - \frac{3\pi}{64} \frac{r}{\lambda} \pi r^2 K_K \frac{dC'_g}{dx} \quad \text{streamline flow}$$

$$\frac{r}{\lambda} \rightarrow 0; J_\infty \rightarrow - \pi r^2 K_K \frac{dC'_g}{dx} \quad \text{Knudsen flow}$$

Fryer (1966) refined the Poiseuille term of Weber's equation by taking into account that a fraction $F(r/\lambda)$ are engaged in wall to wall paths and do not collide with other molecules.

Equation 2.31 becomes (2.38)

$$J_\infty = - \left(\frac{3\pi}{64} \frac{r}{\lambda} \left(1 - F \left(\frac{r}{\lambda} \right) \right) + \frac{\pi}{4} \frac{2r/\lambda}{(1+2r/\lambda)} + \frac{1}{(1+2r/\lambda)} \right) \pi r^2 K_K \frac{dC'_g}{dx}$$

Scott and Dullien (1962) have obtained an approximate solution for $F(r/\lambda)$

$$F \left(\frac{r}{\lambda} \right) \approx \exp \left(-\sinh^{-1} \left(\frac{2r}{\lambda} \right) \right) \quad (2.39)$$

Weber's equation has been modified by Barrer and Nicholson

(1966(b)) for short capillaries, rectangular slits and parallel capillary bundles.

When the condition $\bar{p} \gg \Delta p$ does not hold as in this experimental work, equation 2.31 must be integrated for the flux between $x=0$ and $x=1$, the resulting equation is given in two alternative forms by Ash, Barrer and Nicholson (1963) and Ash, Barrer and Coughlan (1972).

2.4. USE OF THE CAPILLARY MODEL FOR POROUS MEDIA.

There have been many models used to describe porous media. The simplest and probably the most misleading is that of a series of parallel uniform capillaries. The model is misleading because a real porous medium is likely to contain channels which are non-uniform and tortuous. There may be interconnecting of channels and some could exhibit "blind" pore character. Despite the lack of realism much useful progress can be made in a semi-empirical basis, making use of equations derived for gas flow through single capillaries.

A hydraulic radius, r_h , can be defined

$$r_h \equiv \frac{\text{cross-sectional area of capillaries}}{\text{circumference of cross-section}} = \frac{E}{A} \quad (2.40)$$

For capillaries of circular cross-section r_h is equal to $r/2$ where r is the radius of a single capillary and A is the surface area per unit volume of porous media.

Considering viscous and molecular flow Carman (1950) derived an equation for the permeability of a gas flowing through a capillary of uniform cross-section

$$K^{cyl} = \frac{r_h^2 \bar{p}}{k_0 \eta} + \frac{8 r_h \delta}{3 k_1} \left(\frac{2RT}{\sqrt{\pi M \phi}} \right)^{\frac{1}{2}} \quad (2.41)$$

k_0 and k_1 are shape factors. For circular cross-section $k_0 = 2.00$ and $k_1 = 1.00$, η is gas viscosity and δ is a factor which is dependent on pressure.

$$\frac{r \rightarrow \infty}{\lambda}; \quad \delta \rightarrow \delta_1 \equiv \frac{3\pi}{16} \frac{(2-f)}{f} \quad (2.42(a))$$

$$\frac{r \rightarrow 0}{\lambda}; \quad \delta \rightarrow \delta_0 \equiv \frac{2-f}{f} \quad (2.42(b))$$

K^{cyl} can also be written

$$K^{cyl} = \frac{J_{\infty} l}{A_c^{cyl} \Delta C'_5} \quad (2.43)$$

where $A_c^{cyl} = \epsilon A_c$ is the cross-sectional area of the capillaries. Also when a porous medium is considered a structure factor κ must be introduced (Barrer and Strachan, 1955; Barrer, 1967) which allow for a tortuosity and other structural complications.

$$\tilde{K} = \kappa \epsilon K^{cyl} \quad (2.44)$$

substituting for K_{cyl} and writing $r_h = \epsilon/A$

$$\tilde{K} = \frac{\kappa \epsilon^3}{k_0 A^2 \eta} + \left(\frac{8 \delta \kappa}{3 k_1} \right) \frac{\epsilon^2}{A} \left(\frac{2RT}{\pi M \phi} \right)^{\frac{1}{2}} \quad (2.45)$$

This can be compared with the equation obtained by Carman and Arnell (1948) which can be written as (Grove, 1967)

$$\tilde{K} = \frac{\epsilon^3}{k A^2 \eta} + \frac{\delta 8 \epsilon^2}{k' 3 A} \left(\frac{2RT}{\pi M \phi} \right)^{\frac{1}{2}} \quad (2.46)$$

where k is the so called Kozeny constant and k' is also a constant. The two quantities k and k' are related to k_0 and k_1

$$k = k_0 k_t^2 \quad (2.47(a))$$

$$k' = k_1 k_t^2 \quad (2.47(b))$$

k_t is the tortuosity defined (Grove, 1967)

$$k_t = \frac{l_e}{l} \quad (2.48)$$

where l_e is the length of a tortuous path traversed by a gas flowing through a membrane of length l . In equation 2.46 $1/k_t^2$ replaces κ in Barrer's equation (2.45). The use of the structure factor κ is preferred to use of $1/k_t^2$ since differs from unity not only because the channels are tortuous but also because of a number of other reasons associated with the structure of the porous medium (Barrer, 1967). For instance there are changes of shape of cross-sections corresponding to $k_0 = 2.00$ and $k_1 = 1.00$. Channels may have bottlenecks and there will be blind pores by-passed in the

steady-state. The term tortuosity for k_t implies that any deviation of $1/k_t^2$ from unity is entirely associated with tortuous channels. Other authors (for example Satterfield and Cadle, 1968) define $\tau = k_t^2$ as the tortuosity factor.

Ash, Barrer and Coughlan (1972) have integrated Weber's expression for the gas flow through a single capillary for the flux between $x=0$ and $x=1$. The resultant equation for the permeability was split into its three terms.

$$K^{cyl} = K_p^{cyl} + K_c^{cyl} + K_k^{cyl} \quad (2.49)$$

subscripts p, c and k refer to Poiseuille, conduction and Knudsen components respectively. For a porous medium with permeability $\tilde{K}'$ defined

$$\tilde{K}' = \frac{Jl}{\epsilon A_c \Delta C'_g} = \frac{\tilde{K}}{\epsilon} \quad (2.50)$$

three structure factors K_p , K_c and K_k were introduced

$$\tilde{K}'_p = \frac{K_p}{\epsilon} = K_p K_p^{cyl} \quad (2.51(a))$$

$$\tilde{K}'_c = \frac{K_c}{\epsilon} = K_c K_c^{cyl} \quad (2.51(b))$$

$$\tilde{K}'_k = \frac{K_k}{\epsilon} = K_k K_k^{cyl} \quad (2.51(c))$$

For the porous medium

$$\tilde{K} = \epsilon K' = \epsilon (K_p K_p^{cyl} + K_c K_c^{cyl} + K_k K_k^{cyl}) \quad (2.52)$$

Substituting for r with $2\epsilon/A$ and letting $f=1$ Ash, Barrer and Coughlan obtained

$$\begin{aligned} \tilde{K} = & \frac{\epsilon^3 K_p}{2A^2} \bar{p} + \frac{2\pi\epsilon^2}{3A} K_c \left(\frac{2RT}{\pi M \phi} \right)^{\frac{1}{2}} \\ & + \frac{2\epsilon\eta}{34p} \left(\frac{RT}{M \phi} \right) \left(\frac{K_k - \pi K_c}{4} \right) \\ & \cdot \ln \left(\frac{1 + \frac{4\epsilon}{A} \frac{1}{\eta} \left(\frac{2M \phi}{\pi RT} \right) p_0}{1 + \frac{4\epsilon}{A} \frac{1}{\eta} \left(\frac{2M \phi}{\pi RT} \right) p_1} \right) \end{aligned} \quad (2.53)$$

The first term of equation 2.53 is equal to the first term of equation 2.45 if $\kappa_p = 2\kappa/k_0$. For small pressures

$$\ln \left(\frac{1 + \frac{4\epsilon}{A} \frac{1}{\eta} \left(\frac{2M\phi}{\pi RT} \right) p_0}{1 + \frac{4\epsilon}{A} \frac{1}{\eta} \left(\frac{2M\phi}{\pi RT} \right) p_1} \right) \approx 4 \frac{\epsilon}{A} \frac{1}{\eta} \left(\frac{2M\phi}{\pi RT} \right)^{\frac{1}{2}} \Delta p \quad (2.54)$$

and hence

$$\bar{p} \rightarrow 0; \quad \tilde{K} \rightarrow \kappa_k \quad \frac{8}{3} \frac{\epsilon^2}{A} \left(\frac{2RT}{\pi M\phi} \right)^{\frac{1}{2}} \quad (2.55)$$

which corresponds to the low pressure limit of equation 2.45 when $\kappa_k = \delta_0 \kappa/k_1$.

Barrer and Strachan (1955) were the first to define an overall structure factor but a later definition by Barrer and Gabor (1959) is perhaps more useful. They defined the structure factor in terms of the ratio of diffusion coefficients. For a particular flow regime i the respective structure factor κ_i is given by

$$\kappa_i = \frac{D_i}{D_i^{\text{cyl}}} \quad (2.56)$$

where D_i is the diffusion coefficient for the porous media and D_i^{cyl} is the diffusion coefficient for the same flow regime, i , when the gas is flowing through a circular capillary of radius $2\epsilon/A$. Barrer and Gabor were considering the situation where gas phase flow was occurring only in the Knudsen regime but where there was also an extra flow (called by many authors "Surface flow") associated with the flow of adsorbed molecules. Four structure factors were defined κ_g , κ_{gs} , κ_s and κ_{ss} . Structure factor κ_g and κ_s are for the gas phase transport and the extra flow respectively and are defined for the transient state (the diffusion coefficients are obtained from the time-lags L_1^a). κ_{gs} and κ_{ss} are the corresponding structure factors for the steady state. In the work of Barrer and Gabor in actual fact κ_{gs} was defined by

$$D_{gs} = \kappa_{gs} \beta D_g^{cyl} \quad (2.57(a))$$

and κ_{ss} by

$$D_{ss} = \kappa_{ss} \beta D_s^{cyl} \quad (2.57(b))$$

where D_{gs} and D_{ss} are respectively the gas phase diffusion coefficient and the extra flow diffusion coefficient for the steady state (section 2.6) D_g^{cyl} and D_s^{cyl} are the gas phase and extra flow diffusion coefficients for a circular cylindrical capillary. D_g^{cyl} is equal to D_k (see equations 2.30 and 2.31) but D_s^{cyl} cannot be evaluated on any apriori basis β is given by

$$\beta = \frac{e_s}{A_s} \frac{A}{\epsilon} \quad (2.58)$$

where e_s is the porosity of "steady state pores" and A_s is the surface area of "steady state pores". e_s and A_s were assumed to differ from ϵ and A because of blind pores and crevices which were thought to play little part in the steady state flow. In later work by Barrer and his coworkers (for example Ash, Baker and Barrer, 1967; Ash, Barrer, Clint, Dolphin and Murray, 1973) the structure factor is combined with β and the equations defining κ_{gs} and κ_{ss} become

$$\kappa_{gs} = \frac{D_{gs}}{D_g^{cyl}} \quad (2.59(a))$$

$$\kappa_{ss} = \frac{D_{ss}}{D_s^{cyl}} \quad (2.59(b))$$

which are consistent with the general equation 2.56. It should be stressed that there are differences in notation for different workers, for instance κ_{gs} and κ_{ss} as defined by equations 2.59(a) and (b) are sometimes called κ_g and κ_s (for instance Nicholson and Petropoulos, 1968).

Introduction of structure factors is a useful empirical way of relating equations derived for the flow of gases through single capillaries to experimental results for the flow of gases through real porous media. However, much work has been

done to produce a capillary model for porous media by introducing various structural features of real pores which cause deviations from the simple bundle of capillaries in parallel (Nicholson and Petropoulos, 1974), Hiby and Pahl (1956) considered molecular flow through a repeatedly bent tube as a model for porous media. The effect of tortuosity of pores is to reduce the possibility of long diffusion paths and causes the total pore length to exceed l , the length of a single straight capillary. Adzumi (1937 (b)) considered two straight capillaries of different radii and lengths in series. The study of such a system has been extended by Barrer and Nicholson (1965) and the application of the serial model to porous media was considered. A parallel capillary model of a porous medium was examined by de Bethune and Rowell (1963). Four independent pore radii were defined the hydraulic radius (r_h), the sigma radius ($r_\Sigma = 1/A$, recalling that A is the surface area per unit volume of porous medium); the "Adzumi" radius ($r_{PK} = r^4/r^3$) and the Knudsen radius ($r_K = r^3/r^2$). Several pore size distributions were considered, two single Gaussian distributions and a double Gaussian distribution (first proposed for a porous system by Flood, Tomlinson and Leger, 1952(b)). Another improvement which can be made to the capillary model of a porous medium is to consider non-circular cross-sections. This approach was followed by Flood, Tomlinson and Leger (1952 (a,b)); however, unfortunately the work was based on Knudsen's erroneous expression (equation 2.15).

Nicholson and Petropoulos (1968) examined gas phase flow and gas phase and extra flow (which they termed surface flow) in a serial capillary model of a microporous media. From the point of view of the treatment adsorption was considered as only occurring in the Henry law range and it was assumed that there was no blockage or constriction of the pores due to adsorbed material. An expression for K_{gs} , (called K_g by Nicholson and Petropoulos) as defined by equation 2.59 (a) was obtained in terms of a pore radius distribution function and a tortuosity factor. Two pore radius distributions were considered a chi-square and a Gaussian distribution.

Nicholson and Petropoulos (1973(a)) obtained expressions for K_{gs} and K_{ss} for both a serial model and a parallel capillary model and considered various radius distributions. For a serial model $K_{gs} < 1$ and K_{ss} is positive and for a parallel bundle of capillaries $K_{ss} = 1$ and $K_{gs} > 1$. Neither the parallel model or the serial model are very realistic for most systems. The serial model does, however, serve to indicate the importance of bottlenecking (Nicholson and Sing, 1979) and can perhaps be used to represent pores in some types of wood. A capillary model in which the capillaries are interconnected in three dimensions to form a network has also been examined by Nicholson and Petropoulos (1971, 1974). The model consisted of a number of junctions joined together by cylindrical tubes along the sides and face diagonals of cubic unit cells. The network structure was varied by the systematic removal of tubes. Normalised structure factors $\bar{K}_{gs}$ and $\bar{K}_{ss}$ (designated $\bar{K}_g$ and $\bar{K}_s$ by Nicholson and Petropoulos) were considered

$$\bar{K}_{gs} = \frac{K_{gs}}{K_{gs}^0} \quad (2.60(a))$$

$$\bar{K}_{ss} = \frac{K_{ss}}{K_{ss}^0} \quad (2.60(b))$$

in which K_{gs}^0 and K_{ss}^0 are structure factors corresponding to the network where all the capillaries have the same radius, r . For a isotropic network K_{gs}^0 and K_{ss}^0 both equal $1/3$. $\bar{K}_{gs}$ and $\bar{K}_{ss}$ were evaluated by computer for a 3-dimensional network with a Gaussian radius distribution (Nicholson and Petropoulos, 1971, 1974) and also for 2-dimensional networks with a number of other radius distributions (Nicholson and Petropoulos; 1974, 1975 (a), 1977 (a)). Structure factors have also been calculated for the interdiffusion of two gases in random capillary networks and the transition from the Knudsen flow regime to the Poiseuille flow regime (Nicholson and Petropoulos; 1977 (b), 1978).

2.5. THE "DUSTY GAS" MODEL AND OTHER MODELS OF POROUS MEDIA

A porous material can be represented by a model composed of spheres distributed randomly in space (Deryagin and Bakanov; 1957; Bakanov and Deryagin, 1960). The flow of a gas through such a model porous medium can be regarded as the mutual diffusion of two gases with the "molecules" of one gas having an infinitely greater mass than the molecules of the other gas, the gas proper.

The term "dusty gas" was coined by Evans, Watson and Mason (1961) who independently proposed a similar model to the one described above. The system can be treated by means of classical kinetic theory of multicomponent mixtures. For a binary gas mixture diffusing through a porous medium the model can be treated as a ternary gas mixture (Evans, Watson and Mason, 1962). An equation for the Knudsen diffusion coefficient was derived (Evans, Watson and Mason, 1961)

$$\frac{1}{D_K} = \frac{16}{3} \left(\frac{n_d \tau}{\epsilon} \right) \left(\frac{M\phi}{2\pi RT} \right)^{\frac{1}{2}} \pi \sigma^2 \Omega_{1d}^{(1.1)*} \quad (2.61)$$

where n_d is the number of "dust" particles per unit volume, σ is the radius of the particles (the collision radius), $\Omega_{1d}^{(1.1)*}$ is the reduced collision integral for diffusion (Hirschfelder, Curtiss and Bird, 1964), for rigid spheres the collision integral is equal to unity.

Breton and Massignon (1963) also used a "dusty gas" model as a basis for a theory of gaseous separation by a porous wall.

A number of other workers have also used the model of a bed of spherical particles as representing porous media and the transport of gases through the resulting voids has been considered (for example Weissberg, 1963; Strieder and Vallejo, 1975; Evans, Abbasi and Sarin, 1980). These workers have not treated the porous material as being simply another component of the gas mixture.

A number of other models of porous material have been proposed. Flood, Tomlinson and Leger (1952(b)) considered

a lattice of empty cubic cells joined together into a channel network by narrower empty rectangular necks. A lattice of equal rectangular parallelepipeds of phase A embedded in a continuous matrix of phase B has been examined by Barrer and Petropoulos (1961). These models are somewhat idealised and it is difficult to represent real porous media by them.

2.6. THE EFFECT OF ADSORPTION AND THE HELIUM CALIBRATION METHOD

The total flux may be represented as the sum of two components; a gas phase flux, J_g , which would be present for the gas in the complete absence of adsorption and a flux J_s , which is associated with the presence of a mobile adsorbed film having a concentration gradient along it (Barrer and Grove, 1951(b))

$$J_{\infty} = J_g + J_s \quad (2.62)$$

the flow J_s is termed "extra flow" or perhaps less correctly "surface flow" (Nicholson and Sing, 1979). Work concerning the nature of this extra flow and various theoretical treatments are reviewed by Field, Watts and Weller (1963); Barrer (1967); and Nicholson and Sing (1979).

By analogy with Fick's equation (equation 2.3) a gas phase diffusion coefficient, D_{gs} , and a diffusion coefficient associated with the extra flow, D_{ss} , can be defined.

$$\frac{J_g}{A_c} = -D_{gs} \frac{dC_g}{dx} \quad (2.63(a))$$

$$\frac{J_s}{A_c} = -D_{ss} \frac{dC_g}{dx} \quad (2.63(b))$$

It can easily be shown that the overall diffusion coefficient, D , is given by (Ash, Baker and Barrer, 1967; Ash, Barrer and Lowson, 1973)

$$D = \frac{D_{ss} + \left[\left(\frac{dC'_s}{dC'_g} \right) \frac{A}{\epsilon} \right] D_{gs}}{1 + \left(\frac{dC'_s}{dC'_g} \right) \frac{A}{\epsilon}} \quad (2.64)$$

A second diffusion coefficient D_2 can be defined by the time lag L_1^2 (Barrer, 1948)

$$L \frac{a}{l} = \frac{l^2}{6D_2} \quad (2.65)$$

This transient diffusion coefficient can also be split into a gas phase diffusion coefficient, D_g and a diffusion coefficient associated with the extra flow, D_s (Barrer and Grove, 1951 (b))

$$D_2 = \frac{D_g + \left[\left(\frac{dC'_s}{dC'_g} \right) A/\epsilon \right] D_s}{1 + \left(\frac{dC'_s}{dC'_g} \right) A/\epsilon} \quad (2.66)$$

The permeability $\tilde{K}$ can also be split into a gas phase permeability, $\tilde{K}_g$ and a permeability associated with the extra flow $\tilde{K}_s$

$$\tilde{K} = \tilde{K}_g + \tilde{K}_s \quad (2.67)$$

The component associated with the extra flow is usually evaluated by the "helium calibration method". Helium is used as a reference gas, which is assumed to be nonsorbed at working temperatures and pressures. If Knudsen flow occurs it can be seen from equation 2.32 that the gas phase permeability of any species of molar mass M is given by

$$\tilde{K}_g = \tilde{K}_{He} \left(\frac{M_{He}}{M} \right)^{\frac{1}{2}} \quad (2.68)$$

where $\tilde{K}_{He}$ is the overall helium permeability and M_{He} is its molar mass. This equation applies for the flow of helium and the sorbed gas flowing at the same temperature. It should also be stressed that under Knudsen flow conditions $\tilde{K}_g = K_g$ and $\tilde{K}_{He} = K_{He}$. The permeability associated with the extra flow is calculated from the difference between $\tilde{K}$ and $\tilde{K}_g$. It is well known that the helium calibration method should be treated with caution (Barrer and Gabor, 1960) since not all the "surface flow" as determined above can be attributed to the adsorbed phase since there are some evaporative flights due to irregularities within the surface, there is also the effect of blocking by adsorbed molecules of the gas phase (Ash, Barrer and Pope, 1963 (b); Pope, 1963; Ash, Barrer and Lowson, 1973). This blocking effect is particularly important in the separation of gas mixtures (Ash, Barrer and Pope, 1963 (b); Ash, Barrer and Lowson, 1973; Hamilton

1980; Ash and Hamilton, to be published). Three possible divisions of flow into gas and surface phase have been proposed (Ash, Barrer and Sharma, 1976). For these reasons Ash, Barrer and their coworkers prefer the term "extra flow" to "surface flow".

Recently the helium calibration method has come under some scrutiny for another reason and it arises from the assumption that helium is a nonsorbed gas. Hwang and Kammermeyer (1966(a; b), 1967) studying the flow of gases through Vycor porous-glass membranes found for some gases including helium, that $\tilde{K} (M/T)^{\frac{1}{2}}$ (henceforth designated $\tilde{K}_T$) exhibited a minimum with temperature. Clearly considering equation 2.32 for a nonsorbed gas where Knudsen flow conditions predominate $\tilde{K}_T$ is expected to be independent of temperature. Hwang and Kammermeyer interpreted their results in terms of a surface diffusion mechanism, Hill (1955) considered a model for localized adsorption in which the surface was represented by a square lattice of sites separated by a potential energy barrier of height $E^\ddagger$. This model was applied in the consideration of surface diffusion by Hill and his approach was extended by Hwang and Kammermeyer (1966(a)) and later by Nicholson and Petropoulos (1973(b)). A working equation was developed by Hwang and Kammermeyer which was found to fit their results quite well. Using our notation for permeability

$$\tilde{K} \left(\frac{M}{T} \right)^{\frac{1}{2}} = A + B \exp \left(\frac{\Delta}{T} \right) \quad (2.69)$$

More correctly K should be written in equation 2.69 rather than $\tilde{K}$, but where K is independent of pressure the two permeabilities are identical. In the analysis of Hwang and Kammermeyer A is a geometry constant for a given porous membrane, it is independent of the flowing gas species and the temperature. B and Δ are constants for a particular gas and porous medium combination.

$$\Delta = \frac{E^* - E^\ddagger}{R} \quad (2.70)$$

E^* is the minimum molar potential energy for the adsorbed molecules, and $E^\ddagger$ is the molar activation energy or surface diffusion. Hwang and Kammermeyer conclude that even helium exhibits significant surface flow. A number of workers have criticised Hwang and Kammermeyer's conclusions (Satterfield and Cadle, 1968; Satterfield, 1969; Brown and Haynes, 1969) largely on the basis that the evidence for "surface flow" of helium at ambient temperatures is insufficient. Hwang and Kammermeyer (1968, 1969) have defended their results and conclusions. There is only limited experimental evidence concerning the adsorption and surface flow of helium. Steele and Halsey (1954, 1955) observed some adsorption of helium on a charcoal and porous glass, however, even at liquid nitrogen temperatures this adsorption was small. Appreciable amounts of helium at room temperature have been observed to be adsorbed on activated carbons, brown coal char and carbon blacks, whereas with other carbons such as low temperature coke and graphite little or no adsorption can be detected (Maggs, Schwabe and Williams, 1960; Kini and Stacy 1963). Kammermeyer and Rutz (1959) investigating the flow of gases through porous glass found that the computed gas flow of hydrogen (computed from helium data) was less than the observed flow. This was opposite to what was expected if hydrogen was exhibiting surface flow and helium was nonsorbed. It is, however, stressed that the calculated flow is within the experimental accuracy of the observed flow. Ash, Baker and Barrer (1967) reported a constant value for $\tilde{K}_T$ of helium in the temperature range 30°C to -195°C through constrained Graphon and Black Pearls membranes, with a small increase at the temperature of liquid oxygen and liquid nitrogen associated with the beginnings of adsorption and the resultant extra flow. Only a 3% decrease of $\tilde{K}_T$ for helium was found by Ash, Barrer and Lowson (1970) over the temperature range 300°C to -195°C for flow through a constrained Graphon membrane. Horiguchi, Hudgins and Silveston (1971) found almost a 50% increase in $\tilde{K}_T$ for helium flowing through a Graphon membrane in the temperature range 110°C to 0°C. The flow of

gases through three magnesium chromite membranes was studied by Ciesmak-Galland and Delafosse (1977). For one of the membranes they found a decrease in the value of $\tilde{K}_T$ at 299°C by a factor of almost three to the value of 32°C. With the other two compacts $\tilde{K}_T$ was independent of temperature. They conclude that this strange result is due to wall effects inherent to the plug constitution rather than due to extra flow of helium. Using the helium calibration method Haul and Hübner (1974) obtained in some cases negative value for D_s of n-pentane through Aerosil. A result which they interpreted partly in terms of blockage and partly in terms of the pentane flow being outside the Knudsen regime. The helium calibration method also led to negative values of D_s for cyclopentane (Haul and Hübner, 1975). In most studies at normal temperatures $\tilde{K}_T$ for helium is found to be independent of temperature and the helium calibration method leads to positive value for permeabilities and diffusion coefficients associated with the extra flow.

There are also a number of experimental results where adsorption is too small to be considered measurable which have shown that $\tilde{K}_T$ (or a related quantity) is dependent upon both gas and temperature for single capillaries (Berman and Lund, 1958; Lund and Berman, 1958, 1966 (a); Hanley and Steele, 1964; Barrer and Nicholson, 1965 (a)).

The approach of Hill (1956) and Hwang and Kammermeyer (1966(a)) has been developed by Nicholson and Petropoulos (1973(b)) in considering the flow of gas through a parallel sided slit. They introduce several new features such as the specification of the functional form of the adsorption potential energy, $E(z)$ (z is a component in the direction of the axis perpendicular to the slit sides). Secondly a division of the flux into two parts, J_g comprising those adsorbed molecules which have insufficient energy to cross the adsorption barrier the J_g the remaining molecules which can cross the desorption barrier. Two Henry's law constants k_s^+ and k_g are defined corresponding to the two divisions.

These constants are dependent upon the partition functions in the direction of z , normal to the walls of the slit and those for a direction parallel. The z direction partition functions are determined using a Hamiltonian (Nicholson and Petropoulos, 1973 (b); Nicholson and Sing, 1979)

$$H_z = E(z) - E_0 + \frac{p_z^2}{2m} \quad (2.71)$$

where E_0 is the depth of the potential well at the saddle point for a molecule of mass m having a component of momentum p_z in the z direction. For the adsorbed phase p_z lies between $-p_z^0$ and p_z^0 , for the gas phase p_z lies outside these limits

$$p_z^0 = (2m[E_m - E(z)])^{\frac{1}{2}} \quad (2.72)$$

E_m is the potential energy at the centre of the slit. The gas phase concentration and the surface phase concentration varies across the slit as a consequence of the theory. The former is least dense at the surfaces whereas the latter is most dense near the surface. Both phases become more uniform with increasing temperature. The total flux ratio could be written as

$$\phi = \frac{J}{J_g} = \frac{B_g k_g + B_s k_s^*}{J_g} \quad (2.73)$$

$B_g \simeq 1$, B_s is the product of the surface mean free path and a constant.

For a strongly adsorbed gas or low T in a sufficiently wide slit ($E_m \rightarrow 0$) the equation derived reduces to an equation similar to that derived by Hill for ϕ_s (Nicholson and Petropoulos, 1973(b), Nicholson and Sing 1979).

$$\phi_s = \frac{J_s}{J_g} = \frac{k_2 k T \exp(E^* - E)}{2 m \nu_y \nu_z k_3 d^2} \quad (2.74)$$

ν_y, ν_z are vibration frequencies of activated molecules at the top of the energy barrier, d is the half width of the slit, k_2 and k_3 are geometrical constants. However, for higher temperatures equation 2.74 show a reversal of

temperature trend, which is not shown by more detailed calculations. This confirms a contention made by Nicholson and Petropoulos that equation 2.74 is invalid in the region where it predicts a minimum in ϕ_g , as in equation 2.69 which also assumes simple harmonic vibration partition functions and predicts a minimum of a plot of $\tilde{K}_T$ against T at a temperature equalling $(E^* - E^\ddagger)/R$.

For narrow slits the temperature trend of ϕ_g is not altered by variation of d but $\phi_g = \bar{J}_g'/J_g$ (J_g' is the gas phase flux inside the pore model, J_g is the gas phase flux of a nonsorbed gas) may be more than unity for low temperatures and approach unity as T approaches infinity. For wider slits ϕ_g increases towards unity as the temperature becomes large. At the same time ϕ_s approaches zero so it is clear that ϕ may pass through a minimum. As d becomes still larger the temperature dependence of ϕ becomes smaller since ϕ_g approaches unity and ϕ_s becomes insignificant. Differences in the results of Ash, Barrer and Lowson (1970) and Hwang and Kammermeyer (1966(a)) can be resolved in terms of differences in pore size. Nicholson and Petropoulos' theory can be criticised on several grounds (Nicholson and Petropoulos (1975(b); Nicholson and Sing, 1979) A simple slip geometry is too specialized to represent a real porous medium. Transition state theory is difficult to justify in the context of diffusion. The division of fluxes implies a division of molecular trajectory types whereas in actual fact all the molecules travel in the potential field due to the adsorbent.

An alternative explanation to that of Hwang and Kammermeyer's concerning surface diffusion of helium was suggested by Brown and Haynes (1969). They pointed out that Knudsen's and Smoluchowski's derivation of their respective flow equations (equation 2.27 and 2.28) ignore the effect of interactions between the walls of the porous medium and the flowing gas molecules. Sandler (1972) tried to take these interactions into account in his study of the flow of gases through porous media under Knudsen flow conditions. Sandler was using the "dusty gas" model, and his starting point was equation 2.61. He looked at nature of the reduced collision

integral where inelastic collisions were occurring. Assuming an interaction energy between the gas molecule and the porous medium with the form

$$E = Ar^{-n} - Br^{-m} \quad (2.75)$$

where A , and B are parameters describing the scale and the magnitude of the interaction, r is the separation between the gas molecule and the "dust" particle, n and m are the indexes of the repulsive and attractive components of the interaction energy respectively. Using the expression obtained by Hassé and Cook (1929) for the viscosity of a gas and assuming that the reduced viscosity collision integral was proportional to the reduced diffusion collision integral Sandler obtained an expression for the Knudsen permeability of a gas. Using our notation this equation can be written

$$K_k = C_{n,m} \left(\frac{T^{(4+3n-2m)/2n}}{S_{n,m} + T^{(n-m)/n}} \right) \quad (2.76)$$

$C_{n,m}$ is a constant depending both on the gas and the membrane $S_{n,m}$ is a "generalized Sutherland constant". Sandler actually defined his permeability Q_k in terms of a pressure gradient but it is related to the Knudsen permeability defined in this work by the relation

$$K_k = Q_k RT \quad (2.77)$$

The validity of equation 2.76 can be tested with the experimental data by plotting $(T^{(4+3n-2m)/2n})/\tilde{K}$ against $T^{(n-m)/n}$ which should give a straight line with a gradient of $1/C_{n,m}$ and an intercept of $S_{n,m}/C_{n,m}$. Equation 2.76 can give a minimum when $\tilde{K}_T$ is plotted against temperature.

With the approach followed by Sandler it is difficult to include geometrical effects also it provides no insight into the concept of surface flow (Nicholson and Petropoulos, 1975(b); Nicholson, Petrou and Petropoulos, 1979).

Rhim and Hwang (1976) examined the Knudsen flow of gases in a parallel slit with a potential field resulting from the wall. The work involved the numerical solution of the Boltzmann equation. It was found that the external potential field enhanced the gas velocity near the walls and

retards that in the bulk phase. The results do not give any indication of a temperature minimum. Groome and Pothering (1979) considered the flow of gases through two parallel plates where interaction occurs between the gas molecules and the surface, their work also involves the solution of the Boltzmann equation. Assuming a square well potential they obtain a separation into gas phase diffusion and surface phase diffusion of the form

$$D = D_g + K_{eq} D_s \quad (2.78)$$

K_{eq} is the gas-solid equilibrium partition function given by

$$K_{eq} = \exp \left(\frac{\xi}{kT} \right) \quad (2.79)$$

where ξ is the potential energy of interaction well depth. Again their results do not give any indication of a temperature minimum.

An alternative approach has been developed (Nicholson and Petropoulos, 1975 (b), to be published; Nicholson Petrou and Petropoulos, 1979) in which molecular trajectories are calculated directly. The method is based on a generalisation of von Smoluchowski's molecular path tracing (M.P.T.) method, (see section 2.3). The equations of motion for a molecule travelling in a potential field due to the wall were solved for both parallel slit (Nicholson and Petropoulos, 1975 (b); Nicholson, Petrou and Petropoulos, 1979) and a circular cylinder (Nicholson and Petropoulos, 1975 (b), to be published) for a slit of length l and width b

$$\frac{J}{b\Delta C_g} = \frac{1}{b} \frac{m}{\pi kT} \int_0^b \int_{-\infty}^{\infty} \int_0^{\infty} x v_x \exp \left(\frac{-E(z)}{kT} \right) \cdot \exp \left(\frac{-mv^2}{2kT} \right) dv_x dv_z dz \quad (2.80)$$

x is the component of a molecular trajectory in the direction of flow, z is the component of a molecular trajectory at right angles to the direction of flow, v_x and v_z are the

respective component of the velocity whose modulus $v = (v_x^2 + v_z^2)^{1/2}$, m is the molecular mass, k is Boltzmann's constant, $E(z)$ is the potential function. A similar equation was obtained for a circular capillary of length l and radius R (Nicholson and Petropoulos, to be published).

$$\frac{J_{\infty l}}{\pi R^2 \Delta C_g} = \frac{\bar{K}}{\pi R^2} = 2 \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^{2\pi} \int_0^R \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} x v_x \exp \left(\frac{-E}{kT} \right) \cdot \exp \left(\frac{-mv^2}{2kT} \right) dv_x dv_r dv_{\theta} r dr d\theta \quad (2.81)$$

r is the distance measured normal to the surface from the centre of the slit, θ is the angular coordinate of a cylindrical coordinate system, v_r and v_{θ} are the respective components of the velocity whose modulus $v = (v_x^2 + v_r^2 + v_{\theta}^2)^{1/2}$. Numerical computation of equation 2.80 and 2.81 were made assuming various potential functions. When the wall was infinitely repulsive and there is no attractive component in the potential field the Knudsen value for the flux was obtained ($J = J_g$). When the attractive component was introduced it was found that $\phi = J/J_g$ decreased initially with increasing temperature and passed through a temperature minimum. For a sufficiently large adsorption well depth $\ln \phi$ became a linear function of $1/T$. The temperature minimum of ϕ can be attributed to two opposing trends (Nicholson and Sing, 1979) as the well depth increases (or T decreases) the trajectory length becomes less than the linear Knudsen trajectory length, and under the same conditions the concentration close to the wall increases. The minimum becomes deeper with increasing $1/R$. For increasing R the minimum broadens continuously, but tends to deepen at first and then become shallower (Nicholson and Petropoulos, to be published).

The results for the slit model have been shown to be in good agreement with a Monte-Carlo calculation, assuming the same potential function (Nicholson, Petrou and Petropoulos, 1979). The theoretical results for a cylindrical

capillary have been shown by Nicholson and Petropoulos (to be published) to be consistent with the experimental results of Hwang and Kammermeyer (1966(a)) and Ash, Barrer and Lowson (1970). Also on the high temperature side of the minimum ϕ for Helium can be greater than ϕ for a heavier molecule as has been observed by Hwang and Kammermeyer (1966(a)). Nicholson and Petropoulos conclude that the use of the helium calibration method in assessing "surface flow" is severely limited.

2.7. INTERACTIONS BETWEEN GAS MOLECULES AND SOLID SURFACES

There are a number of review articles and monographs which discuss in part the interaction between gas molecules and solid surfaces (for example Young and Crowell, 1962, chapter 2; Avgul and Kiselev, 1970; Sing, 1973; Steele, 1974 chapter 2). Before such interactions are discussed it is pertinent to deal with interactions between single molecules, since gas-surface interactions are essentially made up of many molecule-molecule interactions.

Lennard-Jones (1924) proposed an expression in the form of equation 2.75 to represent the energy of interaction between two uncharged atoms or molecules with a spherically symmetrical charge distribution. The expression consists of two terms: a repulsive term and an attractive term. The repulsive term arises from distortions of the electronic distributions caused by bringing the molecules together

$$E_{\text{rep}} = A r^{-n} \quad (2.82)$$

where A is a constant characteristic of the interacting species. The reference energy level corresponds to infinite separation of the two molecules.

The attractive term is brought about by dispersive forces. The vibrations of the molecule in the ground state produce momentary dipole and multipole moments. These instantaneous moments induce in the neighbouring molecule resonant moments in phase with the first molecule and there is an attractive interaction between the two molecules, the dispersive term is

$$E_{\text{dis}} = -B r^{-m} \quad (2.83)$$

B is a constant dependent on the two interacting molecules, m is equal to 6 and n is often taken as 12. The interaction energy, E is then given by the Lennard-Jones 6-12 potential

$$E(r) = Ar^{-12} - Br^{-6} \quad (2.84)$$

The repulsive term is sometimes taken to be given by

$$E_{\text{rep}} = A' \exp(-ar) \quad (2.85)$$

a and A' are positive constants characteristic of the interacting species. In which case the potential function becomes the 6-exp or modified Buckingham potential (Young and Crowell, 1962).

$$E(r) = A' \exp(-ar) - Br^{-6} \quad (2.86)$$

Equation 2.84 can be written in a number of ways. It can be written in terms of the depth of the potential energy minimum ϵ^* and the equilibrium distance r^* between the two interacting molecules or atoms (for example Young and Crowell, 1962; Sing, 1973)

$$E(r) = \epsilon^* \left[\left(\frac{r^*}{r} \right)^{12} - 2 \left(\frac{r^*}{r} \right)^6 \right] \quad (2.87)$$

$$E(r^*) = -\epsilon^* \quad (2.88)$$

$E(r^*)$ is the minimum potential energy; it is a negative quantity. The equation can also be written in terms of the separation distance $r_0 = (1/2)^{1/6} r^*$ corresponding to zero potential energy (for example Steele, 1974)

$$E(r) = 4\epsilon^* \left[\left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right] \quad (2.89)$$

The dispersion energy constant, B is given by

$$B = 2\epsilon^* r^{*6} = 4\epsilon^* r_0^6 \quad (2.90)$$

B is often designated C (Young and Crowell, 1962; Steele, 1974) or A_{12} (Ash, Barrer, Clint, Dolphin and Murray, 1973). A number of expressions have been derived for B. For the interaction of two oscillating molecules 1 and 2 London (1930(a)) obtained the expression below for the dispersion

energy constant

$$B_L = \frac{3}{2} \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{\alpha_1 \alpha_2}{(1/(h\nu_1) + 1/(h\nu_2))} \quad (2.91)$$

α_1 and α_2 (Cm^2V^{-1}) are the polarizabilities of molecules 1 and 2, ν_1 and ν_2 (Hz) are the characteristic frequencies, h is Plank's constant ($6.62620 \times 10^{-34} \text{Js}$) and ϵ_0 is the permittivity of a vacuum ($8.854185 \times 10^{-12} \text{Fm}^{-1}$). The energies $h\nu_1$ and $h\nu_2$ are approximately equal to the ionization energies I_1 and I_2 of molecules 1 and 2 respectively, and equation 2.91 is often written

$$B_L = \frac{3}{2} \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{\alpha_1 \alpha_2}{(1/I_1 + 1/I_2)} \quad (2.92)$$

Slater and Kirkwood (1931) derived an alternative expression for the constant

$$B_{SK} = \frac{3}{4} \frac{eh}{\pi m^{\frac{1}{2}}} \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{\alpha_1 \alpha_2}{(\alpha_1/n_1)^{\frac{1}{2}} + (\alpha_2/n_2)^{\frac{1}{2}}} \quad (2.93)$$

e ($1.602192 \times 10^{-19} \text{C}$) and m ($9.10955 \times 10^{-31} \text{kg}$) are the protonic charge and electronic mass respectively, and n_1 and n_2 are the number of electrons in the outer-shells of molecules 1 and 2. A third equation is the Kirkwood-Müller expression (Kirkwood, 1932; Müller, 1936)

$$B_{KM} = - \frac{1}{(4\pi)^2 \epsilon_0} \frac{6 mc^2}{N_A} \frac{\alpha_1 \alpha_2}{(\alpha_1/\chi_1) + (\alpha_2/\chi_2)} \quad (2.94)$$

χ_1 and χ_2 ($\text{m}^3 \text{mol}^{-1}$) are the diamagnetic susceptibilities of the molecules 1 and 2, N_A is Avogadro's constant ($6.02217 \times 10^{23} \text{mol}^{-1}$) and c is the speed of light in a vacuum ($2.997925 \times 10^8 \text{ms}^{-1}$). The values of the physical constants quoted above were taken from McGlashan (1971).

When the interaction between an adsorbate molecule and an adsorbent surface is considered the energy is obtained by summing the pair-wise interaction potential for every atom

in the adsorbent and every atom in the adsorbate. Barrer (1937) starting from the Lennard-Jones 6-12 potential and using the Kirkwood-Müller formula for the dispersion energy constant calculated the interaction energy of hydrogen, argon and nitrogen with graphite. He summed numerically over 100 atoms of the basal face of the graphite. However, Barrer used r^* the equilibrium distance between the gas molecule and an isolated carbon atom in the graphite in the calculation, and not the equilibrium separation of the molecule from the lattice. The values for the energy potential are hence too inaccurate for comparison with experimental heats of adsorption (Young and Crowell, 1962). Kiselev and coworkers (see for example Avgul, Isirikyan, Kiselev, Lygina and Poshkus, 1957; Avgul and Kiselev, 1970; Kiselev, Poshkus, Grumadas, 1979, see also Sing, 1973), used an expression for the interaction potential between simple and complex molecules with the basal plane of graphite of the form

$$E(z) = -B_{ij1} \sum r_{ij}^{-6}(z) - B_{ij2} \sum r_{ij}^{-8}(z) - B_{ij3} \sum r_{ij}^{-10} - C_{ij} \sum r_{ij}^{-6}(z) + A_i \sum \exp(-r_{ij}/\rho_{ij}) \quad (2.95)$$

r_{ij} is the distance of the centre of either the adsorbed molecule i (or for a complex molecule its atom or group i) from the centres of the carbon atoms in the graphite lattice j , z is the distance of the centre i from the plane that passes through the centres of the outer layer of carbon atoms and ρ_{ij} are constants for the individual interactions. B_{ij1} , B_{ij2} and B_{ij3} are dispersion force constants calculated from Kirkwood-Müller type equations, B_{ij1} represents dipole - dipole interactions, B_{ij2} represents dipole-quadrupole interactions and B_{ij3} represents quadrupole - quadrupole interactions. C_{ij} is a constant of inductive interaction and represents the interaction between a permanent dipole moment in the adsorbed molecule and the induced moment in the solid atoms. The final term allows for short range repulsion, A_i adjusted to satisfy the condition $(\partial E/\partial z)_{z=z^*} = 0$. The summations of r_{ij}^{-6} , r_{ij}^{-8} , and r_{ij}^{-10} were made over 100 - 250 centres j

and $\exp(-r_{ij}/\rho_{ij})$ was summed at 40 to 50 centres j (Avgul, Isirikyan, Kisilev, Lygina and Poshkus, 1957). The remaining interaction was estimated by integration. It was estimated that the dipole-quadrupole and the quadrupole-quadrupole terms contributed about 10% and 1% respectively to the total value of the dispersion interaction; the contribution of the dipole-induced dipole term amounts to at most 5%. Kisilev's results are generally in excellent agreement with experimental values of the gas-solid energy.

The calculation of the gas-solid interaction potential can be simplified by replacing the summation procedure by an integration procedure. London (1930(b)) derive an expression for the interaction by integrating the dispersion term

$$E_{\text{dis}} = - \int_{\substack{\text{all} \\ \text{space}}} Br^{-6} \bar{n} \, dV \quad (2.96)$$

where dV is a volume element and $\bar{n}$ is the number density of solid atoms per unit volume. For a solid of uniform density

$$E_{\text{dis}} = - \frac{\bar{n} \pi B}{6z^3} \quad (2.97)$$

where z is the perpendicular distance between the gas molecule and the solid. A similar process can be followed for the total interaction (Hill, 1960) to obtain

$$E_s = \frac{2}{3} \pi \bar{n} \, \epsilon^* r_0^3 \left[\frac{2}{15} \left(\frac{r_0}{z} \right)^9 - \left(\frac{r_0}{z} \right)^3 \right] \quad (2.98(a))$$

or (for example Young and Crowell, 1962)

$$E_s = \frac{\pi \bar{n} \, \epsilon^* r^*{}^3}{3} \left[\frac{1}{15} \left(\frac{r^*}{z} \right)^9 - \left(\frac{r^*}{z} \right)^3 \right] \quad (2.98(b))$$

If $z_0 = (2/15) r_0$ is the perpendicular distance corresponding to zero energy and $z^* = (1/5) r^*$ is the perpendicular distance at which E_s is a minimum, equation 2.98 (a) becomes

$$E_s = 5\pi \bar{n} \, \epsilon^* z_0^3 \left[\left(\frac{z_0}{z} \right)^9 - \left(\frac{z_0}{z} \right)^3 \right] \quad (2.99(a))$$

equation 2.99(b) becomes

$$E_s = \frac{5}{9} \pi \bar{n} \epsilon^* z^{*3} \left[\left(\frac{z^*}{z} \right)^9 - 3 \left(\frac{z^*}{z} \right)^3 \right] \quad (2.99(b))$$

The minimum energy of interaction (Ash, Barrer, Clint, Dolphin and Murray, 1973)

$$E_s(z^*) = - \frac{10 \pi \bar{n} \epsilon^* z^{*3}}{9} = - \frac{\pi B \bar{n}}{9 z^{*3}} \quad (2.100)$$

The integration can also be carried out in two dimensions to give the interaction between a single gas molecule and a plane (Steele, 1974; Everett and Powl, 1976)

$$E_p = 4 \pi \bar{n} \epsilon^* r_0^2 \left[\frac{1}{5} \left(\frac{r_0}{z} \right)^{10} - \frac{1}{2} \left(\frac{r_0}{z} \right)^4 \right] \quad (2.101(a))$$

$$E_p = \pi \bar{n} \epsilon^* r^{*2} \left[\frac{1}{5} \left(\frac{r^*}{z} \right)^{10} - \left(\frac{r^*}{z} \right)^4 \right] \quad (2.101(b))$$

If $z_0 = (2/5)^{1/6} r_0$ and $z^* = (1/2)^{1/6} r^*$ equations 2.101(a) and (b) can be rewritten

$$E_p = 5 \pi \bar{n} \epsilon^* z_0^2 \left[\left(\frac{z_0}{z} \right)^{10} - \left(\frac{z_0}{z} \right)^4 \right] \quad (2.102(a))$$

$$E_p = \frac{4}{5} \pi \bar{n} \epsilon^* z^{*2} \left[\left(\frac{z^*}{z} \right)^{10} - \frac{5}{2} \left(\frac{z^*}{z} \right)^4 \right] \quad (2.102(b))$$

The minimum energy of interactions is

$$E_p(z^*) = - \frac{6 \pi \bar{n} \epsilon^* z^{*2}}{5} = - \frac{3 \pi B \bar{n}}{10 z^{*4}} \quad (2.103)$$

In general for a "n-m potential" that is a potential whose repulsive term has an index of n and whose dispersive term has an index m the energy as a function of z can be given as (Sams, Constabaris and Halsey, 1960; Everett and Powl, 1976).

$$E(z) = \left(\frac{n}{n-m} \right) \left(\frac{n}{m} \right)^{m/(n-m)} \epsilon^* \left[\left(\frac{z_0}{z} \right)^n - \left(\frac{z_0}{z} \right)^m \right] \quad (2.104)$$

and

$$z_0 = \left(\frac{u}{n} \right)^{1/(n-m)} z^* \quad (2.105)$$

Steele (1974) has shown that the 3-9 potential obtained by treating the solid as a continuum is a comparatively poor approximation to the energy obtained by pair-wise summation of the 6 - 12 potential. Treating each layer of adsorbent parallel to the surface as a continuum in order to obtain the 4 - 10 potential and then summing the contribution from each layer is a better approximation. The use of the 3 - 9 potential does however have the virtue of being a simple calculation.

In any calculation of the interaction between an adsorbate and an adsorbent three body interactions should be considered (Steele, 1974; Nicholson and Sing, 1979). The contribution to the total energy made by three body interactions are however difficult to assess.

Recently numerical calculations have been made of the adsorption energy in microporous carbons (Nicholson and Sing, 1979). Theoretical models have been proposed for the calculations of adsorption potentials in parallel sided slit-like pores and also for cylindrical micropores (for example Steele and Halsey, 1955, Nicholson, 1975; Everett and Powl, 1976). For a slit of width $2d$ (Steele and Halsey, 1955; Everett and Powl, 1976)

$$E_{\text{slit}} = \frac{(3)^{3/2}}{2} \epsilon_s^* \left[\left(\frac{z_0}{d+z} \right)^9 + \left(\frac{z_0}{d-z} \right)^9 - \left(\frac{z_0}{d+z} \right)^3 - \left(\frac{z_0}{d-z} \right)^3 \right]$$

$$\epsilon_s^* = - E_s(z^*) \quad (2.105)$$

where z_0 is the distance used in equation 2.99(a), z is measured normal to the surface from the centre of the slit. Everett and Powl (1976) actually obtained an expression for E_{slit} in terms of r_0 and also considered interaction of a adsorbate molecule with single lattice planes of the adsorbent. Nicholson and Paton-Brown (1975, to be published) used an

equation similar to equation 2.106 in their calculations concerning the flow of gases through porous media. In the case of the cylindrical pore model (Nicholson and Sing, 1979) the attractive term and the repulsive term are multiplied by appropriate functions depending on the cylinder radius, R and the distance of the adsorbate molecule from the axis, a . Nicholson (1975) expressed these functions in polynomial form, with the coefficients estimated by means of numerical integration. The expression has been used in theoretical studies of the flow of gases through porous media (Nicholson and Petropoulos, to be published). Everett and Powl (1976) also expressed these functions in terms of polynomials, except the coefficients were given in terms of gamma function combinations. They obtained expressions in both the 4 - 10 potential form, and the 3 - 9 potential form.

The depth of the potential energy minimum can be related to the energy of adsorption ΔE (as defined by Ash, Barrer, Clint, Dolphin and Murray, 1973)

$$\Delta E = RT - q_{st}^0 \quad (2.107)$$

where q_{st} is an isosteric heat of adsorption defined by equation 2.108 and q_{st}^0 is the value of q_{st} corresponding to zero uptake

$$q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T} \right)_{n_s} \quad (2.108)$$

n_s is the absolute uptake of the adsorbate by the adsorbent. The value of ΔE at absolute zero designated ΔE_0 can be given by the expression

$$\Delta E_0 = E(z^*) - E_{zp} \quad (2.109)$$

where E_{zp} is the zero point energy. At higher temperatures the molecules will have higher vibrational energy than E_{zp} but ΔE_0 will remain a good approximation to ΔE (Ash, Barrer, Clint, Dolphin and Murray, 1973).

2.8 SURFACE AREA DETERMINATION

A method commonly used for the determination of surface

area is the B.E.T. method. The theory was first introduced by Brunauer, Emmett and Teller (1938), and the method has been reviewed in a number of monographs (for example Young and Crowell, 1962; Gregg and Sing, 1967).

Brunauer, Emmett and Teller from kinetic considerations derived "B.E.T. equation" which is usually applied in linear form

$$\frac{p}{v(P_0 - p)} = \frac{1}{v_m C} + \frac{(C-1)p}{v_m C P_0} \quad (2.110)$$

where P_0 is the saturated vapour pressure of the adsorbent v ($\text{cm}^3_{\text{STP}} \text{g}^{-1}$) is the volume of gas adsorbed at pressure p , v_m is the volume of gas required to cover the surface with a complete monolayer and C is a constant related to both the net enthalpy and net entropy of adsorption. The B.E.T. equation can also be derived with the aid of statistical mechanics (see for example Aveyard and Haydon, 1973, chapter 5).

The BET plot of $p/v (P_0 - p)$ against p/P_0 is generally linear in the approximate p/P_0 range 0.05 to 0.30, but for graphitised carbon it may not extend beyond $p/P_0 = 0.1$ (Sing, 1973). Various attempts have been made to improve the range of validity of the BET equation by introducing additional parameters (for example Barrer, MacKenzie and MacLeod, 1952; Sing, 1973). This is a means of compensation for the various inadequacies of the theory behind the equation. In the derivation of the expression it is assumed that adsorption is localised in all layers of adsorbed molecules, but at the same time it is supposed that all layers other than the first are liquid-like and have the properties of bulk liquids. It is also assumed that there are no lateral interactions between the stacks of molecules.

The BET surface area, A_{BET} is calculated from v_m assuming an average area a_m occupied by the adsorbate molecule in the completed monolayer. Sing (1973) discusses the use of a number of adsorbates and the respective values of a_m used for BET area determinations. The relationship of the method with

the value of C is also discussed. Despite all its shortcomings the BET procedure is the most frequently used method for assessment of surface area.

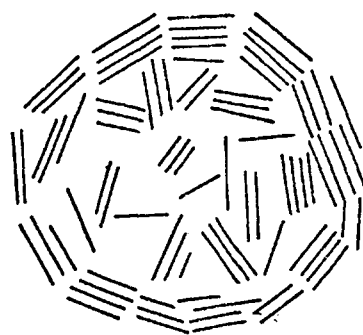
2.9 THE CARBON.

The carbon used in this study was the graphitised form of Sterling S. It is a carbon black produced by partial combustion of natural gas in a furnace (Schaeffer, Smith and Polley, 1953; Dollimore, 1971). Hence it is described as being a "furnace black" as opposed to a "channel black" (such as Spheron 6 the ungraphitised form of Graphon), produced by burning natural gas in an oxygen deficient atmosphere where the flame is directed to steel channels.

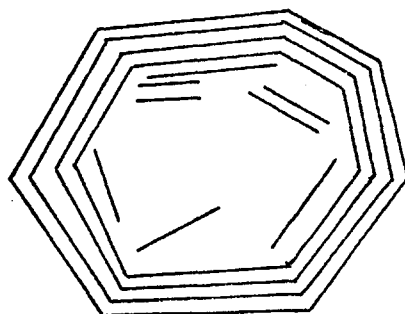
In carbon blacks the carbon atoms are chemically bonded to form plane hexagonal networks called layer planes. These are piled in stacks approximately 0.35 nm apart, some being three to five layers deep, called crystallites (~ 1.5 nm thick and ~ 2 nm diameter). In crystallites the layer planes are arranged parallel and equidistant (Biscoe and Warren, 1942). The orientation is however random with respect to the layer normal. Furnace blacks show less surface crystallite orientation than channel blacks of corresponding particle size (Hess, Ban, Eckert and Chirbo, 1968).

Heat treatment in the region 1000°C to 3000°C brings about a process known as graphitisation. Sterling S is graphitised by heating to 2700°C in an induction furnace. During graphitisation changes in crystallite size and orientation occur, the dimensions and numbers of parallel layer groups increasing. Initially orientation remains random. When the layer diameter increases to above 10 nm the layers begin to position themselves as in graphite (Houska and Warren, 1954). Progressive improvement in layer alignment orientation takes place, starting at the surface and then moving inward at higher temperatures (Riven, 1971). At the surface the layer planes grow to form an outer shell. In the more disordered interior the layer planes grow and migrate and become parallel to the shell, tending to leave a partially occupied void in

Figure 2.2. The Change in Structure of Carbon Black due to the Graphitisation Process.



(a) Before graphitisation.



(b) After graphitisation.

the interior (Figure 2.2). The graphitised black and is said to have a capsular structure. The work of Heckman and Harling (1966) utilizing a technique of oxidative attack supports the concentric crystallite model of the carbon black. Earlier dark-field electron micrography (Hall, 1948) showed that the layer planes near the surface are orientated parallel to the surface. Among the carbon blacks studied by Hall (1948) was Sterling R which appears to have as surface area of similar magnitude to that of Sterling S (Polley, Schaeffer and Smith, 1953).

CHAPTER 3

EXPERIMENTAL TECHNIQUE

3.1 MATERIALS USED.

Hydrogen, nitrogen, helium, neon, argon, xenon and carbon dioxide all more than 99.99% pure and krypton 99.97% pure were "research grade" gases supplied in 1 litre pyrex glass bulbs by British Oxygen Company Special Gases division. Deuterium 99.7% pure was similarly supplied by BOC Prochem division. The National Physical Laboratory supplied methane, ethane and propane of 99.9% purity in 500 cm³ pyrex bulbs.

Sterling S is a graphitised carbon black obtained from the Cabot Corporation, Massachusetts, USA. The graphitised carbon is obtained by heating the ungraphitised form in an induction furnace to 2700 - 3000°C. Some of the physical properties of Sterling S are listed in table 3.1.

Table 3.1 Physical Characteristics of Sterling S.

* Surface Area/ 10 ⁴ m ² kg ⁻¹	2.22
* Helium Density/ 10 ³ kg m ⁻³	2.08
Crystallite Height/ 10 ⁻⁹ m	7.9
Crystallite Width/ 10 ⁻⁹ m	9.1
Ash	0.06%
Volatile	0.0%

* As determined in this work; the remaining data furnished by Cabot Corporation, 1965.

3.2 PREPARATION OF THE POROUS MEMBRANES AND THE SORPTION SAMPLE

The membrane holder assembly is shown in detail in figure 3.1. The membrane holders were manufactured from stainless steel together with the copper cooling coils in the mechanical workshop of this department. The overall length of the stainless steel cylinder was 9cm, its external

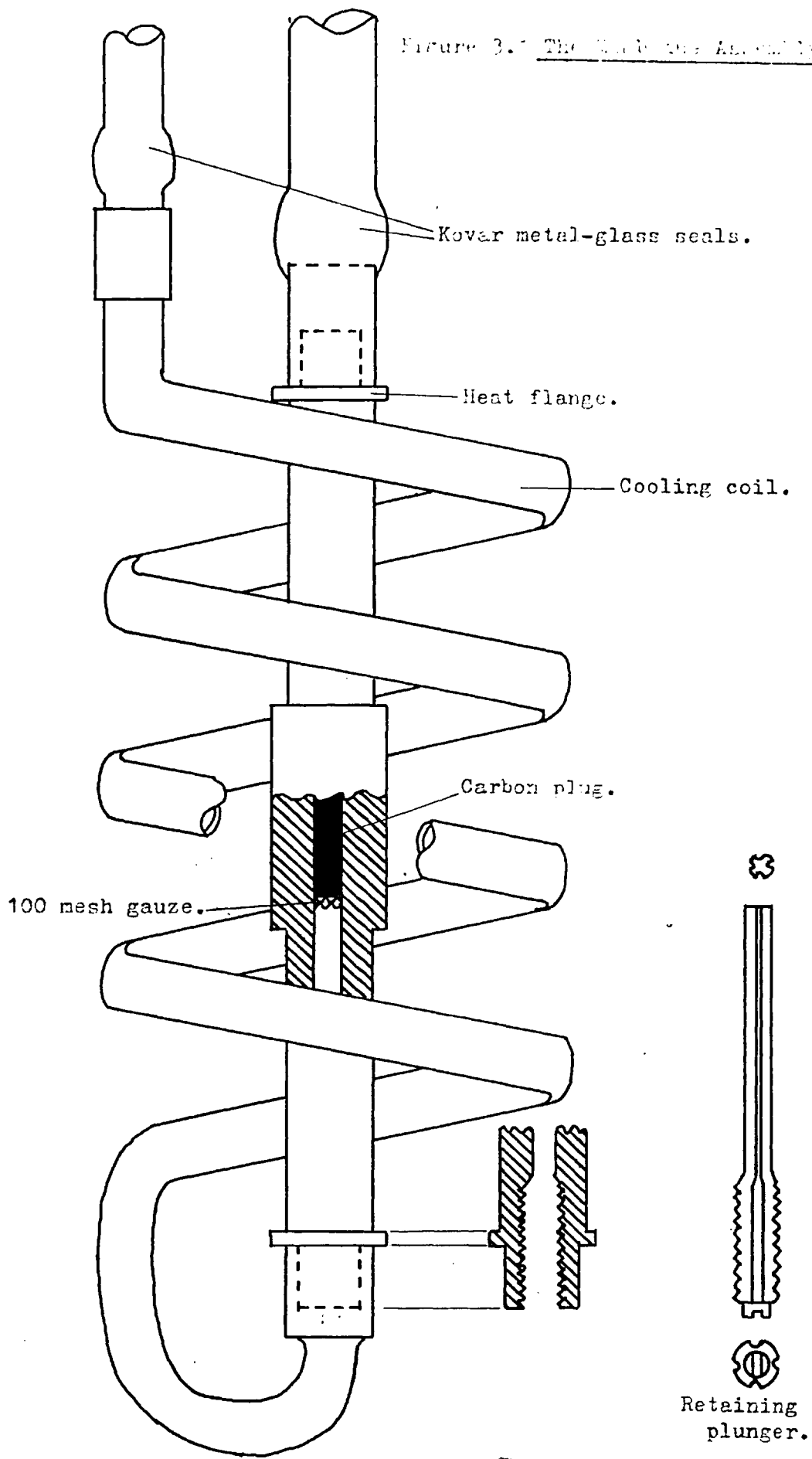
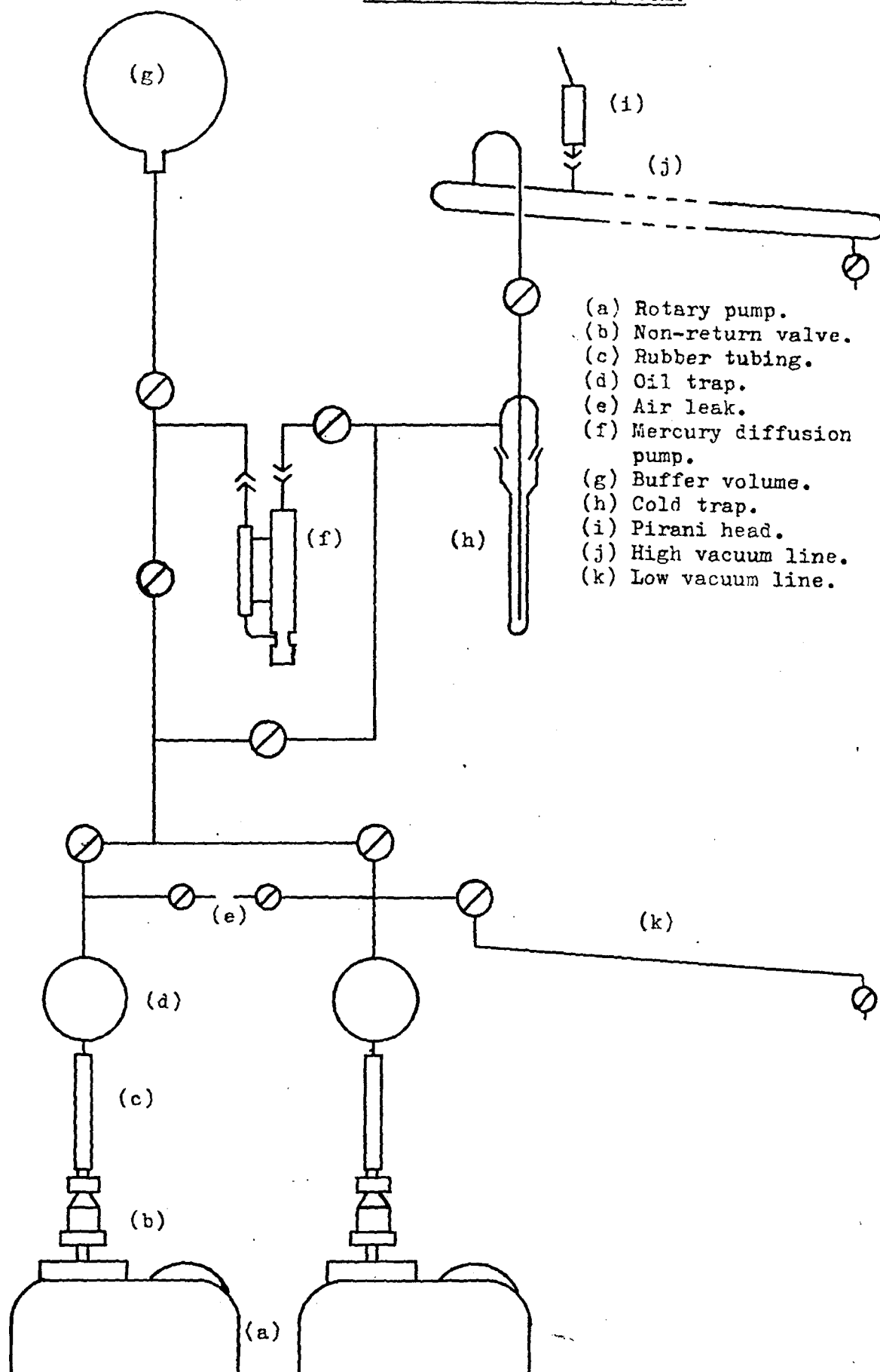
Figure 3.7 The Sublimation Apparatus.

Figure 3.2. A Typical Pumping System.

diameter was 1.25 cm at the ends and 1.6 cm in the centre. The internal diameter was nominally 0.3 cm. The internal cross-sectional area was determined accurately by resting the plug holder on a compression plunger and adding weighed amounts of mercury. The height of the mercury column was measured by lowering a needle attached to the telescope of cathetometer until it touched the mercury. The needle and the holder were made to form part of an electric light circuit and the point of contact was indicated by the bulb lighting. From knowing the mass of mercury forming the column, its height and the density of mercury the cross-sectional area was calculated.

Two membranes were prepared by incremental compaction of Sterling E. For the first, three increments of the powder were weighed out to form a plug of nominal porosity 0.5 and length 1 cm. The membrane was fabricated by compressing the carbon into the holder using hardened steel compression plungers and a $1\frac{1}{2}$ ton Dennison press. A 2 cm dial gauge was used to ensure that each increment was compressed to the desired length. The final combined length was determined by measuring the distance between the ends of the compression plungers with vernier calipers. The total weight of material used was obtained by weighing the holder before and after compaction. By building the plug in increments in this way it was possible to obtain a "reasonably uniform" membrane (Ash and Barrer, 1980). Two layers of stainless steel 100 mesh gauze (supplied by R. Cadish and Sons) were packed up against membrane face. Finally stainless steel length-wise grooved retaining plungers were inserted and screwed home against the mesh to prevent swelling of the compact. A 5 cm wide coil made from 0.3 cm internal diameter copper tubing was silver soldered to the bottom of the plug holder and Kovar metal-glass seals were silver soldered to the inlet and outlet. During soldering the outlets were stoppered and the assembly immersed in water to prevent excessive heating of the plug. Additional protection is provided by the heat

flanges.

A second, more highly compressed (nominal porosity 0.3), Sterling S membrane was similarly prepared, except that the plug was compacted using a Record hand-vice. This was because in order to compact the first membrane a pressure of only 12 lb in $^{-2}$ as indicated by the gauge of the Dennison press was required for compaction of the third increment. The membrane characteristics are shown in Table 3.2.

Table 3.2. Membrane Characteristics.

	Membrane 1	Membrane 2
Weight of Carbon / 10^{-5} kg	6.93	11.37
Number of Increments	3	3
Length, $l/10^{-3}$ m	9.62	10.82
Cross-sectional Area, $A_c/10^{-6}$ m ²	7.27	7.44
Porosity, ϵ/m^3 (m ³ porous membrane) ⁻¹	0.524	0.321
Surface Area, $A/10^7$ m ² (m ³ porous membranes) ⁻¹	2.19	3.13 ⁴
$(2\epsilon/A) / 10^{-8}$ m	4.79	2.05

A sample of Sterling S weighing 11.1244g was used for sorption studies and a second sample weighing 22.7556g was used for helium density determinations.

3.3. GENERAL FEATURES OF THE APPARATUS.

3.3.1. The Pumping System.

Three distinct high vacuum rigs were employed for the studies; two flow apparatus and one volumetric adsorption apparatus.

Each apparatus was constructed from Pyrex glass using wide-bore tubing (>12 mm bore) whenever possible together with large bore high vacuum stopcocks. This was to maximise the pumping speed. A typical pumping system is shown schematically in figure 3.2. A rotary oil pump (Edwards 2SCOA) capable of an ultimate vacuum of 10^{-4} cm Hg backed by a mercury diffusion pump was used to produce an ultimate "sticking" vacuum of between 10^{-6} and 10^{-7} cm Hg.

The diffusion pump was connected to the high vacuum line by a liquid nitrogen cold trap. This prevented mercury contamination of the system and helped achieve a better vacuum by reducing the vapour pressure of mercury, water vapour or other condensable vapours which might be present. On the reference side of the system with the capacitance manometers (see section 3.4.4) two cold traps in series were used to ensure that any traces of mercury vapour, which could condense in the capacitance manometer was excluded.

On the low vacuum side of the diffusion pump there was a buffer volume of between 3 dm^3 and 5 dm^3 , enabling the diffusion pump to operate independently of the rotary pump for a limited period. This was to allow routine maintenance of the rotary pump, such as belt and oil changes (the latter at about six monthly intervals).

Mercury levels in McLeod gauges and manometers were adjusted with the help of a second rotary pump connected to a low vacuum line. This "rough" pump was also used for the preliminary evacuation of the apparatus via a bypass connection. An additive oil (Edwards grade 17) was used in this pump to protect from contamination and oxidation. A non-additive oil (Edwards grade 8A) was used in the high vacuum pump. In the case of the system where measurements were made using capacitance manometers no "rough" pump was required for the reference side. On the measurement side the "rough" pump was connected directly with rubber pressure tubing to a McLeod gauge.

Oil traps (approximately 1 dm^3 capacity) and non-return valves above the rotary pumps were used to prevent oil from being sucked-back into the apparatus in the event of a power failure or broken belt. Each high vacuum system contained a Pirani vacuum gauge (Edwards G5C-2) with a suitable control unit (Edwards 8-2) covering the range 1 to 10^{-5} cm Hg.

3.3.2. Thermostat Baths and Furnaces.

Several different systems of thermostating were used to cover the range of temperatures at which the flow and

adsorption measurements were made:

77.4 K: Liquid nitrogen in a dewar flask.

199 K: "Card-ice slush"; solid carbon dioxide (supplied in pellets by Distillers Company) in a dewar flask containing methylated spirits, the "Card-ice" being in excess.

213 - 273K: For the flow measurement a large dewar flask containing methylated spirits was used, the required temperature being maintained to $\pm 1K$ by adding pellets of solid carbon dioxide. For the adsorption measurements a "leaky dewar" system was employed. Methylated spirits was again used as the thermostating fluid, with pelletized "Card-ice" or liquid nitrogen as refrigerant. The temperature was controlled to $\pm 1K$ using a Sunvic bi-metal thermostat, in conjunction with a Gallenkamp relay and a 25 watt lamp.

273 K: Melting ice stirred in a dewar flask.

293 K: Water in a large dewar flask was utilized as the thermostating fluid. The temperature was maintained to $\pm 0.5K$ using a "Red-Rod" heater connected to a variable voltage transformer, and controlled using a Sunvic or Gallenkamp relay and a mercury contact thermometer. Ice was added if the temperature of the bath was below that of room temperature. The bath was stirred using a paddle stirrer driven by a small electric motor.

308 - 473 K: Silicone oil (Hopkin and Williams MS550), in a 2 litre beaker, insulated using asbestos rope and asbestos paper and surrounded by a 3 litre beaker, was heated by two "Red-Rod" heaters connected to variable voltage transformers. One heater maintained the bath a few degrees below the required temperature. The second heater was used to achieve the required temperature (to $\pm 0.5K$) using a regulator / relay system. The bath was stirred using a paddle stirrer.

Outgassing temperature: Temperatures above 473K were achieved using an electric furnace controlled by a Variac transformer. The furnace consisted of a fused silica casing with a winding of resistance wire, the exterior being surrounded with asbestos rope and asbestos cloth. The inside

of the furnace was packed with asbestos rope.

3.3.3. Thermometers.

A series of mercury in glass thermometers (-20 to 20°C , 0 to 50°C , 0 to 100 to 150°C , 150 to 200°C) with 0.1°C divisions were furnished by Sugden Powell Ltd. Each was supplied with a works certificate. For low temperatures vapour pressure thermometers were used. An ammonia vapour pressure thermometer, made by R.T. Lowson (Lowson, 1968), was used to cover the range -80 to -40°C and a sulphur dioxide thermometer made by M. Rosenblat (Rosenblat, 1980), was used for -20°C . The vapour pressure data was taken from standard handbooks (Weast, 1970 and Ferry and Chilton, 1973). A hexane-in-glass thermometer (-100 to 50°C) was used as a rough check at low temperatures. To monitor the outgassing temperature a 0 to 360°C mercury-in-glass thermometer was employed.

3.3.4. McLeod Gauges.

A McLeod gauge was used on the apparatus with Sterling S membrane 1 for accurate pressure measurement in the range 10^{-4} cm Hg to 10^{-2} cm Hg. McLeod gauges were also used on all three vacuum systems to monitor the vacuum in the system when open to pumping.

The volume of the measurement McLeod gauge was calculated from the weight of distilled water required to fill the bulb. The cross-sectional area of the Veridia precision bore capillary limb was calculated from the length of an accurately weighed mercury slug in several places. The bulb volume was $3.011 \times 10^{-4} \text{ m}^3$ and the capillary cross-sectional area was $3.142 \times 10^{-6} \text{ m}^2$. The working equation for the evaluation of the pressure, p , in cm Hg is

$$p = \frac{l_1 l_2 a}{V - l_1 a} \quad (3.1)$$

where l_1 and l_2 are the lengths (cm), as indicated in figure 3.3.; a is the cross-sectional area of the capillary (cm^2) and V is the bulb volume (cm^3).

The McLeod gauges were made in the glass workshop of this department.

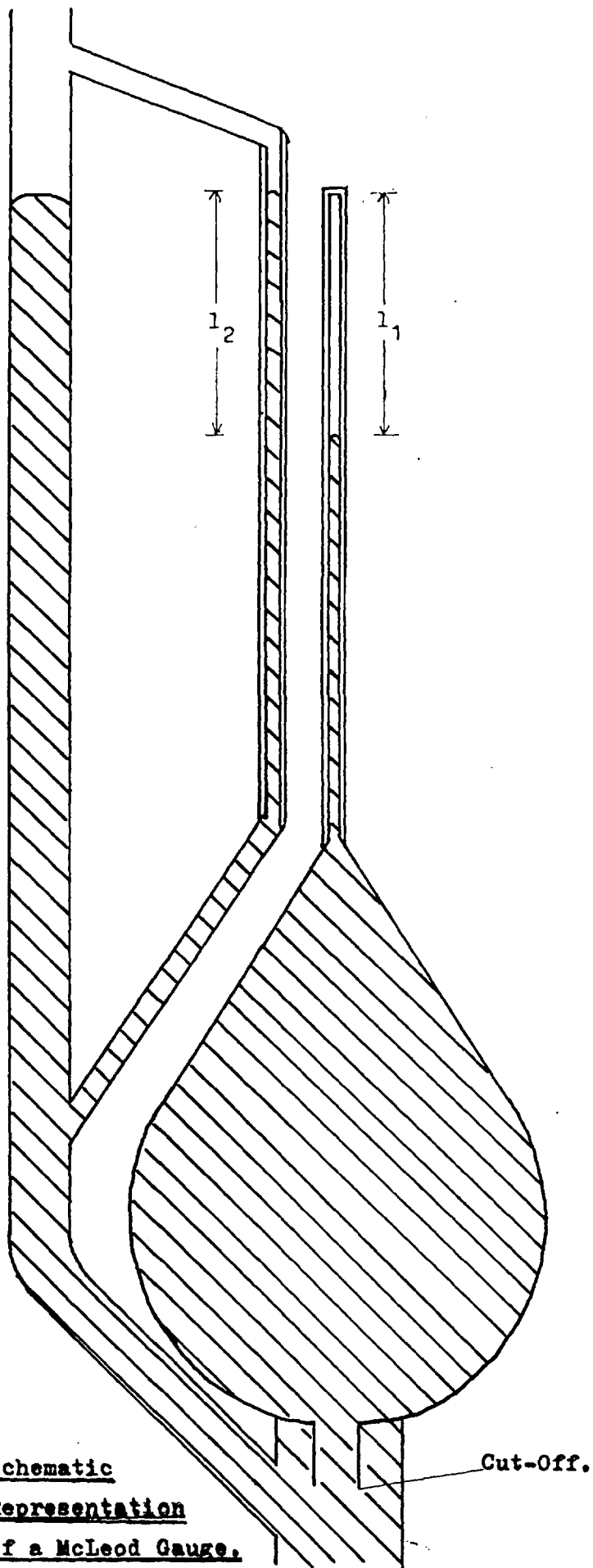


Figure 3.3. Schematic Representation of a McLeod Gauge.

3.3.5 Mercury.

The mercury used in the McLeod gauges and manometers was cleaned using the method employed by Ash (1955) to reduce "sticking problems". The mercury was first filtered through pin-holed filter paper to remove any large particular impurities. The mercury was placed in a 1 dm³ Buchner flask and covered with water to a depth of a few centimeters. Sodium peroxide was added and the mixture was agitated overnight by drawing air through it. The resulting mixture contains acid-free mercury. The aqueous layer was removed and the mercury was washed free of alkali using distilled water. Metal impurities were removed by shaking the mixture with acidified potassium permanganate. An oxide scum is left on the surface (the metal impurities are coprecipitated with the manganese dioxide). The mercury was rewashed with distilled water and filtered into dilute nitric acid. The aqueous layer was removed and the mercury was washed several times with distilled water. After removal of the water layer the mercury was dried using filter paper. It was then heated to 120°C in an evaporating dish in a fume cupboard. Finally the mercury was filtered into dry, clean, storage bottles.

3.3.6 Miscellaneous

Cathetometers (Precision Tool and Instrument Company) were used to measure the differences in mercury levels in McLeod gauges and manometers. Heights were measured to 0.001 cm. The cathetometers were placed on cast-iron tables for stability.

The high vacuum ground glass taps were lubricated with Apiezon - N grease; cones and sockets were sealed with Piccin wax.

A Rone stopwatch was used to measure time.

3.4. THE FLOW APPARATUS

3.4.1. Basic principle.

Two flow apparatus were employed, designated 1 and 2 respectively. Flow apparatus 1 was used with Sterling S membrane 1 (porosity 0.524) and flow apparatus 2 was used

with Sterling S membrane 2 (porosity 0.321). Both apparatus were designed for isothermal work. The boundary conditions for the experiments were

$$C(0,t) = C_0, \quad t > 0$$

$$C(1,t) = C_1(t) \ll C_0, \quad t > 0$$

where C denotes the total concentration of diffusant in the adsorbed and gas phases. The membrane is bounded by the planes $x=0$ and $x=1$, where $x=0$ denotes the ingoing side and $x=1$ denotes the outgoing side.

3.4.2. Flow apparatus 1 - a description.

The apparatus (plate 3.1, figure 3.4) consisted of an ingoing side with gas line, a membrane and an outgoing side. The ingoing side comprised two graduated gas burettes and a 1 dm^3 buffer volume. These were used to maintain a constant ingoing pressure measured on the mercury manometer. This manometer was made from 15 mm precision bore Veridia glass tubing. Two gas bulbs were connected onto the ingoing side, but each was isolated from the rest of the ingoing side by two right-angle stop-cocks and a cold trap (used for recovering condensable gases).

The outgoing side consisted of three 5 dm^3 buffer volumes and a McLeod gauge to measure the outgoing pressure as a function of time. The buffer volumes were calibrated with distilled water before fitting to the apparatus. The dead space volume was calibrated by helium expansion, making use of the gas burettes on the ingoing side. The volumes are given in table 3.3.

Table 3.3. Isothermal Flow Apparatus 1: Outgoing Volumes.

Component buffer volume	Volume 10^{-3} m^3	$\Sigma(\text{Outgoing Volume})^*$ 10^{-3} m^3
Dead space	0.854	0.854
α	5.410	6.272
β	5.365	11.643
γ	5.396	17.049

* The summed outgoing volumes include volumes between the tap and the ground glass joints for each buffer.

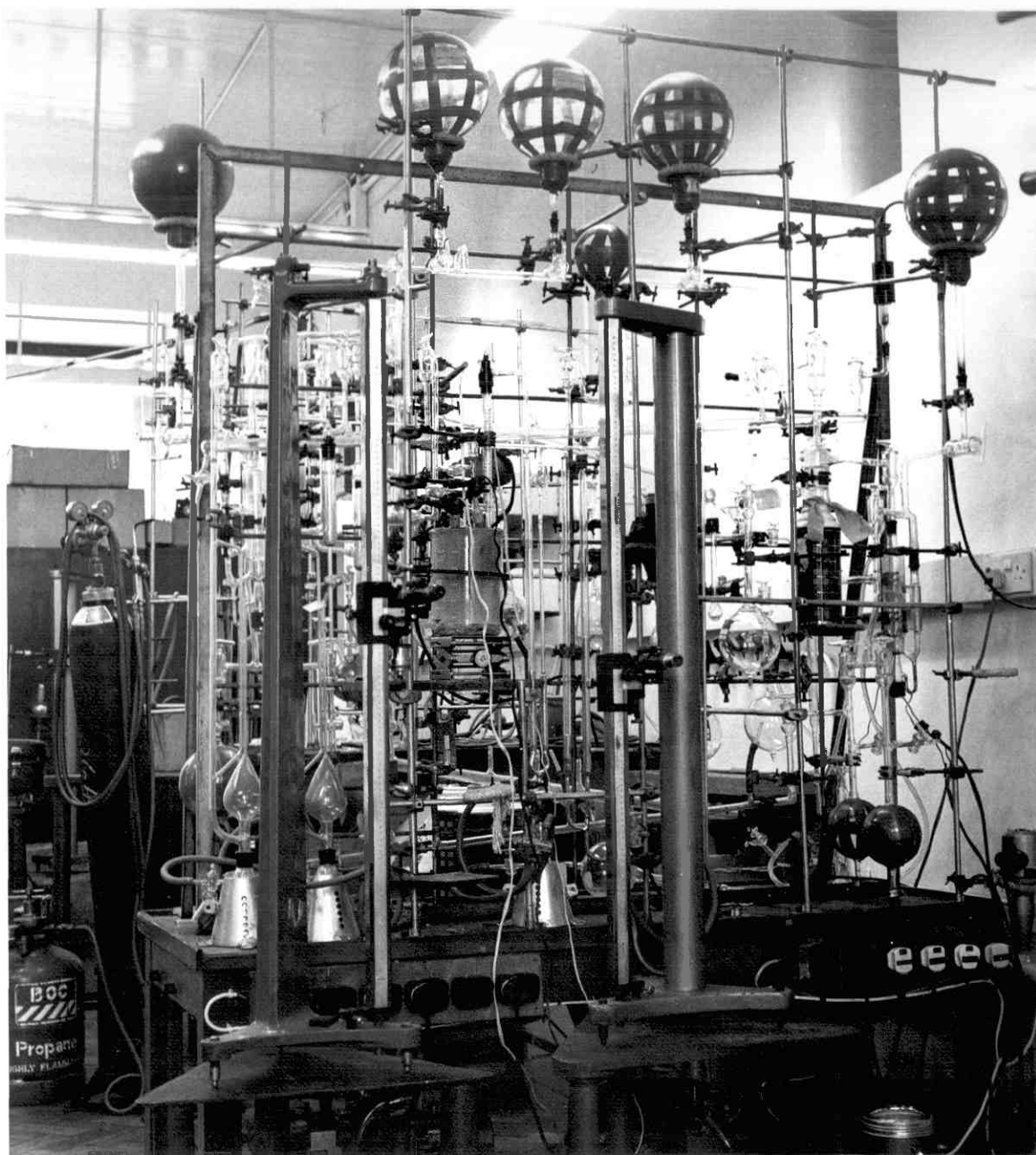


Plate 3.1. Flow Apparatus 1

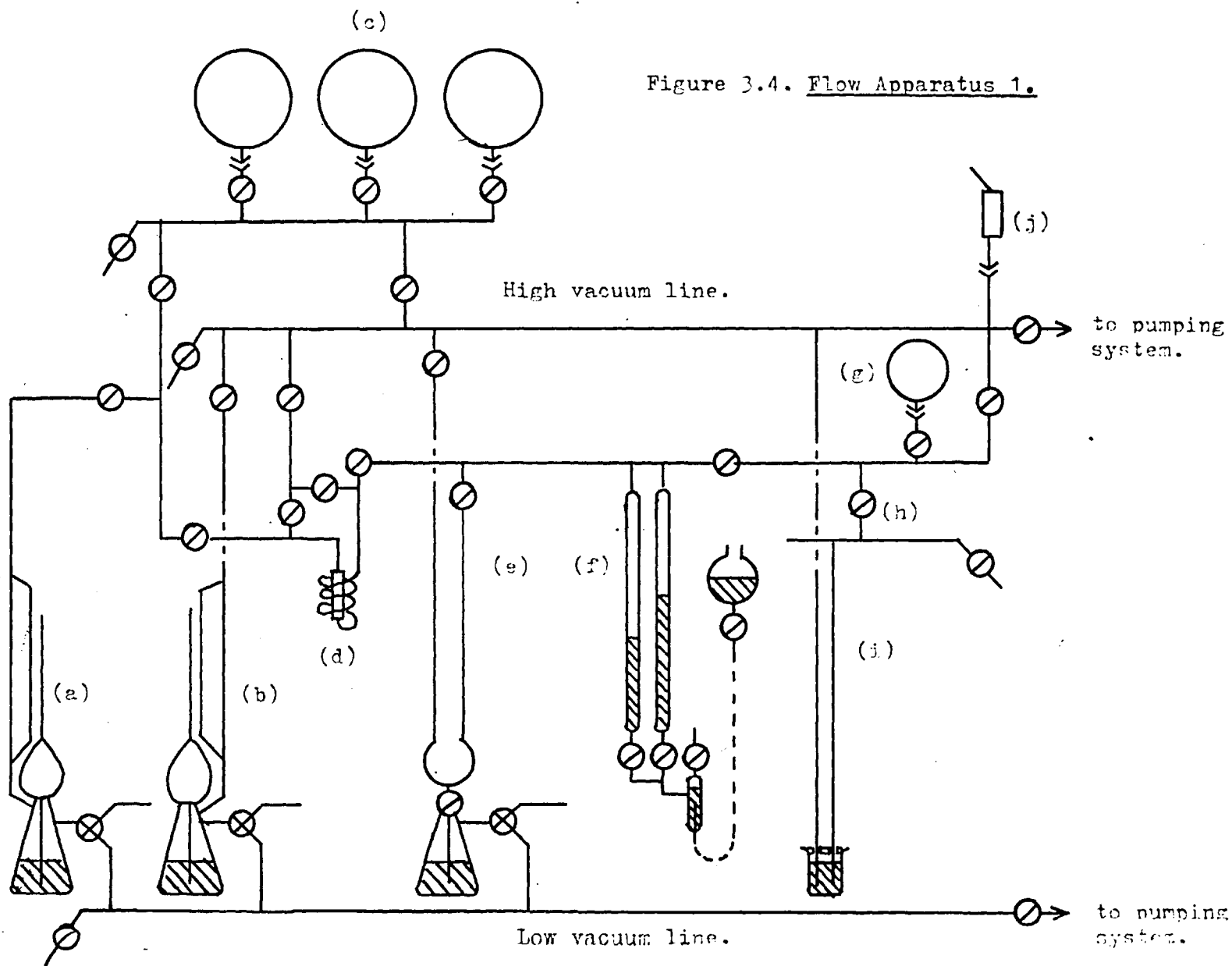


Figure 3.4. Flow Apparatus 1.

- (a) Measurement
McLeod gauge.
- (b) Monitor
McLeod gauge.
- (c) Outgoing buffer
volumes.
- (d) Plug assembly.
- (e) Ingoing mano-
meter.
- (f) Gas burettes.
- (g) Ingoing buffer
volume.
- (h) Gas line.
- (i) Safety mano-
meter.
- (j) Pirani gauge.

3.4.3. Flow apparatus 1 - operation.

The outgassed membrane was thermostatted to the required temperature. Gas was admitted to the ingoing side, with the stop-cock between the ingoing side and the membrane closed. This stop-cock was opened at time $t=0$, and the stop watch started. The ingoing pressure p_0 , was held constant by raising the mercury level in one of the gas burettes. The outgoing pressure, p_1 was measured as a function of time using the McLeod gauge. For each measurement p_1 the pressure p_0 and the room temperature, T_R were also recorded. For each run about ten readings of the outgoing pressure were made. The time elapsed during the course of a run varied from 90 to 120 minutes. The outgoing volume could be varied from one experiment to another, in order to maintain p_1 in the McLeod gauge range, and also to keep p_1 less than 0.1% of p_0 . For convenience the pressures were measured in centimetres of mercury and time, t , in minutes. The working equation for the evaluation of the integral permeability $\tilde{K}$ in $\text{m}^2 \text{s}^{-1}$ is

$$\tilde{K} = V \frac{1}{A_c} \frac{dp_1}{dt} \frac{1}{60} \frac{1}{p_0} \frac{T}{T_R} \quad (3.2)$$

V is the receiving volume (m^3), T is the membrane temperature (K), l (m) and A_c (m^2) are the length and cross sectional area of the membrane respectively, dp_1/dt (cm Hg min^{-1}) is the least mean square evaluation of the slope of a plot of p_1 against t . The working equation used to evaluate the flux, J (mol s^{-1}) is

$$J_\infty = \frac{V}{RT_R} \frac{dp_1}{dt} \frac{1333.2}{60} \frac{1}{e} \quad (3.3)$$

R is the gas constant ($8.3143 \text{ J K}^{-1} \text{mol}^{-1}$), e is ratio of the density of mercury at 273.2 K to density of mercury at T_R (densities taken from Weast, 1970). The numerical factor 1333.2 converts pressure in cm Hg at 273.2K to pascals ($\text{Pa} = \text{Nm}^{-2}$).

The membrane was initially outgassed at 100°C for 24

hours at a pressure of less than 1×10^{-6} cm Hg. Flow experiments were then carried out for a selection of gases with the membrane thermostatted at 35°C . The outgassing temperature was increased in 50°C steps and the flow experiments were repeated each time until an outgassing temperature of 300°C was reached. Flow experiments were then carried out on a range of gases at a range of temperatures.

For the outgassing trials several runs were made for each gas at ingoing pressure ranging from 1 cm Hg to 30 cm Hg. For the experiments investigating the variation of permeability with temperature a set of four or more runs were made at pressures usually less than 7 cm Hg. Measurements were made at comparatively low pressures to ensure that the mean free path of the gases are small compared with the hydraulic radius, $2\epsilon/A$.

The membrane was outgassed at frequent intervals at a temperature of about 300°C . Periodic checks of the helium permeability were made to test for any change in flow characteristics of the membrane. The gas bulbs were occasionally changed to ensure that impurities did not cause anomalies in the results.

3.4.4. Flow apparatus 2 - a description.

The apparatus (plates 3.2 and 3.3; figure 3.5) consisted of a gas line, an ingoing side, and outgoing side and a reference side operating off a separate pumping system. Pressure was measured using capacitance manometers (0 - 100 cm Hg range) was connected between the ingoing side and the reference side, this replacing the mercury-in-glass manometer of flow apparatus 1. Between the outgoing side and the reference side a capacitance manometer of range 0 - 0.1 cm Hg was connected, this replaces the McLeod gauge.

Use of capacitance manometers renders it desirable to avoid the presence of mercury vapour, so no gas burette or Toepler pump was included on the ingoing side to maintain constant pressure. Instead a large 5 dm^3 buffer volume was

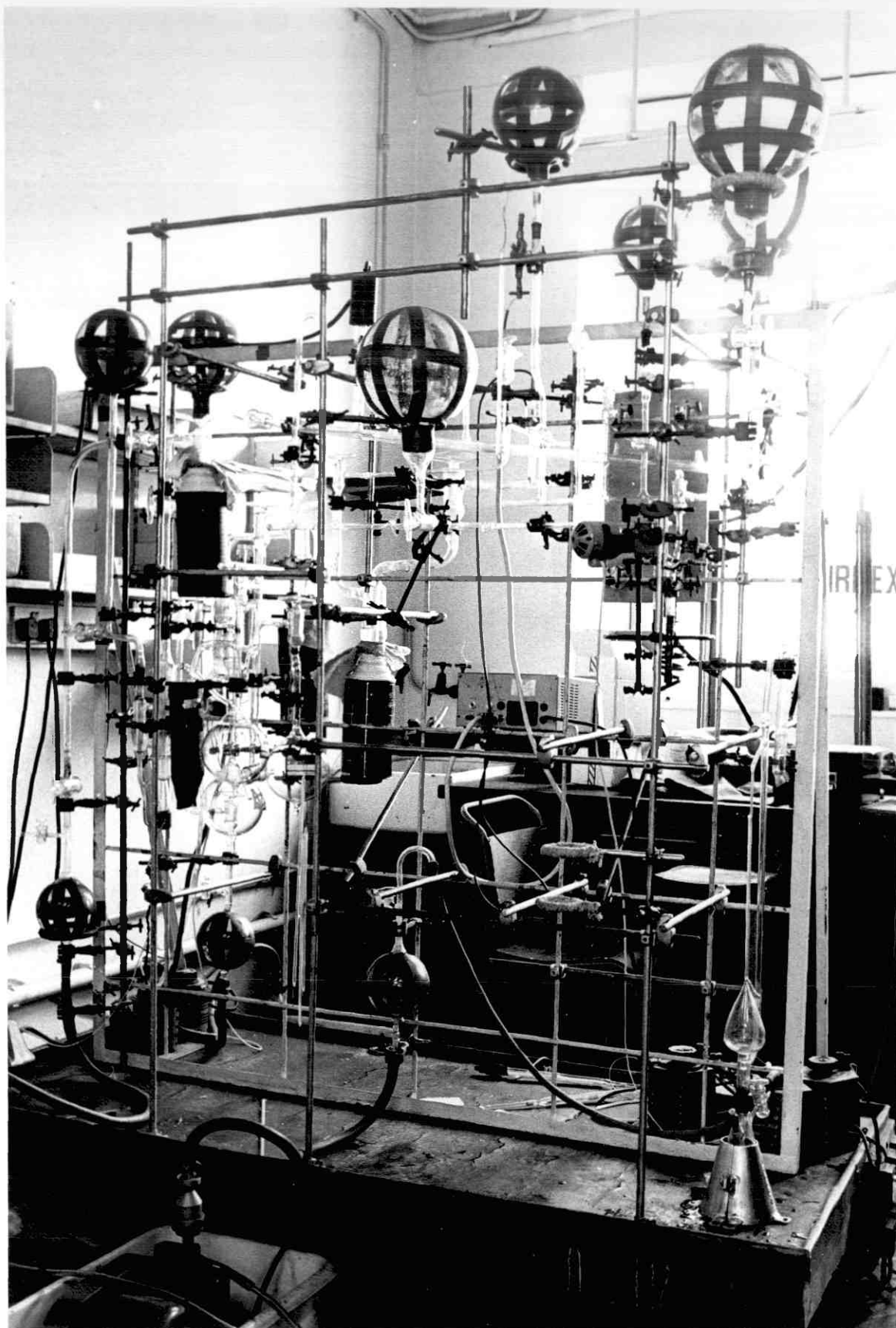


Plate 3.2. Flow apparatus 2

(Showing gas line, ingoing side,
outgoing side, and plug assembly)

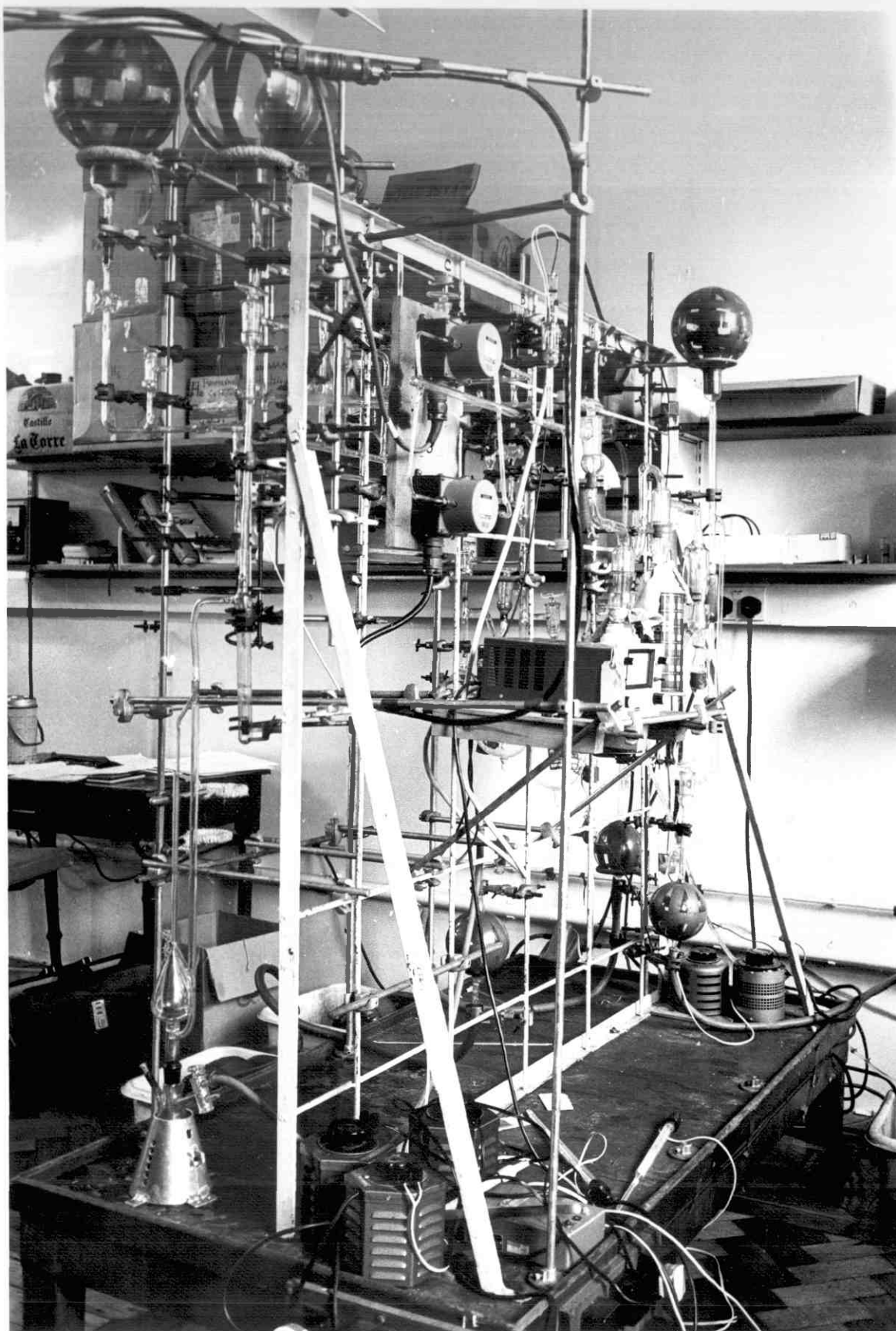
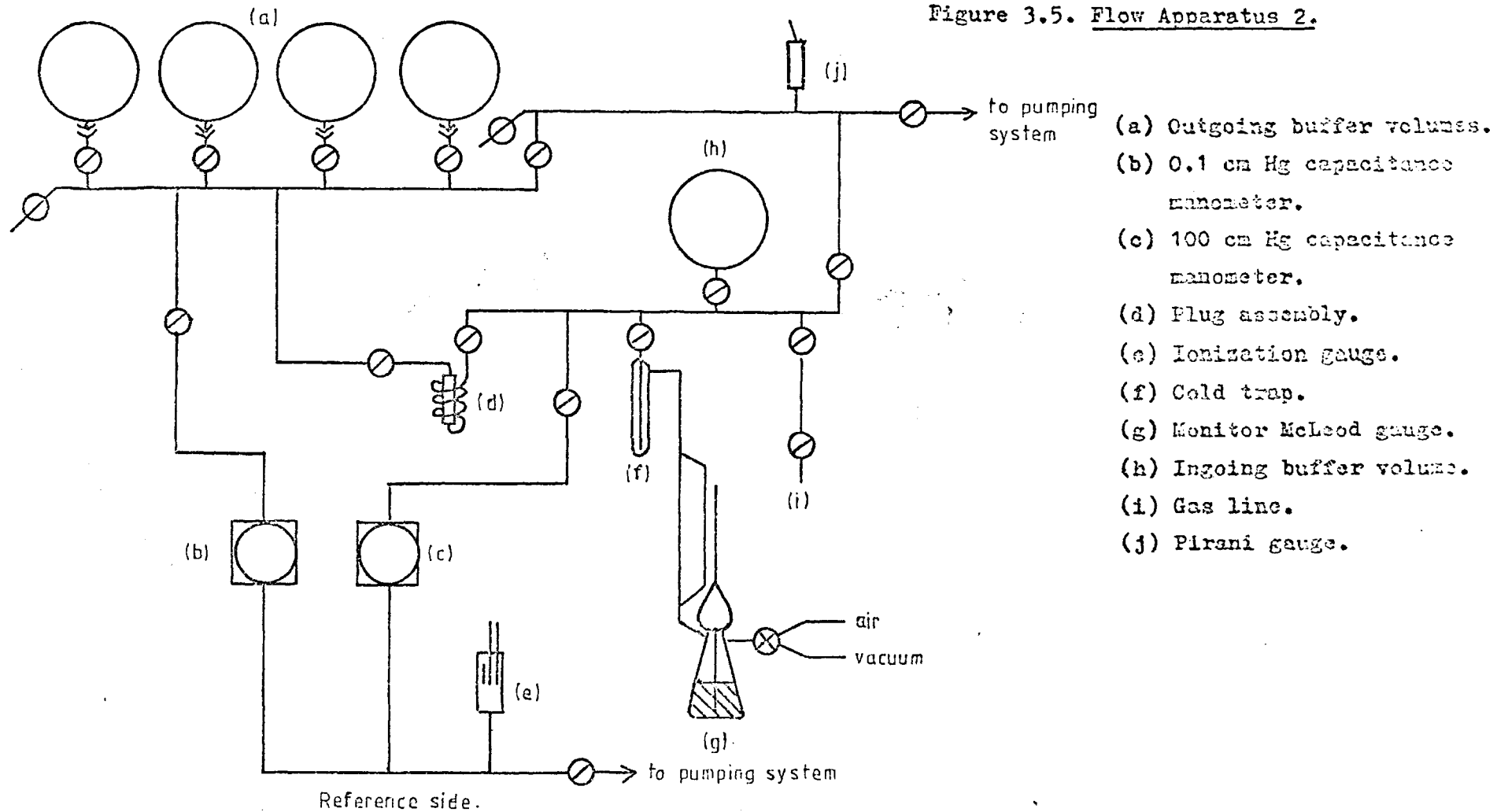


Plate 3.3. Flow Apparatus 2
(Showing reference side with
Baratron heads)

Figure 3.5. Flow Apparatus 2.



included on the ingoing to ensure that any change in pressure was $< 0.1\% p_0$. On the outgoing side there was a range of buffer volumes: a 1 dm^3 bulb, a 2 dm^3 bulb and two 5 dm^3 bulbs. As with flow apparatus 1, the buffer volumes were initially calibrated with distilled water. Connecting volumes were calibrated by helium expansion. The volumes are tabulated in table 3.4, together with the total outgoing volume for each respective buffer. As previously (table 3.3) the total volume includes the volume between the stop-cock and the ground glass joint connecting the buffer to the system.

Table 3.4. Isothermal Flow Apparatus 2: Outgoing volumes.

Component buffer volume	Volume 10^{-3} m^3	Outgoing Volume 10^{-3} m^3
Dead Space	0.188	0.188
A	5.339	5.532
B	5.382	5.591
C	1.056	1.263
D	2.271	2.494

Further outgoing volumes could be achieved by combining two or more buffer volumes.

A monitor McLeod gauge connected to the main vacuum line of the flow apparatus was used solely to demonstrate that a "sticking" vacuum had been obtained. Most of the time it was isolated from the rest of the system but when in use the remainder of the apparatus was protected from mercury vapour by a liquid nitrogen cold trap.

The reference side consisted of a pumping system attached to a single manifold. The pumping system was somewhat different to that described in section 3.3.1 in that there was no "rough" pump. A single rotary pump was connected in

series with a three-stage mercury diffusion pump and two liquid nitrogen cold traps. The cold traps were to remove any mercury vapour and other contaminant vapours from the system. A single 16 mm bore right-angled stop-cock separated the pumping system from the manifold. An ionization gauge head (Edwards IG6G) and control unit (Ion 7) were used to observe the pressure on the reference side. It was desirable that the pressure on the reference side should be small compared with the pressures on the ingoing and outgoing sides of the membrane during a flow experiment. The pressure was kept at 10^{-6} cm Hg or less. The ionization gauge head was periodically outgassed as described in the manufacturers instructions. The reference side of the two capacitance manometers were connected directly onto the manifold.

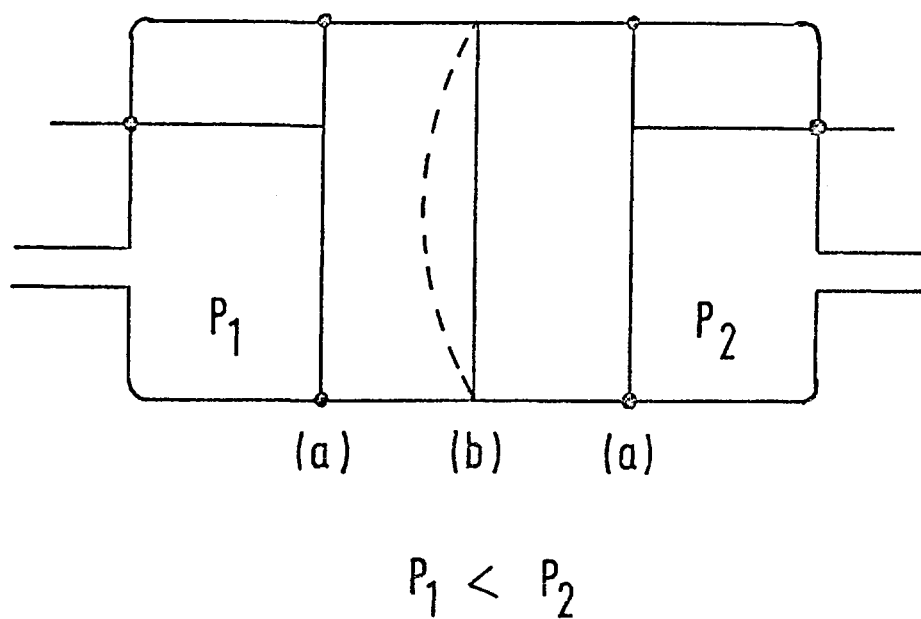
3.4.5. The Capacitance Manometers.

The capacitance manometers used in this work was the "Baratron" pressure meter type 170 manufactured by MKS Instruments Inc. of Burlington, Massachusetts, U.S.A. The capacitance manometer measures absolute pressure unlike Pirani gauges and ionization gauges whose pressure reading depend on the nature of the gas. The pressure head (figure 3.6) consists of a tensioned metal diaphragm positioned between two electrodes. A pressure difference across the diaphragm causes a deflection of the diaphragm and as a result a change in capacitance between the diaphragm and each electrode occurs. These capacitances are part of a bridge circuit balanced by a decade unit.

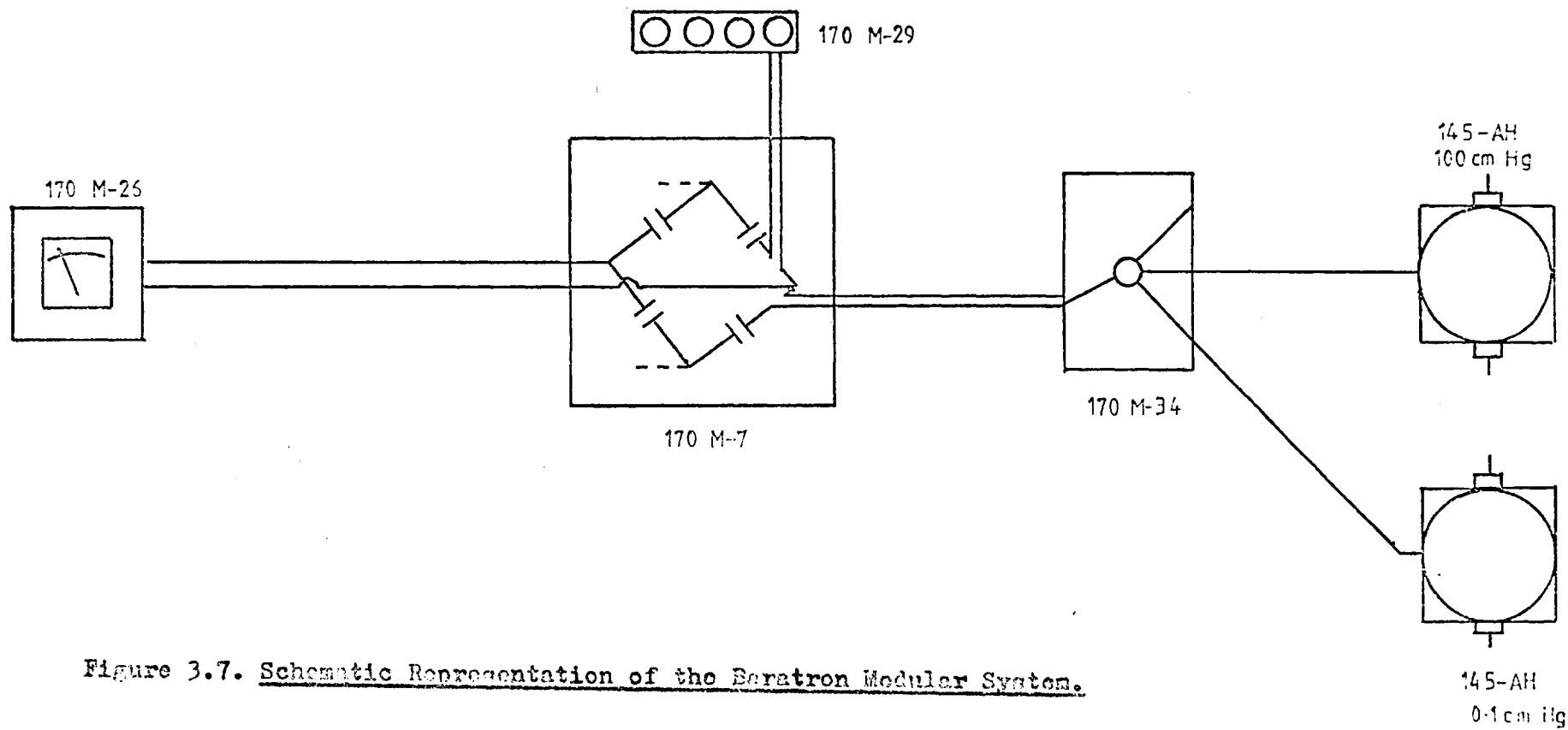
The Baratron system is modular in design and the following modules were incorporated into the system (schematically represented in figure 3.7).

(a) Type 145AH: Head Sensor. In this work two head sensors were used one with a full scale reading of 100 cm Hg and a second with a full scale reading of 0.1 cm Hg. The heads were of all welded metal construction to minimise outgassing and leaks. In order to minimise effects due to changes in room temperature the sensor contained internal heaters

Figure 3.6. Capacitance Manometer Pressure Head.



- (a) Fixed electrodes : nickel deposited on ceramic.
(b) Tensioned metal diaphragm.



regulated to maintain the temperature at 49°C (120°F). Cajon VCR couplings were used to connect the head to the vacuum system via Kovar metal-glass seals. As a built-in safety feature protecting the diaphragm from over pressure the fixed electrodes act as stops against which the diaphragm can rest.

(b) 170 M-7: Electronics Unit. The electronics unit provided the basic power supply to the head and converted the head signal into two 0 - 10V D.C. outputs per range. A precision voltage divider allowed different sensitivities, $\times 1$, $\times 0.1$, $\times 0.01$ and $\times 0.001$ of the full scale range.

(c) 170 M-26: Analog Meter. One of the D.C. outputs from the head was used by the meter and corresponded to the out of balance signal.

(d) 170 M-29: Digital Offset Unit. This unit consisted of three decade switches plus a vernier potentiometer and was used to adjust the D.C. output to zero. The dial readings give the pressure as a percentage of full scale pressure.

(e) 170 M-34: Head Selector Unit. The unit provided the option of powering three heads continuously. It contained zero and quadrature adjustment controls for each head. Capacitance changes of the head at zero differential pressure were corrected by the zero control; high resistance or stray capacitance 90° out of phase with the bridge signal could be allowed for with the quadrature control.

3.4.6 Flow Apparatus 2 - operation.

The basic principle of operation was as described for flow apparatus 1 with minor differences. The ingoing pressure was measured after gas had been admitted to the ingoing face of the membrane using the 100 cm Hg capacitance manometer. The deflection on the analog meter was adjusted to give zero deflection using the digital offset unit. The pressure was obtained from the setting of the digital offset. The outgoing pressure was similarly measured off the 0.1 cm Hg capacitance manometer at various times, t . About ten readings of outgoing pressure were taken during the course of a run of duration of between 60 minutes and 90 minutes.

The ingoing pressure was again measured at the end of a run. The ingoing pressure, p_0 used in calculation was a mean of the initial ingoing pressure reading and the final ingoing pressure reading. Room temperature was measured using a 0 to 50°C mercury in glass thermometer at the end of each pressure measurement. The outgoing volume could be adjusted as described to maintain the outgoing pressures, p_1 within the range of the 0.1 cm Hg capacitance manometer and also to ensure that p_1 was less than 0.1% of p_0 .

The method of calculating the permeability $\tilde{K}$ and the steady-state flux J_∞ was as described in section 3.4.3, using equation 3.2 and 3.3.

The membrane was periodically outgassed at 300°C. However, contamination of the membrane with this system was less likely than with flow apparatus 1 because of the precautions made to ensure the absence of mercury vapour from the system.

Several runs were made for each gas at each temperature at ingoing pressures ranging from 0 to 20 cm Hg.

3.5. THE ADSORPTION APPARATUS.

Two standard volumetric adsorption apparatus (see for example Young and Crowell, 1962 p.284) were used in the measurement of the nitrogen isotherms and helium density measurements. A diagram of a typical apparatus is shown in figure 3.8. The experimental rig was originally built and used by Craven (1976) for a study of sorption kinetics and actually contained four basic adsorption systems. Connections between adsorption bulbs, gas burettes and manometers were constructed from 3 mm bore capillary tubing to minimize the dead volume. The manometers were constructed from precision bore Veridia glass tubing. The burette bulb volumes were originally calibrated by mercury weighings (Craven 1976) and are recorded in table 3.5. The dead space volumes, V_d are also recorded, and were calibrated in this work by helium expansion.

Figure 3.8. A Typical Volumetric Adsorption Isotherm Apparatus.

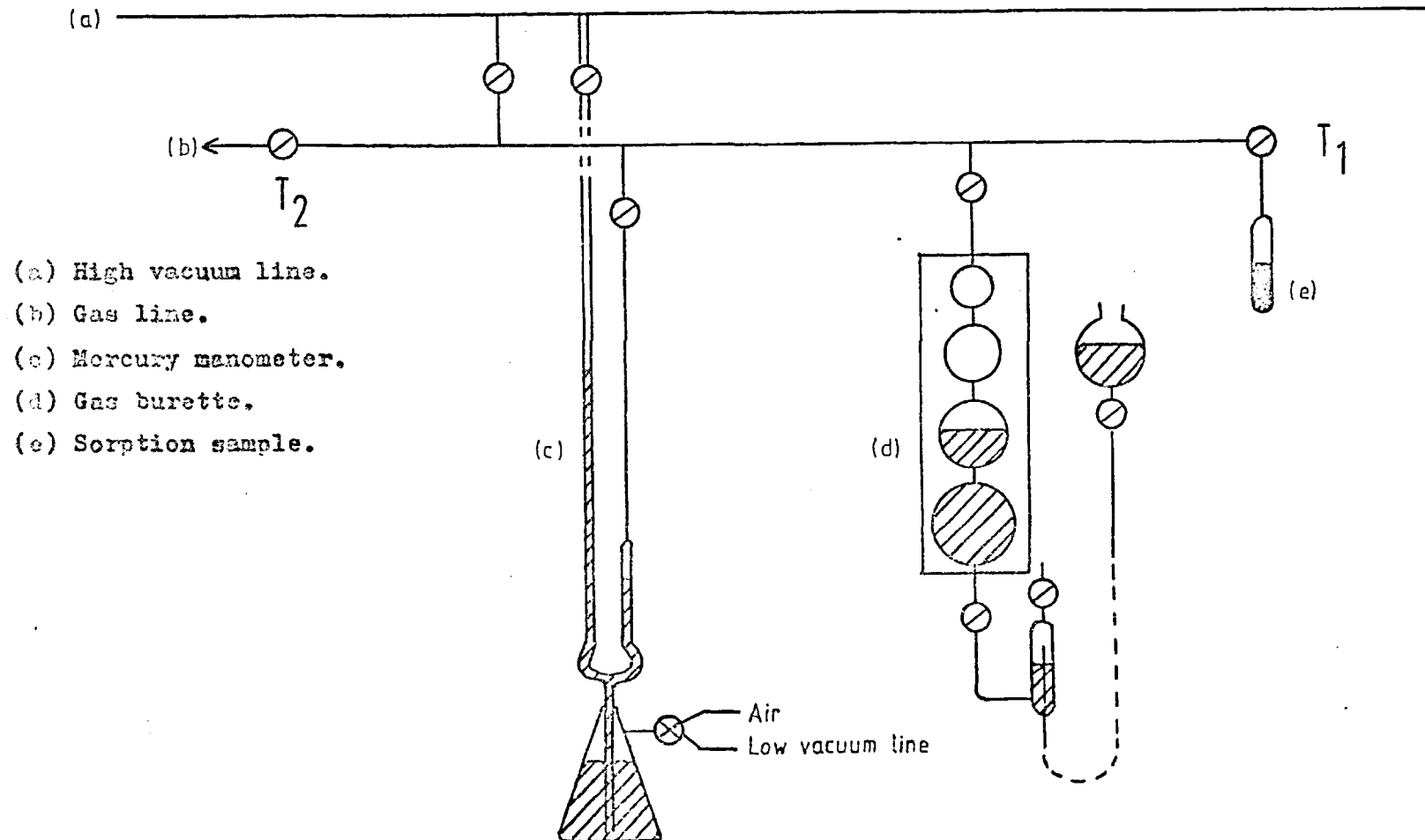


Table 3.5. Calibrated Volumes for Adsorption Apparatus.

	V_{GB1} $10^{-6} m^3$	V_{GB2} $10^{-6} m^3$	V_{GB3} $10^{-6} m^3$	V_{GB4} $10^{-6} m^3$	$\sum V_{GBi}$ $10^{-6} m^3$	V_d $10^{-6} m^3$	A_{man} $10^{-4} m^2$
Apparatus 1	10.272	19.726	33.487	54.155	117.640	36.666	0.271
Apparatus 2	23.779	23.390	43.834	52.686	149.689	51.338	0.361

V_{GBi} is the volume of the i th. bulb of the gas burette (bulb 1 being the top bulb) A_{man} is the cross sectional area of the manometer tubing; V_d is the dead volume.

Apparatus 2 was used to measure the adsorption of nitrogen on Sterling S at 77.4K (Temperature of liquid nitrogen). A sample of Sterling S weighing 11.1244g was used for the adsorption measurements and was outgassed for 60 hours at 300°C. At the isotherm temperature the volume from the sample bulb to the tap, T_1 , connecting the bulb to the burette system was calibrated with helium (assuming helium to be non-adsorbed). This is a temperature dependent "volume" due to the temperature gradient existing between the temperature of the room and that of the sample bulb. The remaining volumes were treated as being at room temperature. The helium was withdrawn and a dose of nitrogen was admitted via tap T_2 (tap T_1 being closed). Tap T_2 was then closed. The amount of nitrogen in the system could be determined from the pressure, volume and room temperature. Tap T_1 was opened, and after waiting an hour for the system to reach equilibrium, the quantity of nitrogen in the gas phase could be determined. The difference between the two values was the amount of nitrogen adsorbed. The pressure was increased either by raising the mercury level in the gas burette or by introducing more nitrogen through tap T_2 with tap T_1 closed. The adsorption isotherm was hence constructed. A BET analysis was made of the results.

The helium density determinations were performed on apparatus 1. The volume of any empty sample bulb was determined by helium expansion. The system was evacuated, and a dose of helium was introduced via tap T_2 . Tap T_2 was then closed and the level of the mercury in the gas burette was progressively raised, with tap T_1 open. At each graduation of the gas burette the pressure, p of helium in the system was measured and room temperature, T_R was recorded. When the bulb volume was plotted against T_R/p the volume of the bulb plus the dead volumes was obtained from the intercept with the volume axis. The mean of two determinations was used in the calculation.

The sample bulb was filled with 22.7556g of Sterling S, The sample was outgassed at room temperature and the volume of the bulb redetermined. The volume occupied by the carbon is given by the difference between the two volume determinations. Two determinations were made.

The experiment was repeated after outgassing the sample for 16 hours at 300°C. Again two measurements were taken.

3.6 ERROR ANALYSIS

As has been pointed out by Hamilton (1980) an objective assessment of errors in the parameters characterizing the flow process is difficult. However, it is right and desirable that some consideration should be given to the analysis of errors involved in the experimental work. In any experiment there are two types of error; random and systematic. The systematic errors arise from the theoretical assumptions, deviations from the required boundary conditions and instrumental errors. Petropoulos and Myrat (1977) have given some consideration to errors involved in permeation time-lag experiments, while Loebenstein and Deitz (1947) considered the magnitude of the experimental error in nitrogen adsorption experiments.

Looking first at the B.E.T. determination of surface area. One source of error arises from the ideal gas assumption. At the temperature of liquid nitrogen (77.4K) it becomes particularly important to correct for deviations from ideality.

Following Young and Crowell (1962, p 284) The equation used for calculating the volume V_a of gas adsorbed (cm^3_{STP}) was

$$V_a = V_t - V_h (1 + \alpha p) - V_b \quad (3.4)$$

where V_t is the total volume of adsorbate admitted to the system, V_h is the volume of helium required to fill the sample bulb and connecting tubing to the equilibrium pressure, p and V_b is the volume remaining in the burette and the dead volume at equilibrium. The correction factor $\alpha = 6.6 \times 10^{-4} (\text{cm Hg})^{-1}$ (Young and Crowell, 1962). Errors are also reduced by keeping the volume of the tubing connecting the sample bulb (at 77.4K) to the rest of the system (at room temperature) to a minimum. Criticisms of the B.E.T. method will be discussed in section 5.3.

The random errors include errors in temperature, pressure and volume measurements. Much of what is said about adsorption measurements also applies to helium density determinations. The pressure in the system can be measured to $\pm 0.002 \text{ cm Hg}$ by means of a cathetometer, whilst the temperature readings can be made to $\pm 0.1\text{K}$; although room temperature can drift by up to $\pm 3\text{K}$ ($\sim 1\%$) during the course of an adsorption isotherm. The burette volumes were originally calibrated by filling with mercury, and the error is better than 0.1% , whereas the volumes calibrated by helium expansion have an uncertainty of about 1% . The mass of carbon can be measured to $\pm 0.0005\text{g}$. These errors combined lead to an error in the volume adsorbed, v ($\text{cm}^3_{\text{STP}}\text{g}^{-1}$) of about $\pm 0.02 \text{ cm}^3_{\text{STP}}\text{g}^{-1}$. This figure for the uncertainty applies for the first dose of gas admitted, for subsequent doses of gas the errors are cumulative (Loebenstein and Deitz, 1947). The final error in the surface area, A , is $\pm 0.3 \text{ m}^2 \text{ g}^{-1}$. Little meaning can be attributed to the value of the constant C since the intercept of the B.E.T. plot (figure 4.2) is small and the error in C is as much as $\pm 2 \times 10^5$.

The random errors lead to an uncertainty in the helium density of approximately $\pm 40 \text{ kg m}^{-3}$ ($\pm 0.04 \text{ g cm}^{-3}$). This value is close to the variation in the four helium density measurements ($\pm 30 \text{ kg m}^{-3}$).

For the flow experiments with apparatus 1, there is a small error associated with deviations from the boundary conditions (equation 2.1 (a, d, e)). This was minimised by ensuring that p_1 was less than $0.2\% p_0$ throughout the duration of the experiment (section 3.4.3). Random errors in membrane dimensions lead to a systematic error in the calculation of permeability. The uncertainties in the cross-sectional area and length of the membrane are $\pm 1.5\%$ and $\pm 1.0\%$ respectively. The mass of carbon used is correct to $\pm 0.5\%$. Taking into account the error in the helium density (see above) the resulting error in $(1 - \epsilon)$ is $\pm 2.5\%$.

Random errors in the permeabilities involve uncertainties in volume, temperature and pressure measurements. The errors in the volume calibrations are as described for the volumes of the adsorption apparatus, those measured by filling with water, $\pm 0.1\%$ and those calibrated by helium expansion $\pm 1\%$. Measurements of the ingoing pressure, p_0 were made to $\pm 0.002 \text{ cm Hg}$, variation of p_0 during the course of an experiment was $\leq \pm 0.1\%$. The outgoing pressure, p_1 was measured using a McLeod gauge. Carr, 1964 reviewed methods for minimizing and correcting systematic errors in McLeod gauge readings. Different capillary depression in the capillary limbs is avoided by making the two limbs from the same piece of precision bore glass tubing. Error due to mercury sticking was minimised by the cleaning procedure (section 3.3.5) also the limbs were tapped before taking a reading. These precautions limit the uncertainty to a maximum of $\pm 1\%$. The error in temperature measurement and the variation in room temperature have been described above. The worst temperature control of the thermostat baths was $\pm 1 \text{ K}$, this figure applying for temperatures below 273 K ; for higher temperatures the temperature control was

better than $\pm 0.5\%$. For a particular experiment the error in dp_1/dt can easily be calculated using a least mean square method (see for example Levitt, 1973 p.21). This quantity includes the errors mentioned above and for experiments taken at random, the estimated uncertainty is $\pm 1\%$ in the slope. The corresponding estimated uncertainties in the integral permeability, $\bar{K}$ and steady-state flux J_∞ are 2% and 1% respectively.

With flow apparatus 2 the errors involved with using capacitance manometers are of a different nature to those associated with mercury-filled gauges. The main source of error is associated with operating a thermostatted measurement head at a different temperature to ambient temperature. This possible thermal transpiration error has been variously estimated to be between 1% (Bromberg, 1969) and 2.6% (Baldwin and Gaerttner, 1973) for pressure measurements between 1×10^{-5} and 0.1 cm Hg. The calibration of full scale output is said to be accurate to $\pm 0.5\%$ (Bromberg, 1969). Capacitance manometer measurements agreed with McLeod gauge reading to within 2% for helium at 10^{-4} cm Hg (Utterback and Griffith, 1966). Taking these factors into account the errors associated with measurements using flow apparatus 2 are probably of the same order as those of flow apparatus 1.

CHAPTER 4

RESULTS

4.1. SURFACE AREA DETERMINATION

Two adsorption isotherms of nitrogen on Sterling S were measured at liquid nitrogen temperature (77.4K), the experimental data being given in Appendix A1 and A2. The two sets of results were combined and plotted in figure 4.1. The isotherm is of the amount adsorbed, v ($\text{cm}^3_{\text{STP}} \text{g}^{-1}$) against equilibrium pressure, p (cm Hg). A gas of known pressure, p_1 was admitted to a known volume, V and the temperature, T_1 was measured. The gas was then introduced to the sample and the resulting pressure, p_2 and the temperature, T_2 measured. The amount of gas before, n_1 ($\text{cm Hg cm}^3 \text{ K}^{-1}$), and after, n_2 , admission to the sample was determined by the expressions (assuming an ideal gas)

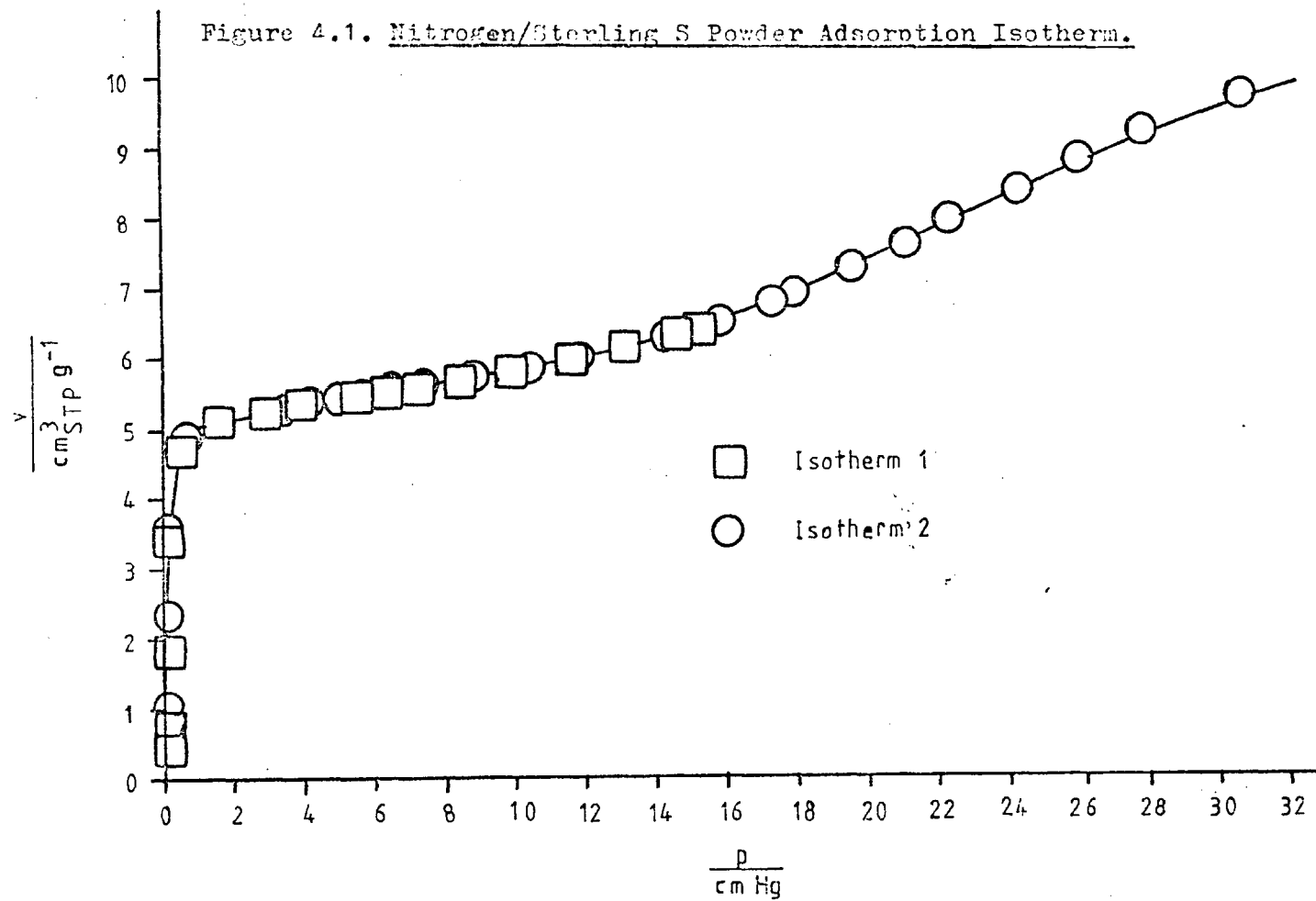
$$n_1 = \frac{p_1 V}{T_1} \quad (4.1)$$

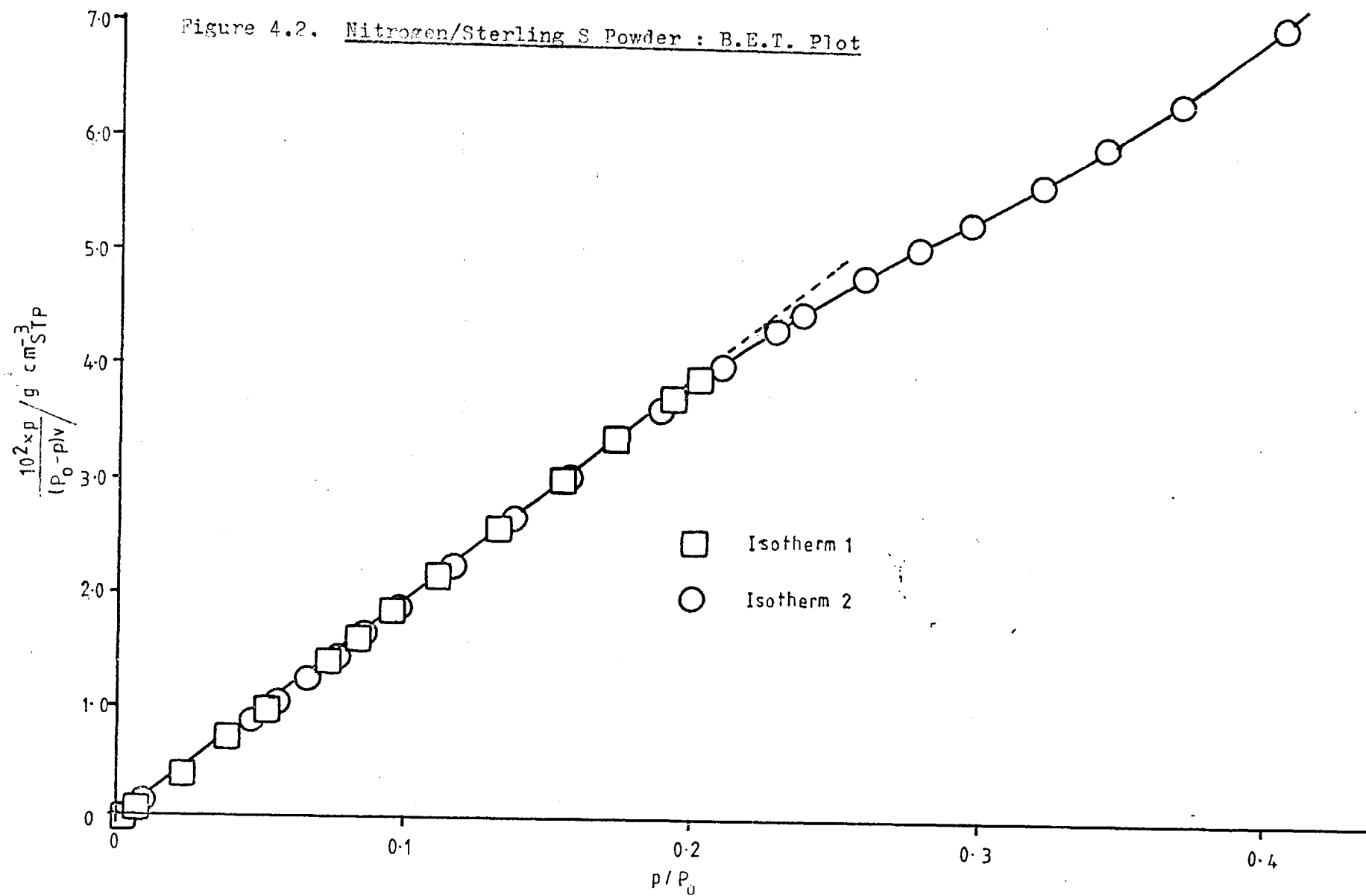
$$n_2 = \frac{p_2 V + \phi_T p_2}{T_2} \quad (4.2)$$

ϕ_T ($\text{cm}^3 \text{ K}^{-1}$) is the temperature dependent volume of the adsorption sample holder accounting for the difference in temperature between the holder and the fixed volume V . This volume ϕ_T was evaluated by helium expansion. The amount of gas adsorbed at the equilibrium pressure p_2 was given by the value of $(n_1 - n_2)$. The value was converted to $\text{cm}^3_{\text{STP}} \text{g}^{-1}$ by the expression

$$v = (n_1 - n_2) \frac{1}{m_{\text{ads}}} \frac{273.15}{76} \quad (4.3)$$

where m_{ads} (g) is the adsorbate mass. A small correction was made to v to account for non ideality of nitrogen (Young and Crowell, 1962).





A B.E.T. plot (figure 4.2) was constructed according to equation 2.110.

$$\frac{p}{(P_0 - p) v} = \frac{1}{v_m C} + \frac{(C-1)}{v_m C} \frac{p}{P_0} \quad (2.110)$$

The graph showed linearity over the range of p/P_0 of 0.01 to 0.13. From the values of the slope and intercept the monolayer capacity was calculated, giving $5.09 \text{ cm}^3_{\text{STP}} \text{g}^{-1}$. The surface area (based upon a value of 0.162 nm^2 , for the mean area occupied by a single nitrogen molecule) was obtained as $22.2 \text{ m}^2 \text{g}^{-1}$ and the value of C was 17,000.

4.2. HELIUM DENSITY DETERMINATION

The density, d_{He} of Sterling S was determined by helium expansion. Two determinations were made after outgassing at ambient temperature and two further results were obtained after outgassing at 300°C . Measurements were made after two different outgassing conditions in order to assess the effect that any structural changes that might occur during outgassing at elevated temperatures has on the density of the material. The mean of the four measurements is 2080 kg m^{-3} . This average value is used in any calculations requiring knowledge of the carbon density.

Table 4.1. Helium Density Determinations

$\frac{T_{\text{OG}}}{\text{K}}$	Determination	$\frac{d_{\text{He}}}{\text{kg m}^{-3}}$
296 (Room Temperature)	1	2070
	2	2120
575	1	2050
	2	2060

4.3. FLOW RESULTS FOR MEMBRANE 1

4.3.1. Introduction

Isothermal flow results under conditions of constant Δp were obtained for twelve gases flowing through Sterling S membrane 1. Studies were made at a number of membrane temperatures between 199K and 473K. The effect of progressively increasing the outgassing temperature on the flow of helium, neon, argon and methane was examined. The stability of the membrane was also investigated by periodic measurements of the permeability of helium throughout the duration of the research programme.

The method used is described in section 3.4.3. The outgoing pressure p_1 was recorded as a function of time and $\tilde{K}$ and J_∞ were obtained from dp_1/dt using equations 3.2 and 3.3. respectively. Typical results for helium are shown in figure 4.3.

4.3.2. Outgassing Trials.

The results of the outgassing trials are shown in figure 4.4 and tabulated in table 4.2. Each point on the graph corresponds to a mean of between three and eleven results (tabulated in detail in Appendix B1) at ingoing pressures, p_0 , in the range of 1cm Hg to 30 cm Hg. Four gases; helium, neon, argon and methane were used for the trials. The membrane was thermostatted at 308.2K. It is clear that as the outgassing temperature, T_{OG} was increased the permeability of each of the four gases increased. The values of $\tilde{K} \text{ M}^{\frac{1}{2}}$ for argon and methane are seen to be less than the value for helium at outgassing temperature of 523 K or lower. These results are discussed in section 5.3.1.

For all subsequent experiments the membrane was periodically outgassed at approximately 573K.

4.3.3. Effect of Pressure.

The flow results for a variety of gases at a number of temperatures are given in detail in Appendixes B2 to B13. Figure 4.5 shows J_∞ plotted as a function of ingoing pressure for the inert gases, where the membrane is thermostatted at

Figure 4.3. Typical Plots of p_1 versus t for Helium Flowing Through Sterling S Membrane 1 : $T/K = 273.2$

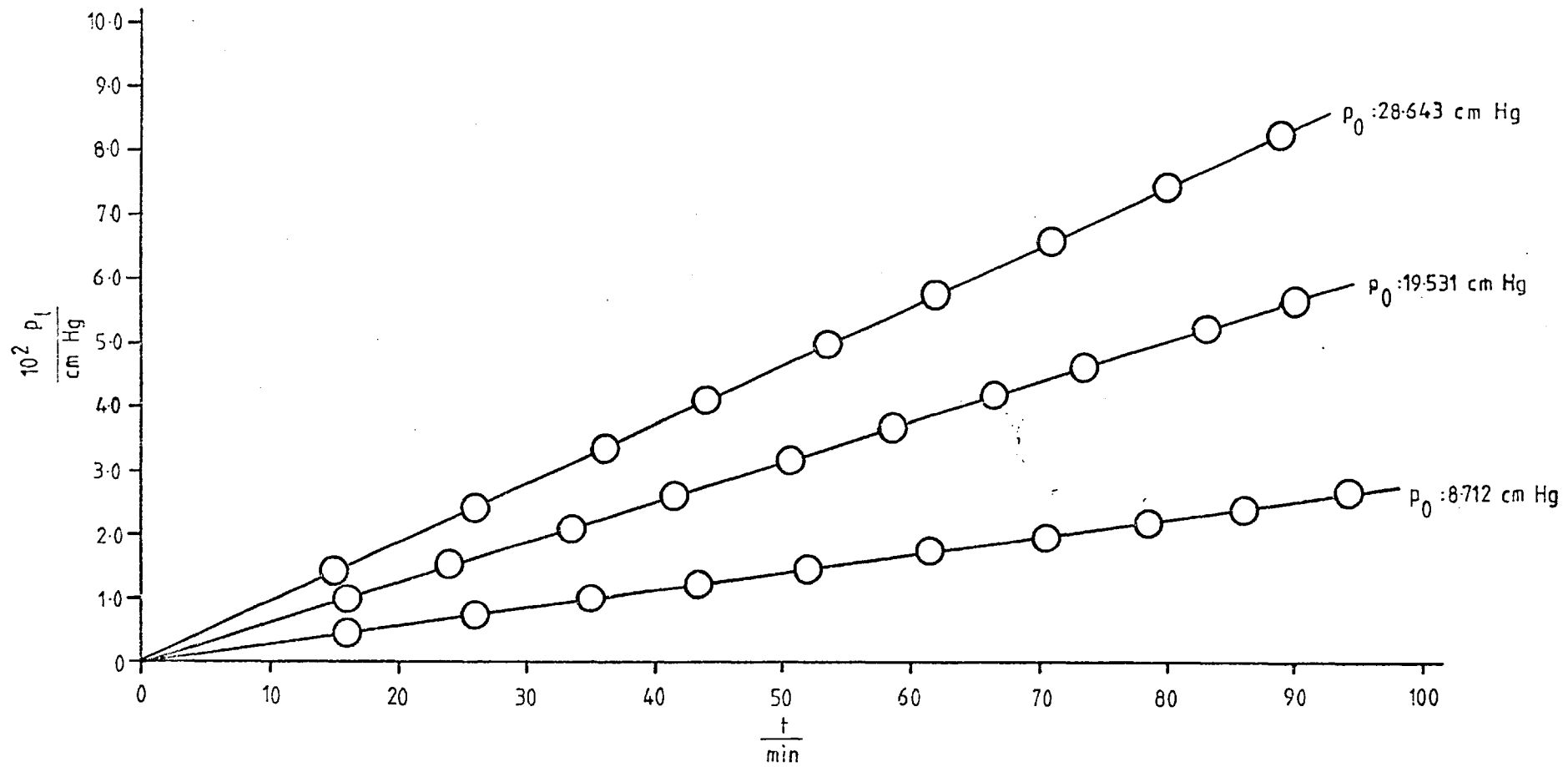
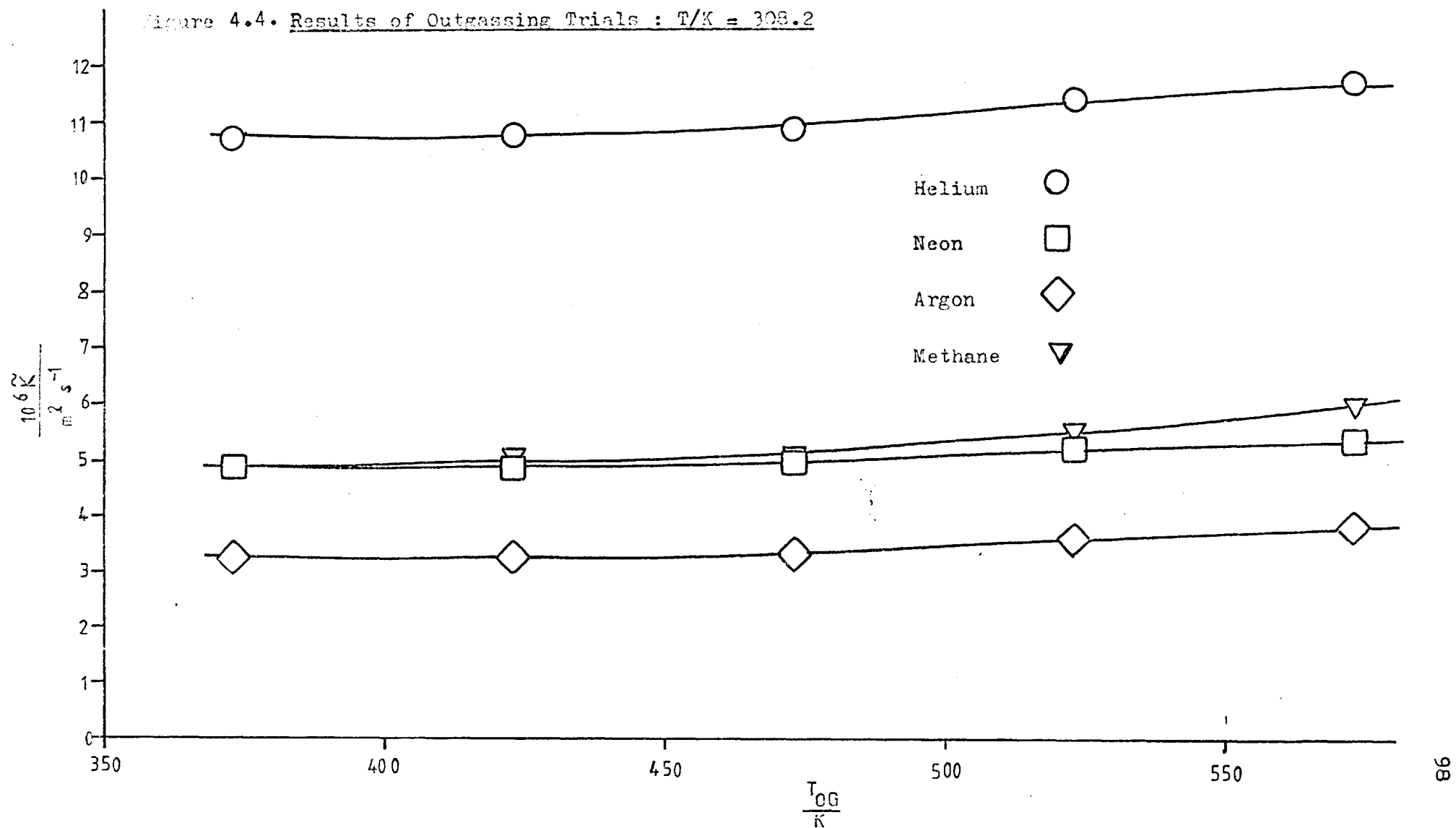


Table 4.2.

Outgassing Trials - $T = 308.2\text{K}$

Gas	$\frac{T_{OG}}{K}$	$\frac{10^{6\gamma} K}{m^2 s^{-1}}$	$\frac{10^{5\gamma \frac{1}{2}}}{m^2 s^{-1} g^{\frac{1}{2}} mol^{-\frac{1}{2}}}$
Helium	373	10.74	2.14 ₉
	423	10.80	2.16 ₁
	473	10.96	2.19 ₃
	523	11.39	2.27 ₉
	573	11.68	2.33 ₇
Neon	373	4.87	2.18 ₈
	423	4.88	2.19 ₂
	473	4.99	2.24 ₂
	523	5.24	2.35 ₄
	573	5.40	2.42 ₆
Argon	373	3.24	2.04 ₈
	423	3.28	2.07 ₃
	473	3.36	2.14 ₄
	523	3.60	2.27 ₅
	573	3.84	2.42 ₇
Methane	373	4.88	1.95 ₅
	423	5.03	2.01 ₅
	473	5.09	2.03 ₈
	523	5.52	2.21 ₁
	573	6.03	2.41 ₅

Figure 4.4. Results of Outgassing Trials : $T/K = 308.2$



308.2K. A similar plot for helium at a number of T values is shown in figure 4.6. Although it is not clear from the graphs but any deviations from linearity which occur are in a positive direction. In other words, the measured flux is greater than predicted from the limiting slope of the J_{∞} versus p_0 curve at zero pressure. Deviations from linearity are very small, less than 1%.

At lower temperatures, however, the permeability of xenon exhibits a clear pressure dependence (figures 4.7 and 4.8). The results for a membrane temperature of 213.2K shows $\tilde{K}$ decreasing with increasing pressure. At temperatures below and above 213.2K any pressure dependence which may exist is masked by experimental scatter. The flux curve (figure 4.3) for 213.2K shows negative deviations from linearity. The dotted line represents the low pressure limit.

Ethane (figures 4.9 and 4.10) and propane gas (figure 4.11 and 4.12) also show permeabilities which are functions of pressure. Ethane shows the dependence at temperatures below 273.2K and propane at temperatures below 308.2K. The permeability - pressure relationship takes a different form in the cases of ethane and propane to that in the case of xenon. For the former two gases the permeability initially increases with pressure but at the same time $(\partial \tilde{K} / \partial p)_T$ decreases and the permeability of propane at 233.2K shows a pressure maximum. The $J_{\infty} - p_0$ curves (figures 4.10 and 4.12) are sigmoid in shape.

Only xenon, ethane and propane show any significant pressure dependence of the permeability in the range of pressure and temperatures studied. Even these three gases do not show this effect at temperatures above 273K.

4.3.4. Effect of Membrane Temperature.

In order that comparison can be made between the flow results of the different gases at the various temperatures, even where there is a pressure dependent effect, a permeability corresponding to zero pressure was extracted (table 4.3). Two methods were employed to obtain this

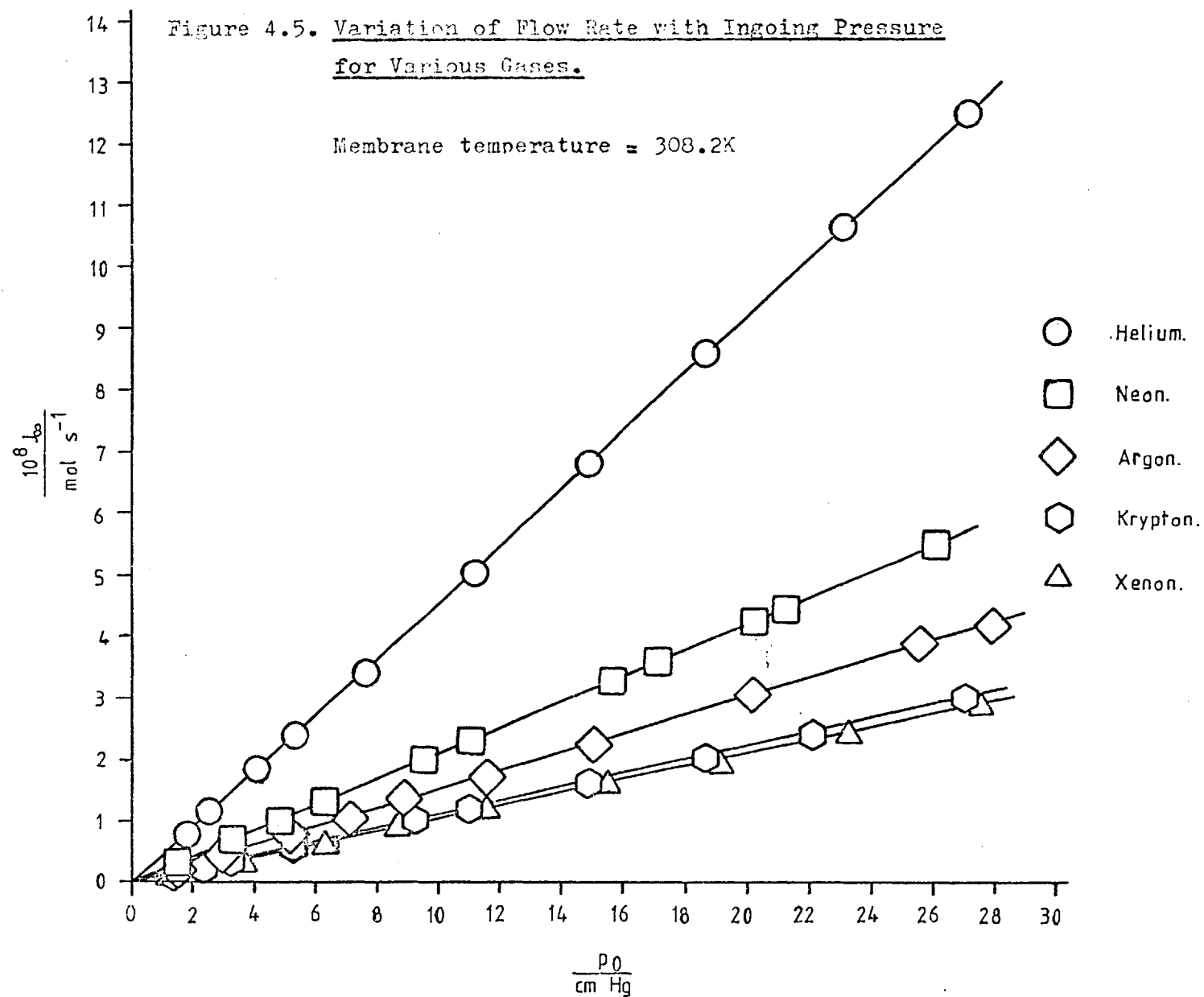


Figure 4.6. Variation of Helium Flow Rate with Ingoing Pressure at Various Membrane Temperatures.

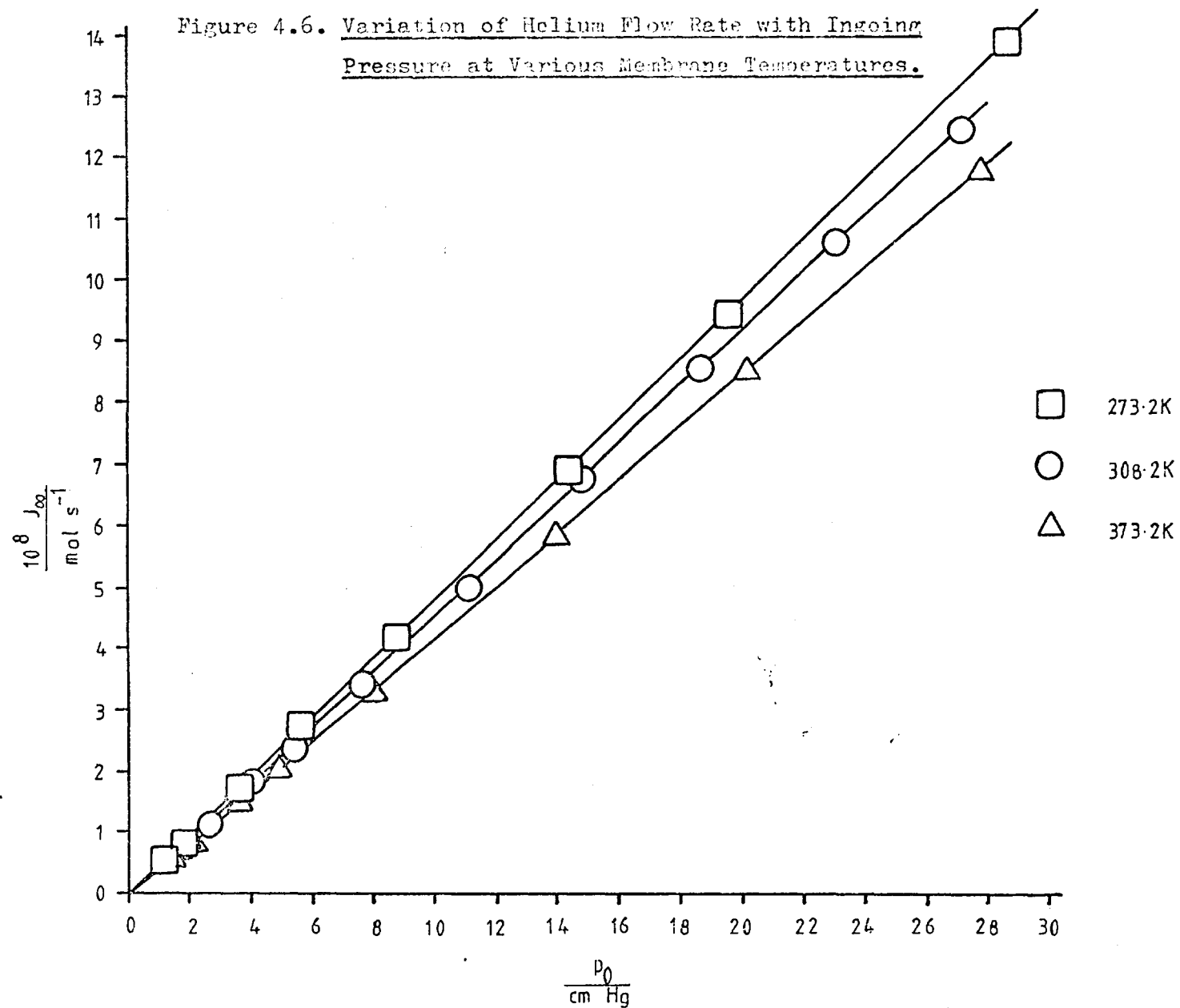


Figure 4.7. Permeability of Xenon as a Function of Pressure.

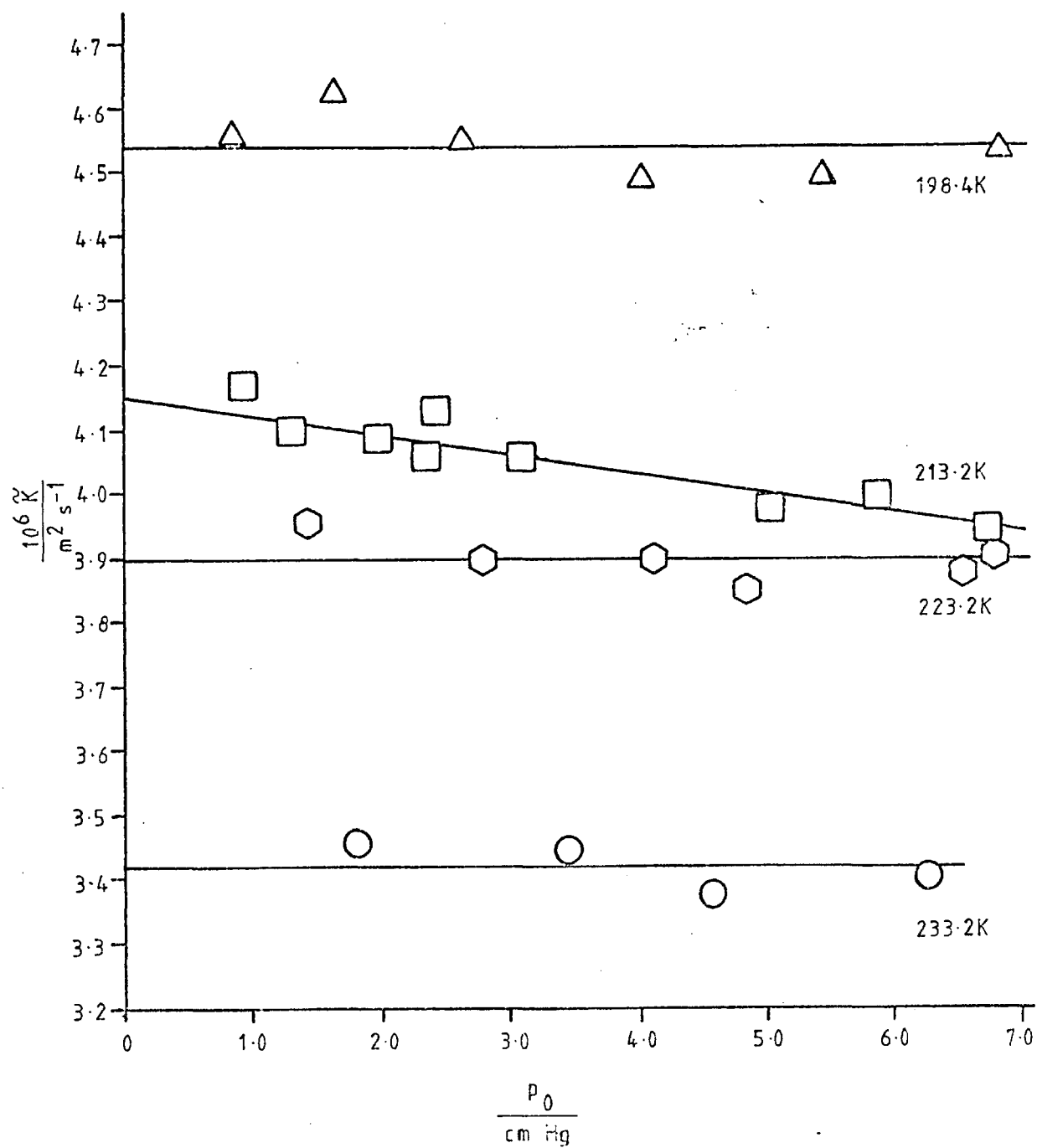
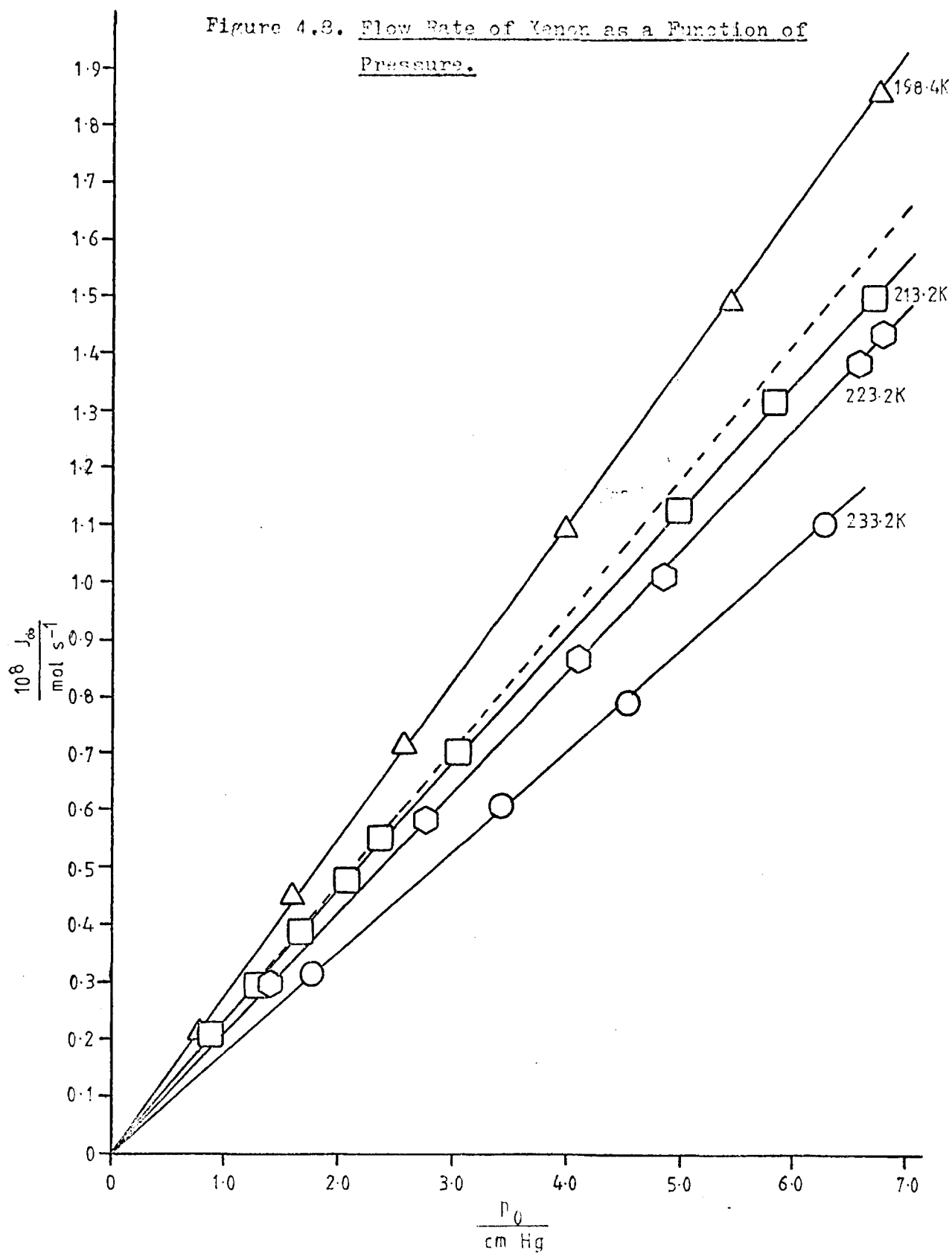


Figure 4.3. Flow Rate of Xenon as a Function of Pressure.



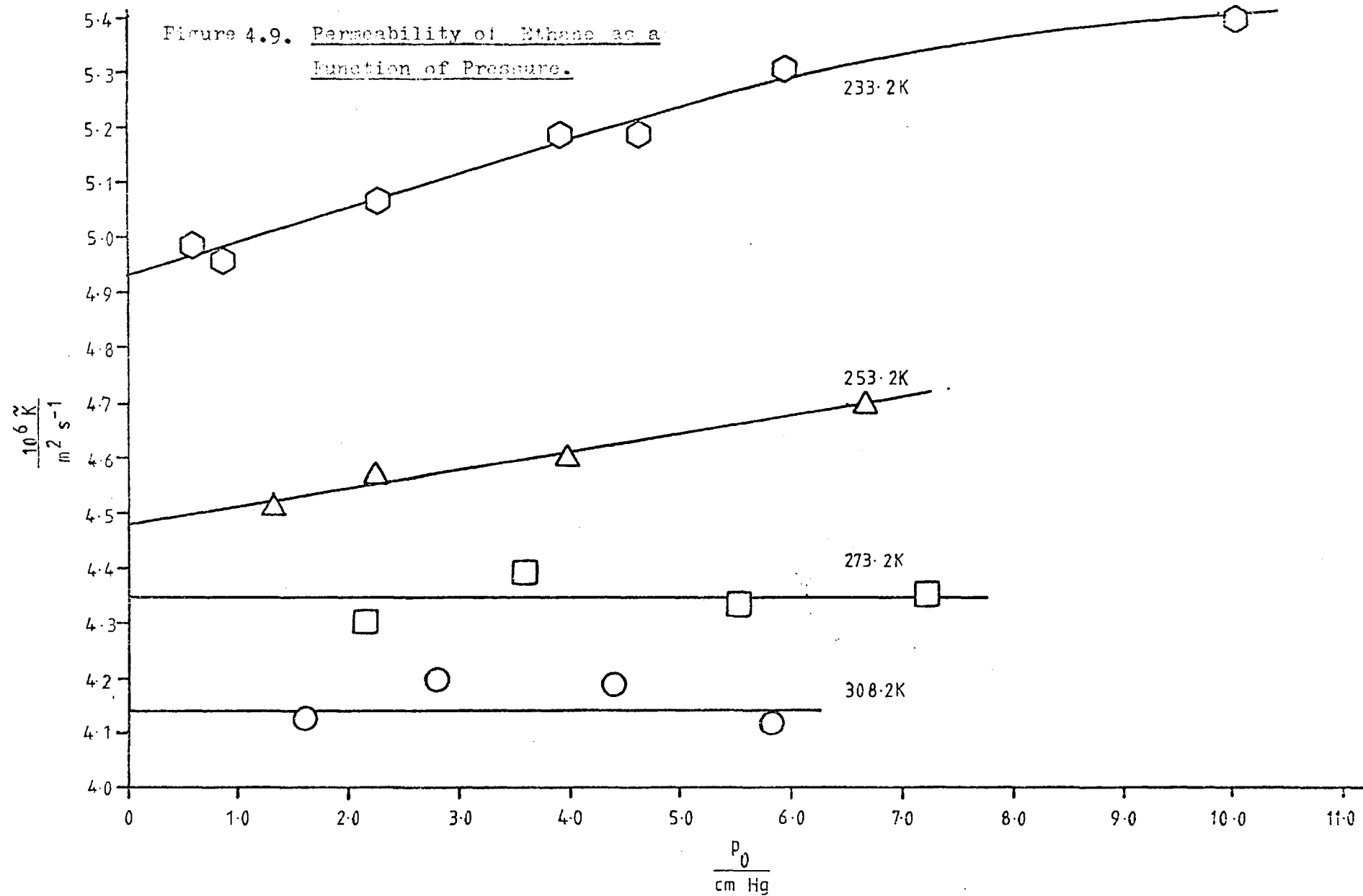


Figure 4.10. Flow Rate of Ethane as a Function of Pressure.

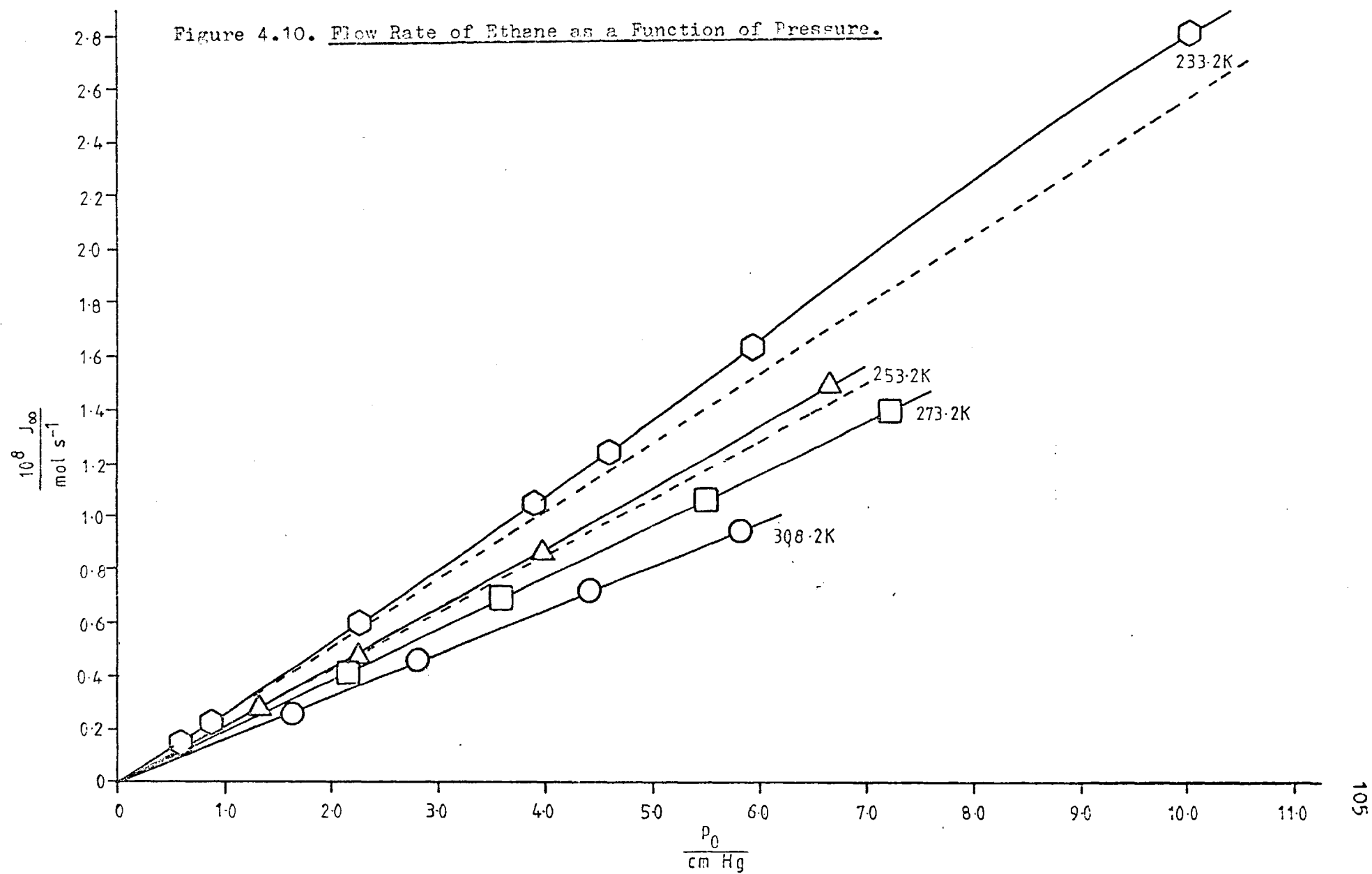


Figure 4.11. Permeability of Propane as a Function
Pressure.

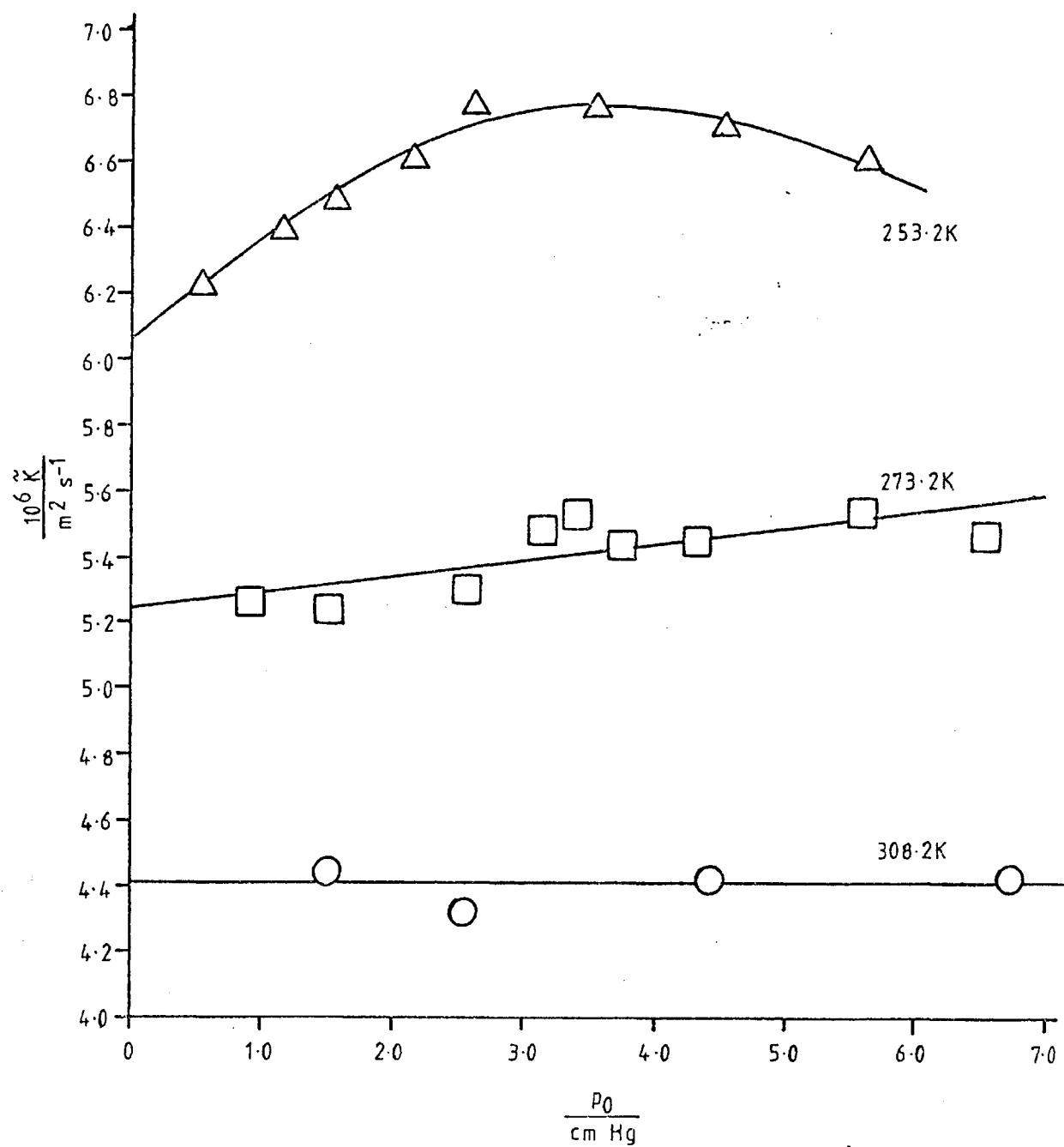


Figure 4.12. Flow Rate of Propane Gas as a Function of Pressure.

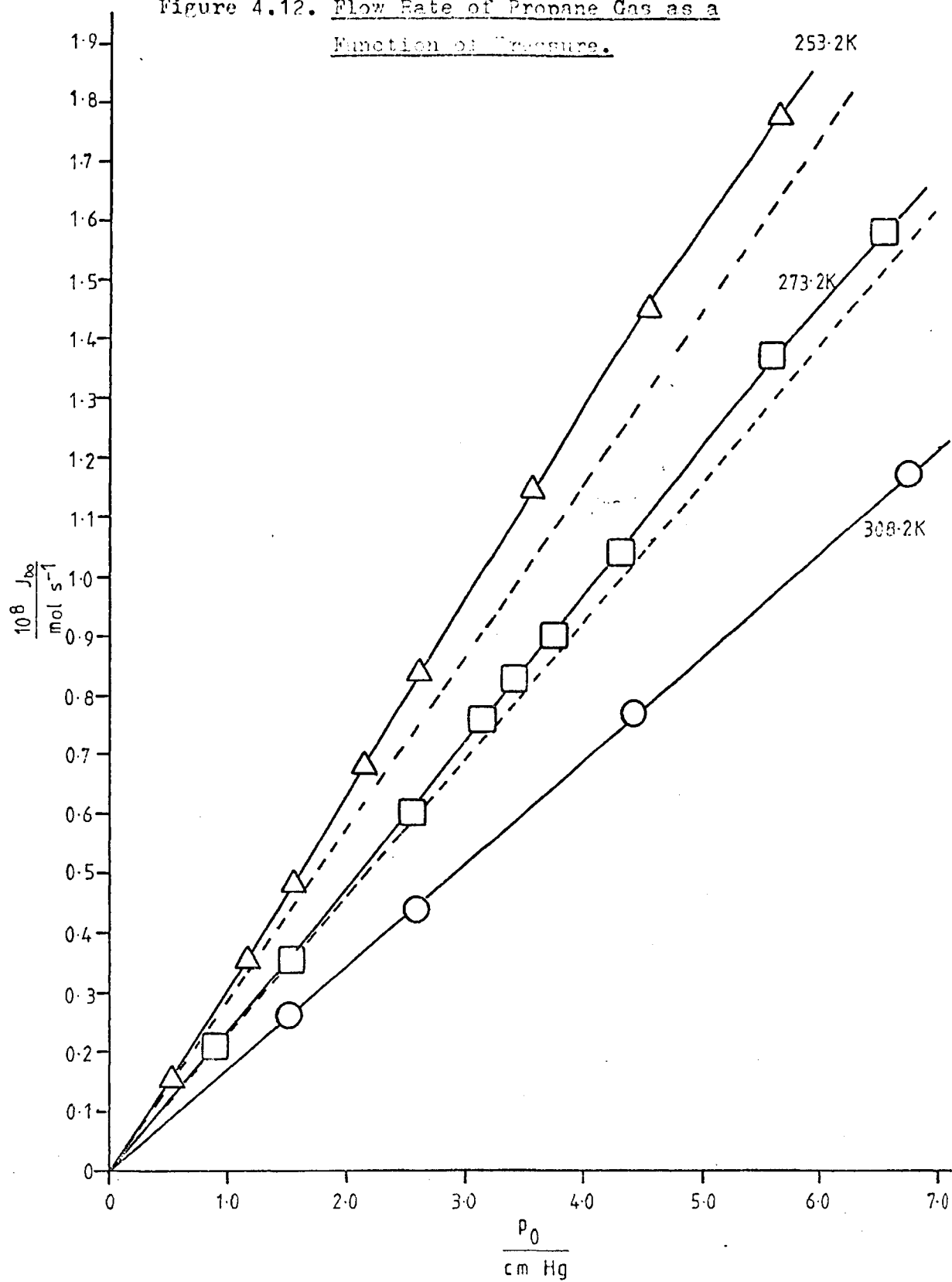


Table 4.3.

Flow Results for Membrane 1

Gas	T K	$\frac{10^6 \tilde{K}_O}{m^2 s^{-1}}$	$\frac{10^7 \tilde{K}_O T^{-1/2}}{m^2 s^{-1} K^{-1/2}}$	$\frac{10^6 \tilde{K}_O M^{1/2} T^{-1/2}}{m^2 s^{-1} g^{1/2} mol^{-1/2} K^{-1/2}}$
Helium	473.2	15.22	7.00	1.40 ₀
	423.2	14.18	6.89	1.37 ₉
	373.2	12.93	6.69	1.33 ₉
	343.2	12.48	6.74	1.34 ₉
	308.2	11.59	6.60	1.32 ₁
	273.2	10.89	6.59	1.31 ₈
	233.2	9.90	6.48	1.29 ₇
	213.2	9.35	6.40	1.28 ₁
	198.9	8.95	6.35	1.27 ₀
Neon	473.2	7.01	3.22	1.45
	423.2	6.56	3.19	1.43
	373.2	6.06	3.14	1.41
	343.2	5.78	3.12	1.40
	308.2	5.38	3.06	1.37
	273.2	5.01	3.03	1.36
	233.2	4.62	3.03	1.36
	213.2	4.30	2.95	1.32
Argon	473.2	5.09	2.34	1.48
	423.2	4.73	2.30	1.45
	373.2	4.32	2.24	1.41
	343.2	4.11	2.22	1.40
	308.2	3.82	2.17	1.37
	273.2	3.55	2.15	1.36
	233.2	3.36	2.20	1.39
	213.2	3.24	2.22	1.40

Table 4.3 (continued)

Gas	T K	$\frac{10^6 \tilde{\nu}_0}{\text{m}^2 \text{s}^{-1}}$	$\frac{10^7 \tilde{\nu}_0 T^{-1/2}}{\text{m}^2 \text{s}^{-1} \text{K}^{-1/2}}$	$\frac{10^6 \tilde{\nu}_0 M^{1/2} T^{-3/2}}{\text{m}^2 \text{s}^{-1} \text{g}^{1/2} \text{mol}^{-1} \text{K}^{-3/2}}$
Krypton	473.2	3.59	1.65	1.51
	423.2	3.35	1.63	1.49
	373.2	3.08	1.59	1.46
	343.2	2.96	1.60	1.46
	308.2	2.79	1.59	1.46
	273.2	2.70	1.63	1.49
	233.2	2.79	1.83	1.68
	213.2	2.93	2.01	1.84
Xenon	199.0	3.12	2.21	2.02
	473.2	3.02	1.39	1.59
	423.2	2.87	1.40	1.60
	373.2	2.69	1.39	1.59
	343.2	2.69	1.45	1.66
	308.2	2.71	1.54	1.76
	273.2	2.81	1.70	1.95
	233.2	3.42	2.24	2.57
Hydrogen	223.2	3.90	2.61	2.99
	213.2	4.16	2.85	3.26
	198.4	4.54	3.22	3.69
	473.2	20.97	9.64	1.36 ₉
	423.2	19.38	9.42	1.33 ₈
	373.2	17.75	9.19	1.30 ₅
	343.2	16.75	9.04	1.28 ₄
	308.2	15.68	8.93	1.26 ₃
Deuterium	273.2	14.28	8.64	1.22 ₇
	233.2	12.96	8.49	1.20 ₅
	213.2	12.22	8.37	1.18 ₈
	473.2	15.10	6.94	1.39 ₃
	423.2	13.87	6.74	1.35 ₃

Table 4.3 (continued)

Gas	T K	$\frac{10^6 \tilde{\nu}_{K_0}}{m^2 s^{-1}}$	$\frac{10^7 \tilde{\nu}_{K_0} T^{-1/2}}{m^2 s^{-1} K^{-1/2}}$	$\frac{10^6 \tilde{\nu}_{K_0} m^{1/2} T^{-1/2}}{m^2 s^{-1} g^{1/2} mol^{-1/2} K^{-1/2}}$
Deuterium	373.2	12.66	6.55	1.31 ₅
	343.2	11.94	6.45	1.29 ₃
	308.2	11.11	6.33	1.27 ₀
	273.2	10.10	6.11	1.22 ₆
	233.2	9.18	6.01	1.20 ₆
	213.2	8.62	5.90	1.18 ₅
Nitrogen	473.2	5.96	2.74	1.45
	423.2	5.51	2.68	1.42
	373.2	5.06	2.62	1.39
	343.2	4.74	2.56	1.35
	308.2	4.42	2.52	1.33
	273.2	4.05	2.45	1.30
	233.2	3.75	2.48	1.30
	213.2	3.62	2.48	1.31
	199.4	3.53	2.50	1.32
Carbon Dioxide	473.2	4.40	2.02	1.34
	423.2	4.02	1.95	1.30
	373.2	3.60	1.86	1.24
	343.2	3.39	1.83	1.21
	308.2	3.17	1.81	1.20
	273.2	2.96	1.79	1.19
	233.2	2.97	1.94	1.29
	213.2	3.07	2.10	1.39
	199.3	3.34	2.37	1.57
Methane	473.2	7.97	3.66	1.47
	448.2	7.68	3.63	1.45
	423.2	7.44	3.61	1.45
	398.2	7.03	3.53	1.41

Table 4.3 (continued)

Gas	T K	$10^6 \tilde{K}_0$ $\text{m}^2 \text{s}^{-1}$	$10^7 \tilde{K}_0 T^{-\frac{1}{2}}$ $\text{m}^2 \text{s}^{-1} \text{K}^{-\frac{1}{2}}$	$10^6 \tilde{K}_0 M^{\frac{1}{2}} T^{-\frac{1}{2}}$ $\text{m}^2 \text{s}^{-1} \text{g}^{\frac{1}{2}} \text{mol}^{-\frac{1}{2}} \text{K}^{-\frac{1}{2}}$
Methane	383.2	6.89	3.52	1.41
	373.2	6.71	3.47	1.39
	343.2	6.36	3.44	1.38
	323.2	6.17	3.43	1.38
	308.2	6.03	3.44	1.38
	293.2	5.85	3.42	1.37
	273.2	5.66	3.43	1.38
	253.2	5.51	3.46	1.39
	233.2	5.50	3.50	1.44
	223.2	5.53	3.70	1.48
	213.2	5.54	3.80	1.52
Ethane	473.2	5.16	2.38	1.31
	423.2	4.78	2.32	1.27
	373.2	4.41	2.28	1.25
	343.2	4.24	2.29	1.25
	308.2	4.14	2.36	1.29
	273.2	4.35	2.63	1.44
	253.2	4.49	2.82	1.55
	233.2	4.93	3.23	1.77
Propane	473.2	4.22	1.94	1.29
	423.2	3.98	1.93	1.28
	373.2	3.85	2.00	1.33
	343.2	4.00	2.16	1.43
	308.2	4.42	2.52	1.67
	273.2	5.25	3.18	2.11
	253.2	6.07	3.82	2.53

limiting permeability. When the permeability was not significantly pressure-dependent the flux, J_∞ was plotted against pressure. The permeability is obtained from the slope $(dJ_\infty / dp_0)_{p_0 \rightarrow 0}$

$$K_0 = \frac{RTl}{A_c} \left(\frac{dJ_\infty}{dp_0} \right)_{p_0 \rightarrow 0} \quad (4.4)$$

K_0 is the limiting value of K at zero pressure. From equation 2.15

$$\tilde{K}_0 = K_0 \quad (4.5)$$

$\tilde{K}_0$ is the low pressure limit of $\tilde{K}$. Where the pressure dependence is more important the second procedure was used. The permeability, $\tilde{K}$ was plotted versus pressure and the required value was obtained by extrapolation to zero pressure.

For each limiting permeability value, $\tilde{K}_0$ the quantity $\tilde{K}_0 M^{1/2} / T^{1/2}$ was evaluated and the results were plotted against membrane temperature, T (figures 4.13 - 4.16). For convenience the units used for M are g mol^{-1} . To convert the tabulated values of $\tilde{K}_0 M^{1/2} / T^{1/2}$ (table 4.3) to units of $\text{m}^2 \text{s}^{-1} \text{kg}^{1/2} \text{mol}^{-1/2} \text{K}^{-1/2}$ it is only necessary to multiply by the factor $0.0316 \text{ kg}^{1/2} \text{g}^{-1/2}$. The first feature of note is that $\tilde{K}_0 M^{1/2} / T^{1/2}$ for helium increases with increasing temperature. Similar results are observed for neon, hydrogen and deuterium. For the remaining gases $\tilde{K}_0 M^{1/2} / T^{1/2}$ passes through a temperature minimum. The results for hydrogen and deuterium are less than the corresponding values for helium over the whole temperature range studied. $\tilde{K}_0 M^{1/2} / T^{1/2}$ for nitrogen, carbon dioxide, ethane and propane respectively is less than the corresponding value for helium over part of the temperature range.

The results for the three hydrocarbons are also plotted in figure 4.17 in the form of $\tilde{K}_0 / T^{1/2}$ versus T . Since $\tilde{K}_0 / T^{1/2}$ is a better measure of the relative flow rates than $\tilde{K}_0 M^{1/2} / T^{1/2}$. It is interesting to observe that $\tilde{K}_0 / T^{1/2}$ for propane lies below that of both methane and ethane at high temperatures. At low temperatures $\tilde{K}_0 / T^{1/2}$ for propane is greater than the values for methane and ethane.

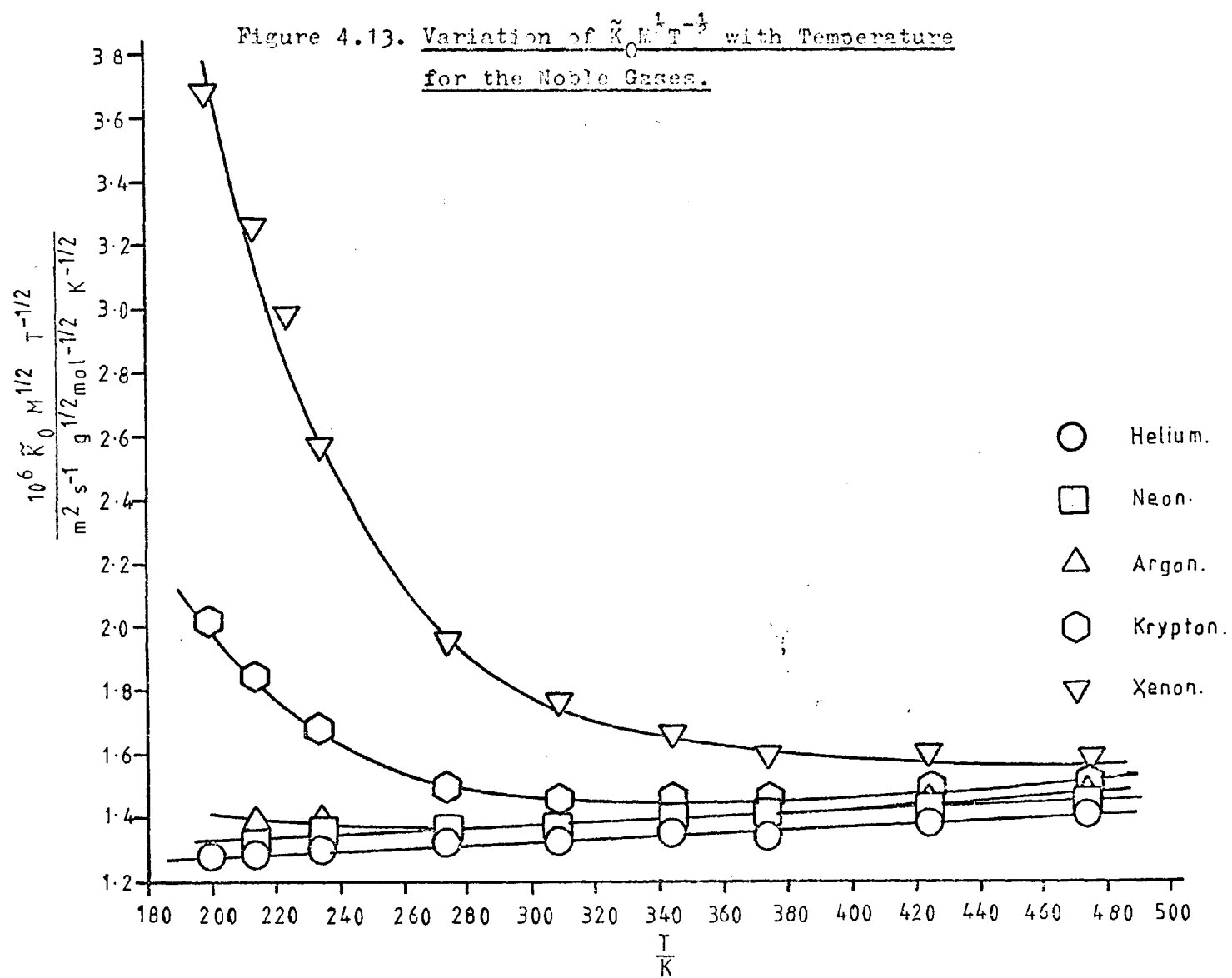


Figure 4.14. Variation of $\tilde{K}_0 M^{1/2} T^{-1/2}$ with Temperature for Helium, Hydrogen and Deuterium.

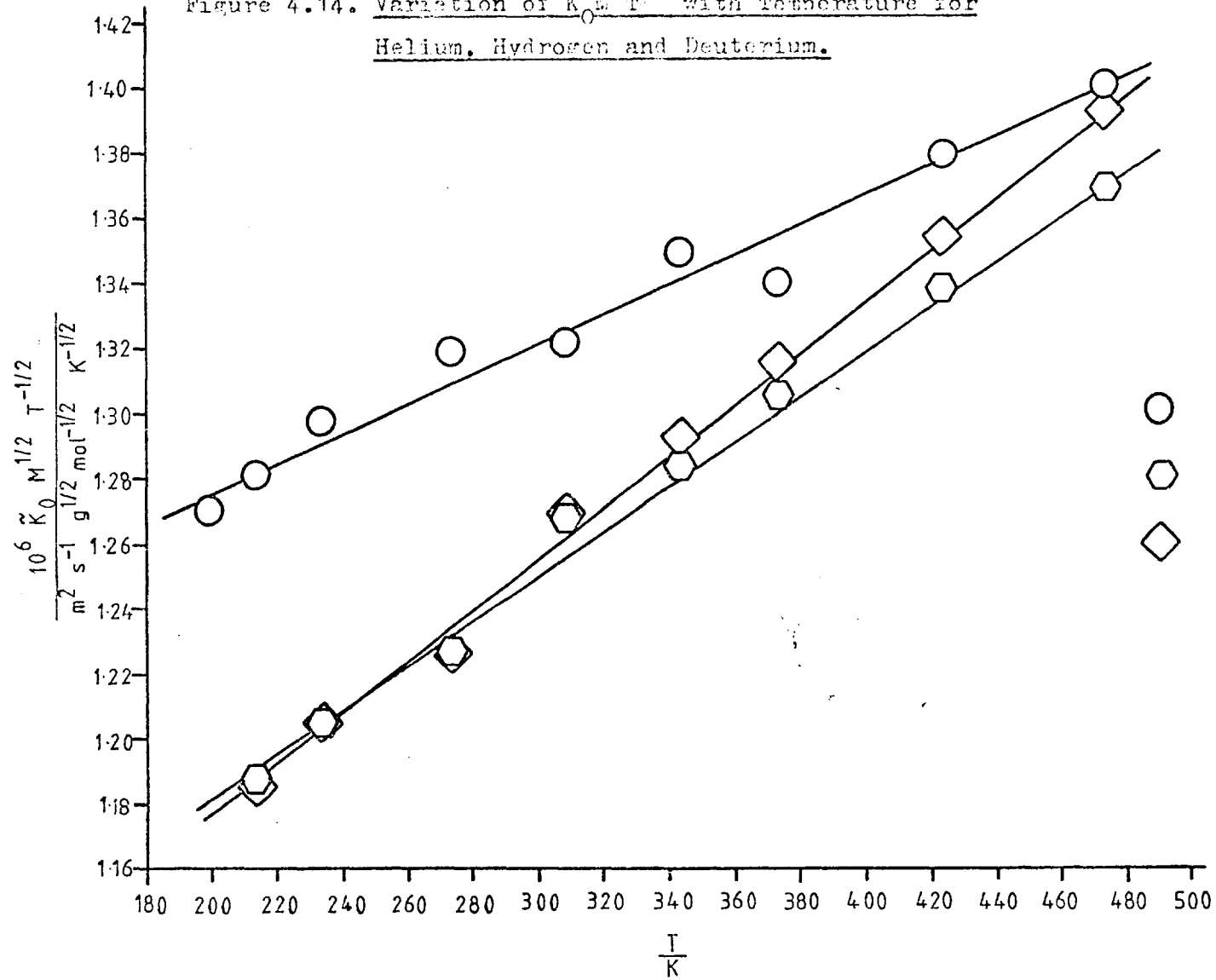
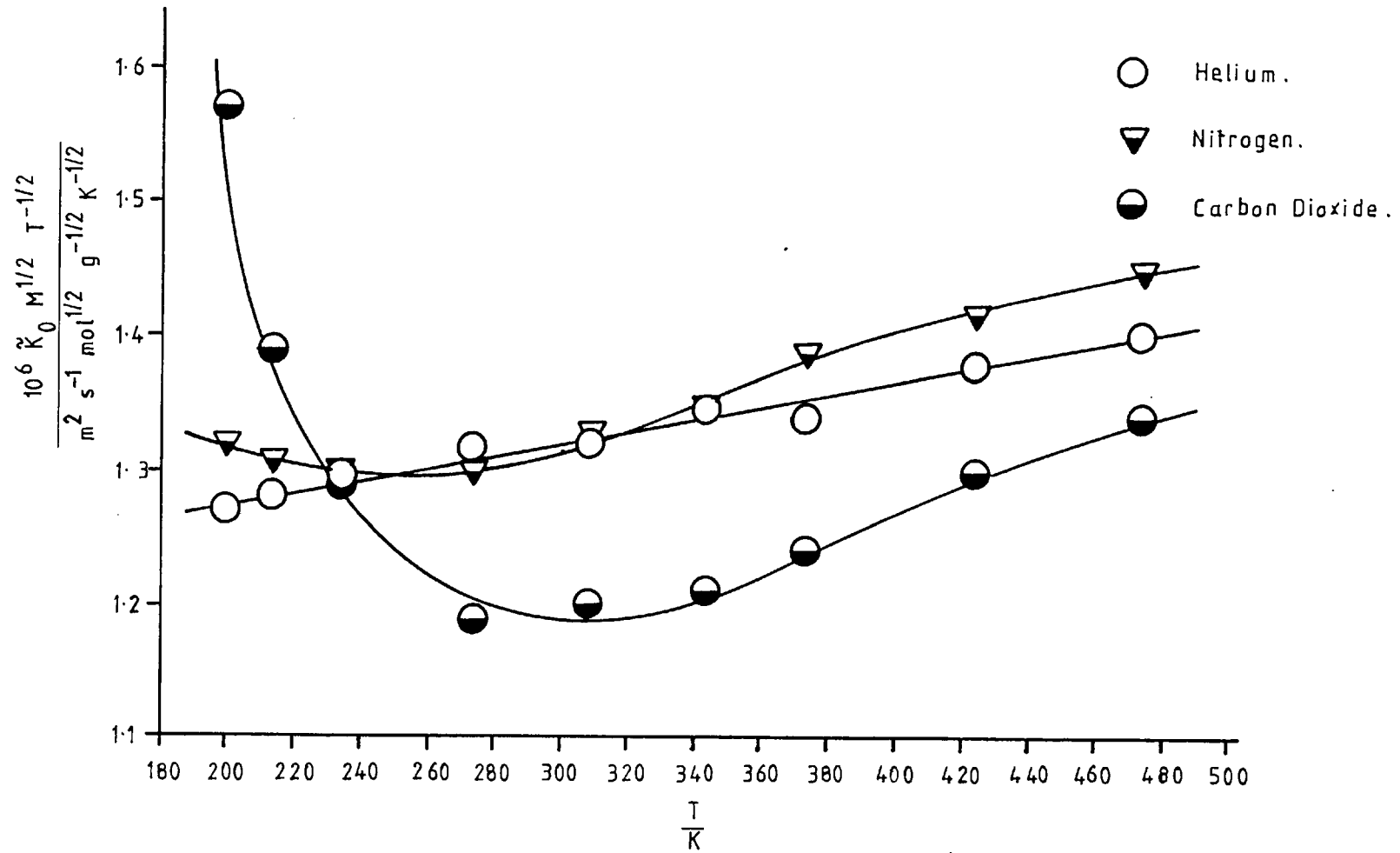


Figure 4.15. Variation of $\tilde{K}_0 M^{\frac{1}{2}} T^{-\frac{1}{2}}$ with Temperature for Helium, Nitrogen and Carbon Dioxide.



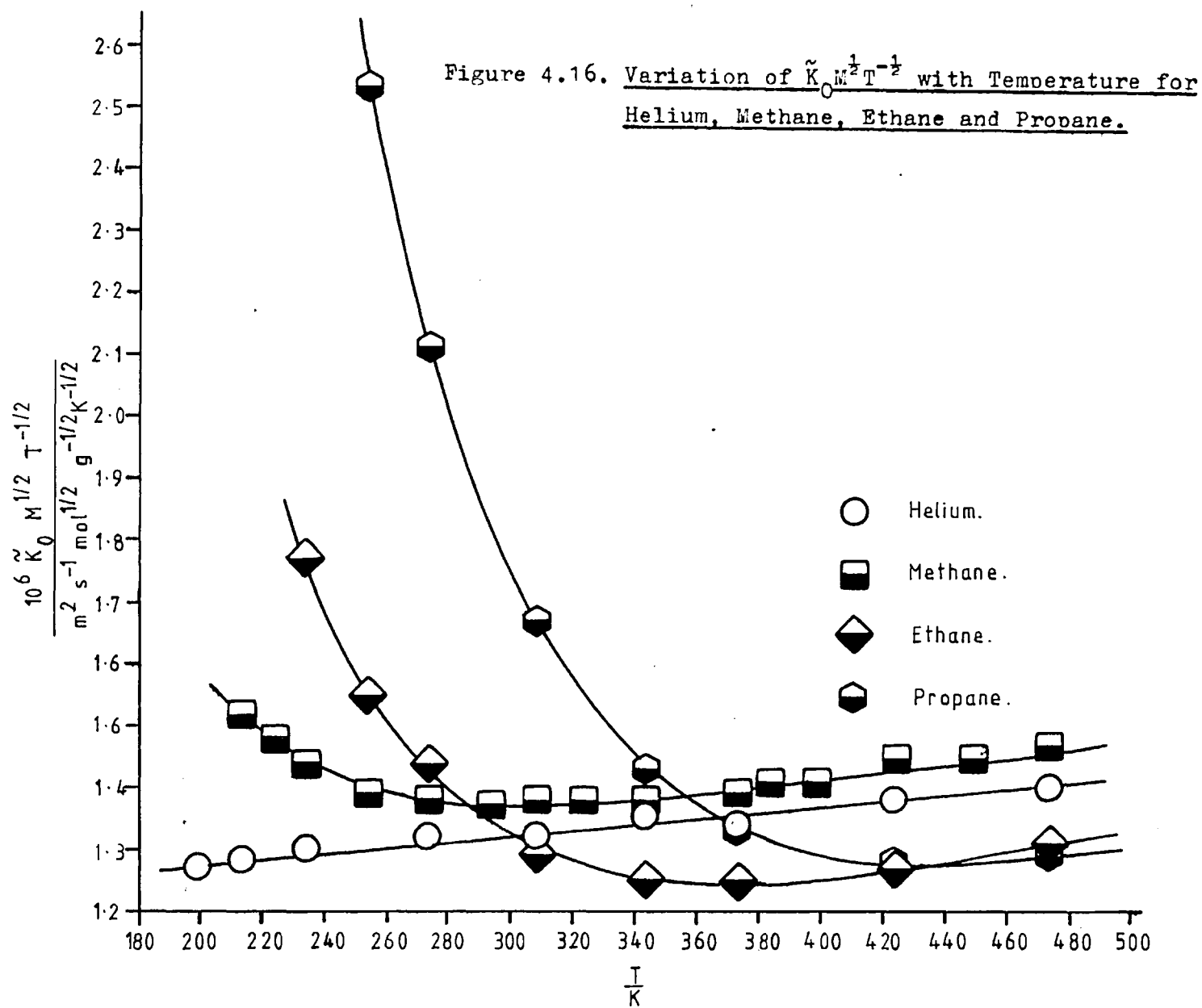
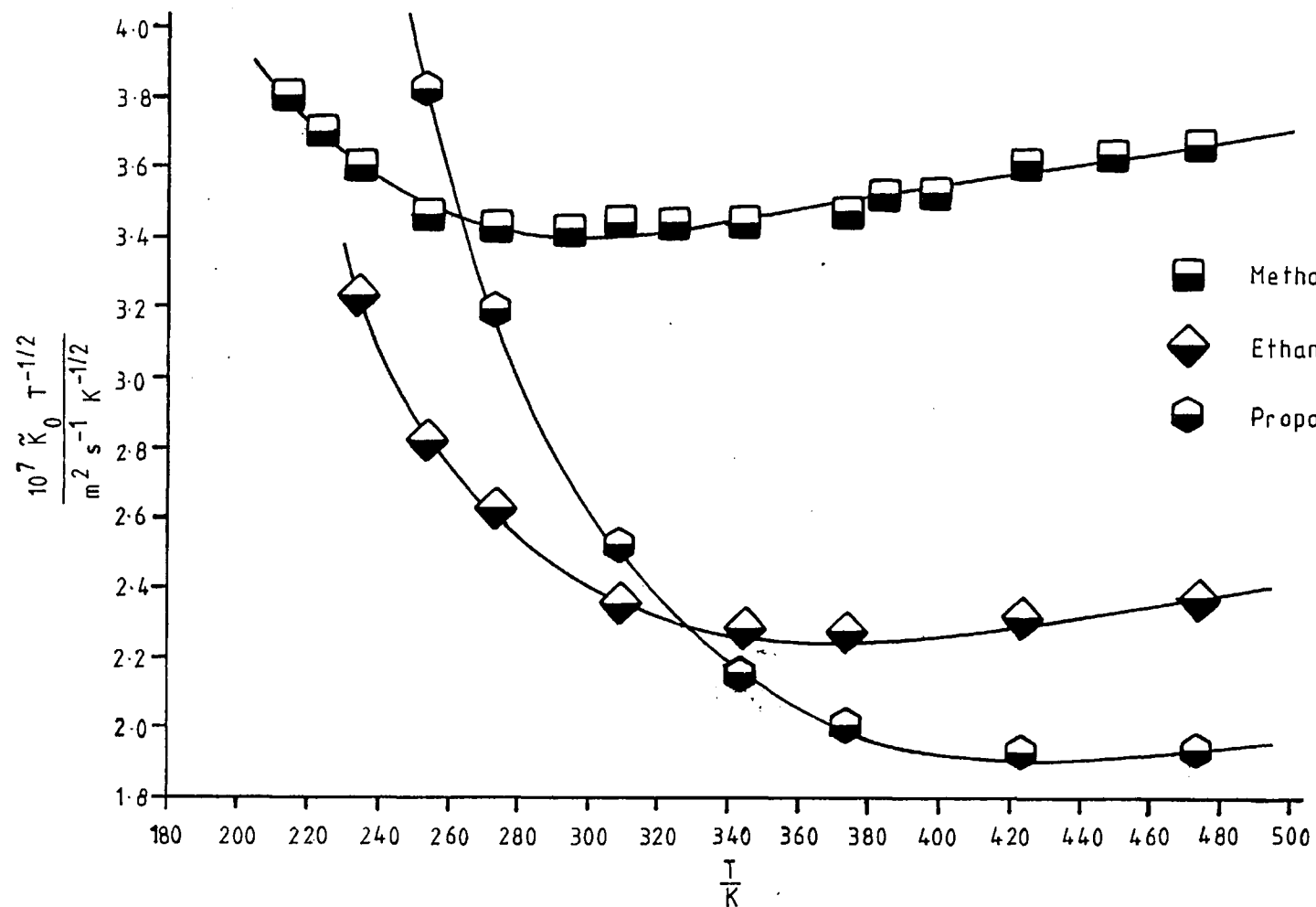


Figure 4.17. Variation of $\tilde{K}_0 T^{-1/2}$ with Temperature
for Methane, Ethane and Propane.



4.3.5. Time-lags.

The time-lags, L_1^a , were found to be too small to be measured accurately. The less strongly adsorbed gases appeared to give largely negative time-lags. Whereas the more strongly adsorbed gases (such as propane) at low temperatures gave more positive time lags. Considering all the gases the time-lags varied between -3 and +3 minutes with most lying between -1 and +1 minute. Considering a given gas at a constant temperature the scatter could be as much as ± 1 minute.

4.3.6. Membrane Stability

Periodic measurements of the helium permeability were made throughout the duration of the experimental programme. This was to check that there was no irreversible ageing of the membrane. Defining $\tilde{K}_i$ as the initial value of $\tilde{K}_0$, the ratio $(\tilde{K}/\tilde{K}_i)_T$ is plotted against experiment number in figure 4.18. The results are also tabulated in Appendix B 14.

4.4. FLOW RESULTS FOR MEMBRANE 2

4.4.1. Introduction.

The isothermal flow of helium and carbon dioxide was studied at four temperatures between 273.2K and 473.2K. The principles of the technique used were basically as for the flow of gases through membrane 1, although the method of pressure measurements was different (section 3.4.5)

As for membrane 1, p_1 was recorded as a function of time and $\tilde{K}$ and J_∞ were derived from the slope. Typical results are shown in figure 4.19. The membrane was outgassed at 573K at frequent intervals.

4.4.2. Effect of Pressure.

The results are tabulated in Appendices C1 and C2. Figure 4.20 shows J_∞ for helium plotted against the ingoing pressure, which is approximately equal to the pressure difference. Figure 4.21 is a similar plot of the results for carbon dioxide. There is no detectable pressure dependence of the permeability over the pressure range considered for either helium or carbon dioxide.

Figure 4.18. Variation of Helium Permeability with Experiment.

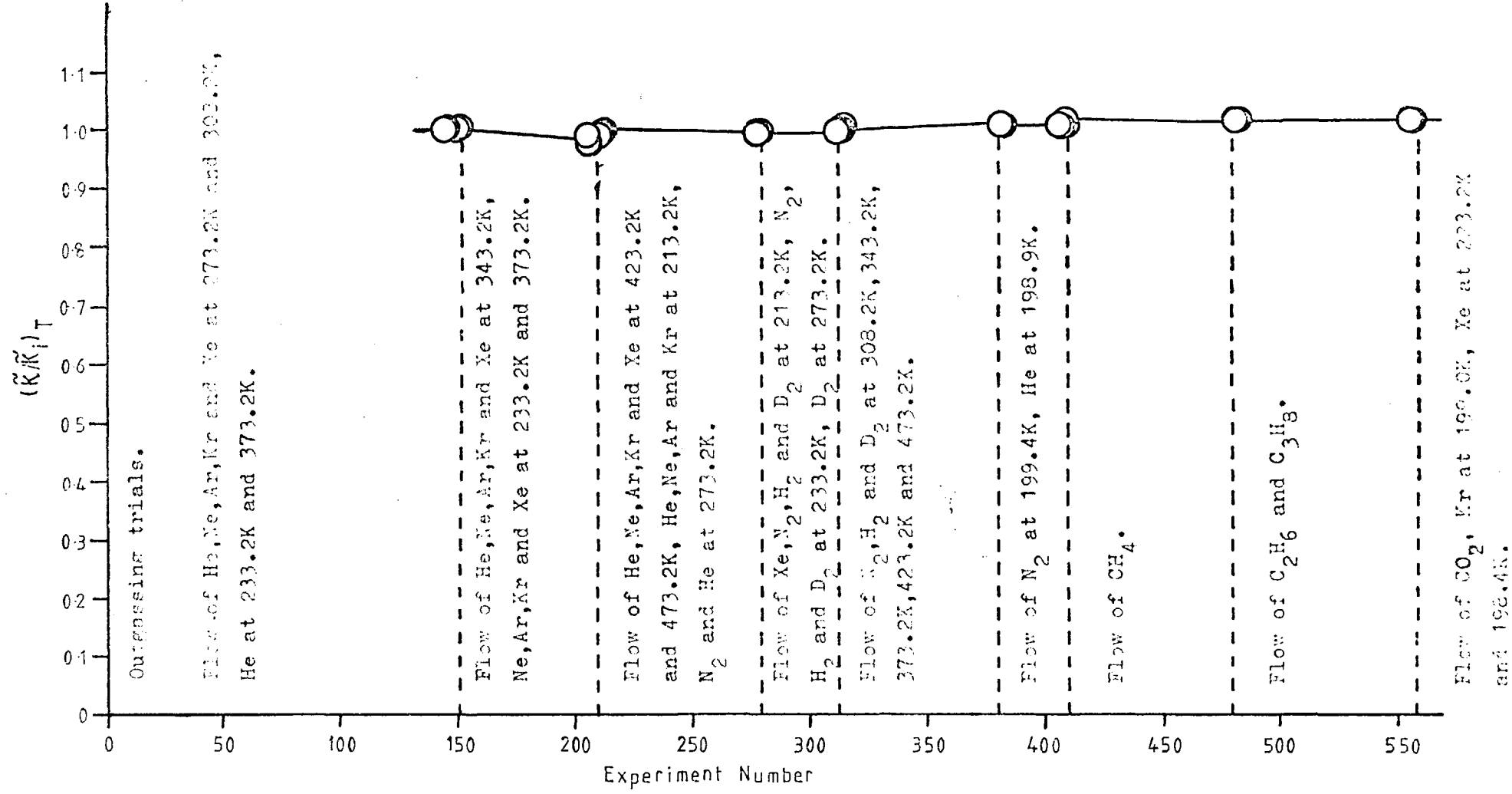


Figure 4.19. Typical Plots of p_L versus t for Carbon Dioxide Flowing Through Sterling S Membrane 2: $T/K = 373.2$

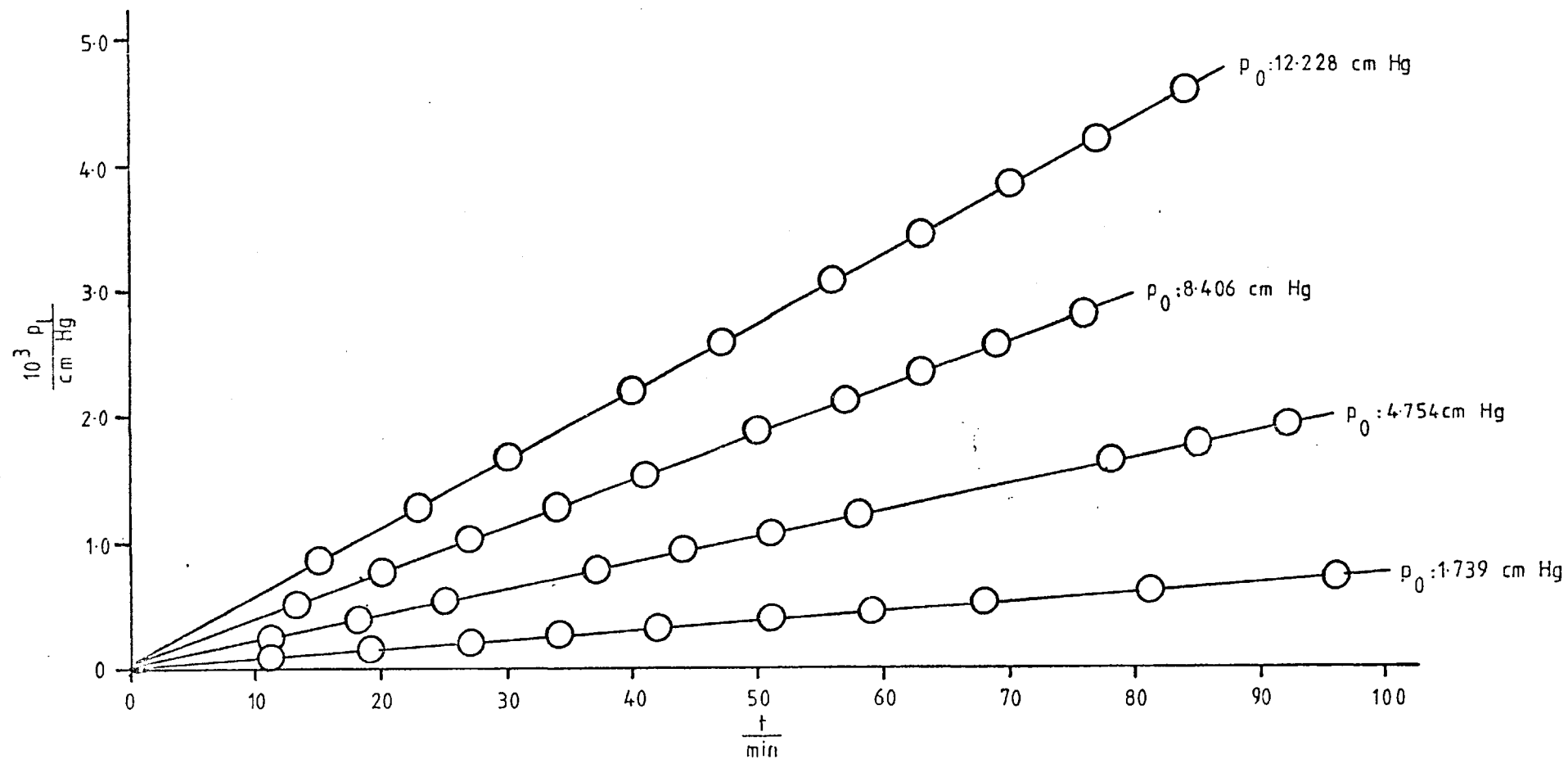


Figure 4.20. Variation of Helium Flow Rate through Membrane 2
as a Function of Pressure.

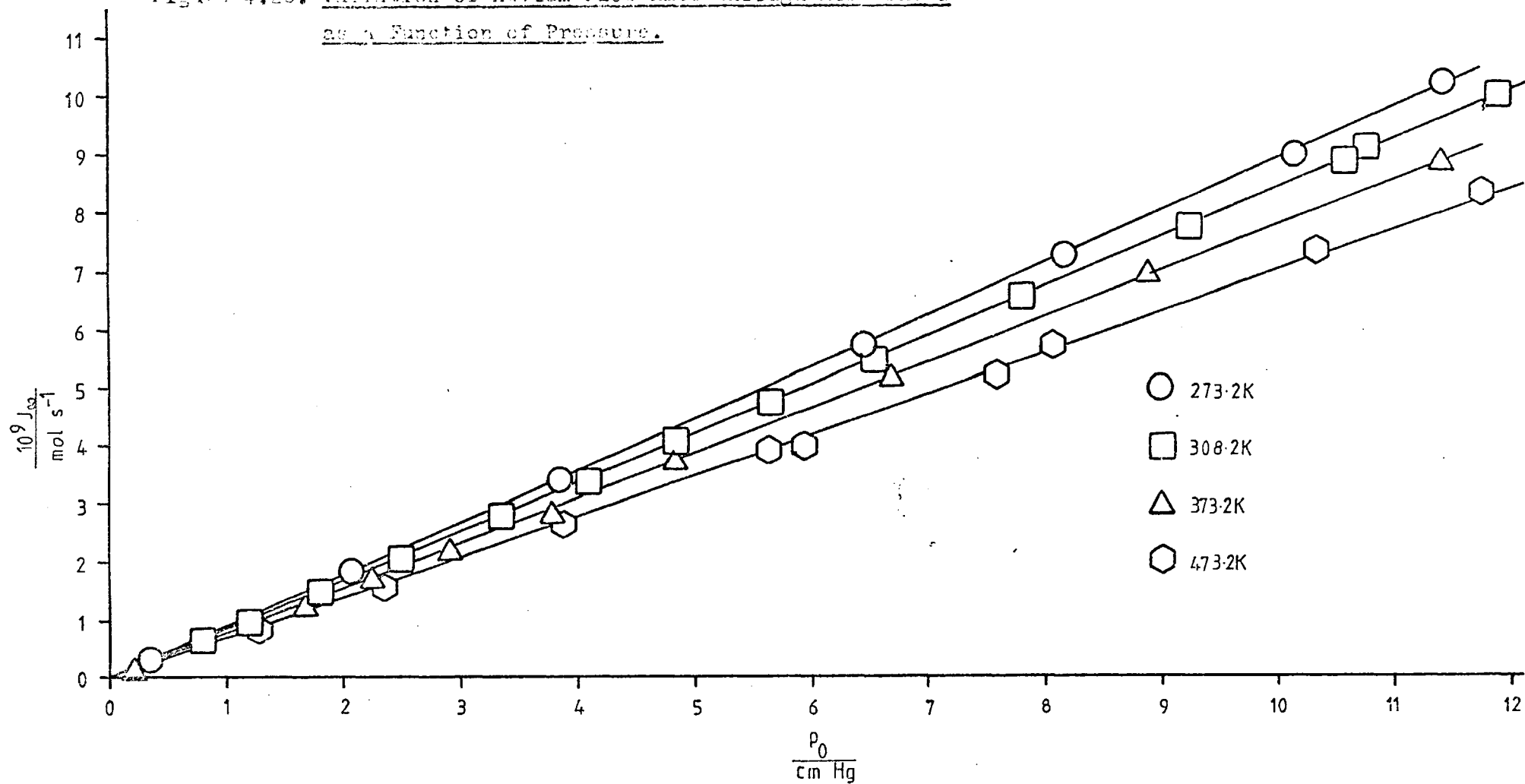
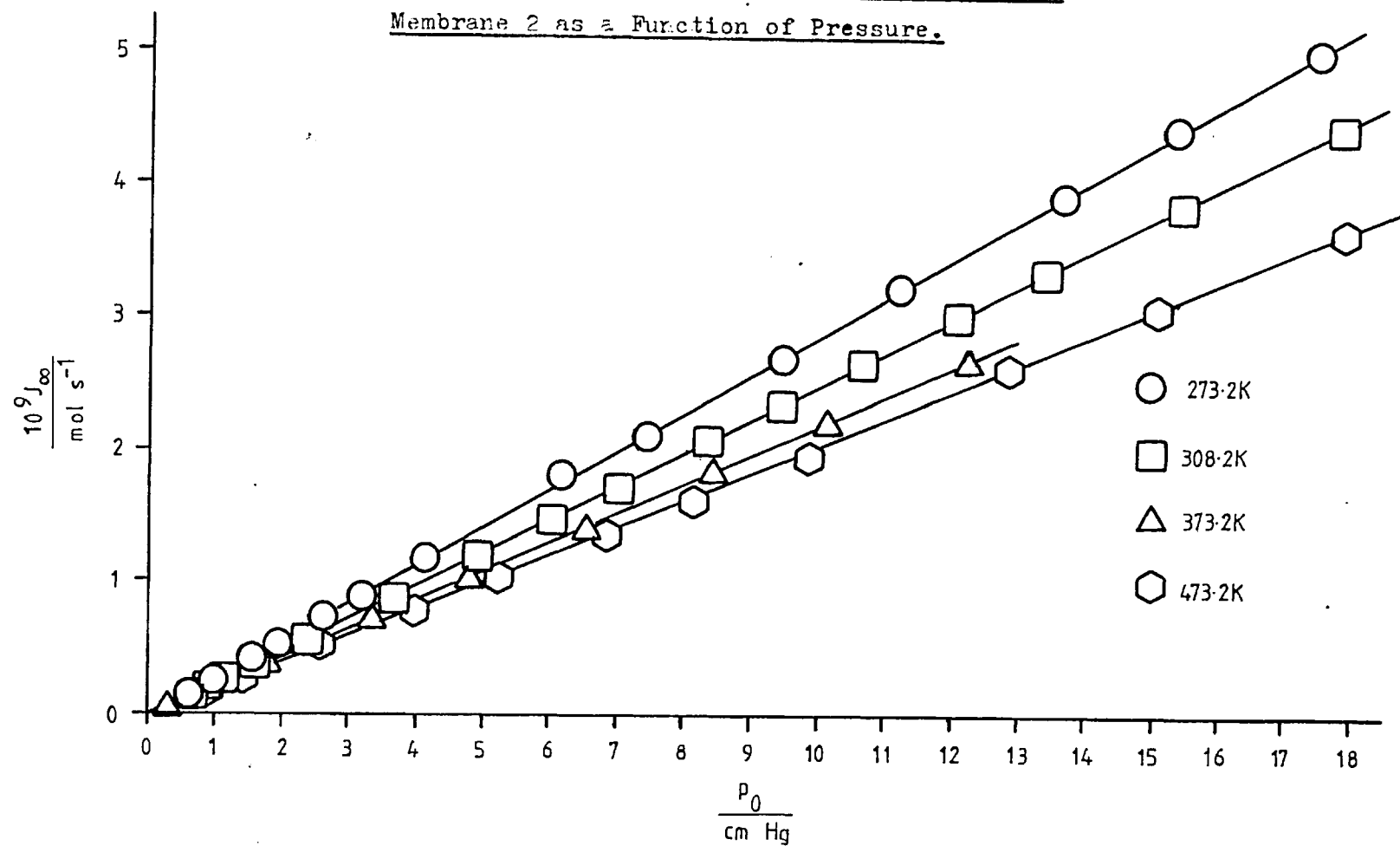


Figure 4.21. Variation of Carbon Dioxide Flow Rate through Membrane 2 as a Function of Pressure.



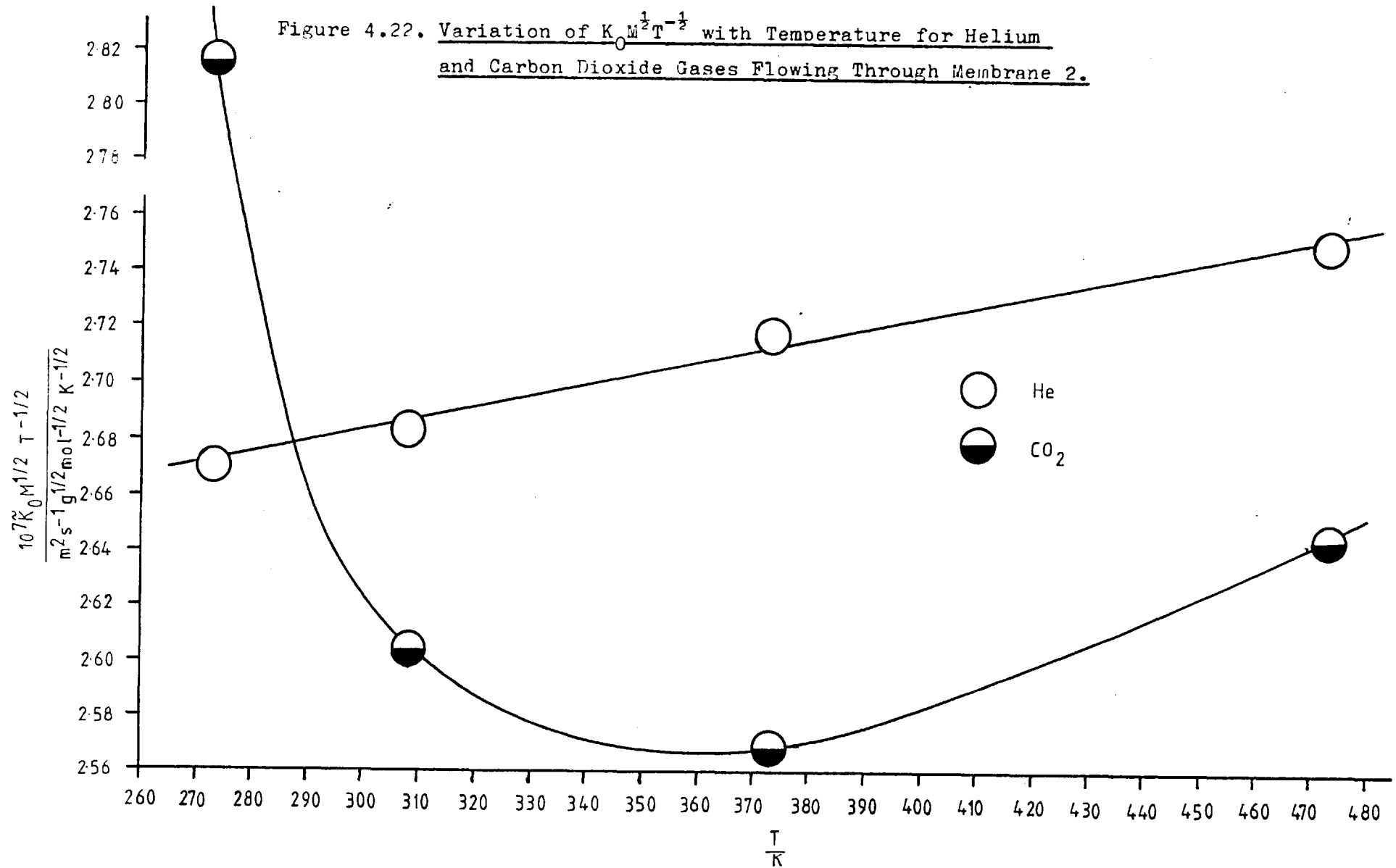
4.4.3 Effect of Membrane Temperature.

The limiting permeabilities were obtained from the slopes of graphs of J_{∞} versus pressure (table 4.4). Figure 4.22 is a plot of $\tilde{K}_0 M^{1/2} / T^{1/2}$ for the two gases against membrane temperature. As with membrane 1 $\tilde{K}_0 M^{1/2} / T^{1/2}$ for helium increases with increasing temperature. Carbon dioxide on the other hand shows a temperature minimum, it is also interesting to note that $\tilde{K}_0 M^{1/2} / T^{1/2}$ for carbon dioxide is less than the value for helium over much of the temperature range.

Table 4.4. Flow Results for Membrane 2.

Gas	T K	$\frac{10^6 \tilde{K}_0}{\text{m}^2 \text{s}^{-1}}$	$\frac{10^7 \tilde{K}_0 T^{-1/2}}{\text{m}^2 \text{s}^{-1} \text{K}^{-1/2}}$	$\frac{10^7 \tilde{K}_0 M^{1/2} T^{-1/2}}{\text{m}^2 \text{s}^{-1} \text{g}^{1/2} \text{mol}^{-1/2} \text{K}^{-1/2}}$
Helium	473.2	2.99 ₂	1.37 ₅	2.75 ₁
	373.2	2.62 ₄	1.35 ₈	2.71 ₈
	308.2	2.35 ₅	1.34 ₁	2.68 ₃
	273.2	2.20 ₆	1.33 ₅	2.67 ₀
Carbon Dioxide	473.2	0.867	0.399	2.65
	373.2	0.748	0.387	2.57
	308.2	0.689	0.392	2.60
	273.2	0.702	0.425	2.82

Figure 4.22. Variation of $K_0 M^{1/2} T^{-1/2}$ with Temperature for Helium and Carbon Dioxide Gases Flowing Through Membrane 2.



CHAPTER 5

DISCUSSION OF RESULTS

5.1. SURFACE AREA RESULTS

The nitrogen-Sterling S isotherm (figure 4.1) was of type II in the B.D.D.T. classification (Brunauer, Deming, Deming and Teller, 1940) with a sharp knee. This type of isotherm is well suited to B.E.T. analysis. The high value of C found here is indicative of localized monolayer formation (Sing, 1973) and under such circumstances the exact value of the average area occupied by the adsorbate molecule, a_m , will be dependent on the substrate structure. However, in this work nitrogen was used with $a_m = 1.62 \times 10^{-19} \text{ m}^2$ as a standard adsorbate. Pierce and Ewing (1964) however suggest $a_m(\text{N}_2) = 2.0 \times 10^{-19} \text{ m}^2$ to be more appropriate for graphites if localized adsorption occurs: the nitrogen molecules being attracted to all sites on the surface, but with slightly stronger attraction at the graphite ring centres, so that a close packing arrangement is not applicable. Electron-microscopic examination of graphitised carbon blacks has given higher values for the surface area than that calculated by the B.E.T. method using $a_m(\text{N}_2) = 1.62 \times 10^{-19} \text{ m}^2$. A value for $a_m(\text{N}_2)$ of $1.9 \times 10^{-19} \text{ m}^2$ is suggested (see Sing, 1973). Krypton and argon have also been used as adsorbents in B.E.T. surface area determinations using suitable values of a_m fixed by adsorption measurements on materials with a known geometric area (Sing, 1973). The value of $a_m(\text{N}_2) = 1.62 \times 10^{-19} \text{ m}^2$ was chosen since it is a value often quoted in the literature and so is useful for comparison purposes, and there is no direct evidence suggesting an alternative value of $a_m(\text{N}_2)$ for this particular graphitised carbon.

Little meaning can be attributed to the absolute value of C obtained in this work, in view of the large experimental uncertainty (section 3.6); it is sufficient to say that C is large (i.e. $>10^4$). The large value of C is associated with a large difference in the average life-time of an adsorbate molecule in the first layer and the average

life-time in second and higher levels. The average life-time being larger in the first adsorbate layer than in higher layers (Gregg and Sing, 1967, chapter 2).

The simple B.E.T. theory assumes that the surface is energetically uniform. This is a reasonable assumption for a homogeneous graphitised carbon. The theory only takes into account interactions acting normal to the surface. Yet lateral molecule-molecule interactions cannot remain negligible at higher coverages, where the average separation of adsorbate molecules is less than a single diameter, (Gregg and Sing, 1967). Neglecting lateral interactions is in contradiction to the postulate that the heat of adsorption in the higher layers is equal to the latent heat of condensation of the bulk liquid. The postulate that all sorbate molecules in layers other than the first have liquid-like evaporation-condensation properties has also been criticised, (Barrer, MacKenzie and MacLeod, 1952). It is reasonable that the adsorption potential diminished as the distance from the surface increases. Barrer, MacKenzie and MacLeod (1952) modify the B.E.T. isotherm by making molecules more and more volatile the higher the layer. The assumption that the number of adsorbed layers become infinite when the saturated vapour pressure is reached is also doubtful in many cases (Gregg and Sing, 1967).

Despite all the limitations of the B.E.T. theory it is useful in a qualitative sense in that type II and type III isotherms can be described. The B.E.T. analysis has been widely applied to type II isotherm, but the B.E.T. area should not be calculated from a type III isotherm (Gregg and Sing, 1967 pp93 et seq; Sing, 1973).

It is pertinent to compare the surface area, A_{BET} , found in this work for Sterling S with other values found in the literature. Comparison can also be made with the surface area of other carbons used in permeability studies. There have been a few determinations of the surface area of Sterling S in either the ungraphitised or the graphitised form (Beebe, Biscoe, Smith and Wendell, 1947; Schaeffer, Smith and Polley, 1953; Cabot Corporation Technical data sheet, 1965).

The literature values of A_{BET} are summarized in table 5.1.

Table 5.1 Surface Area of Sterling S from B.E.T.

N_2 Isotherms - a_m $1.62 \times 10^{-19} \text{ m}^2$

Nature of Sterling S	A_{BET} $10^4 \text{ m}^2 \text{ kg}^{-1}$	Reference
Ungraphitised	2.4	Beebe, Biscoe, Smith and Wendell (1947)
	2.7	Schaeffer, Smith and Polley (1953)
Graphitised (after heat treatment at 2700°C)	2.5	Schaeffer, Smith and Polley (1953)
	2.37	Cabot Corporation Technical data sheet (1965)
	2.22	This work

A_{BET} as measured in this work is somewhat smaller than other literature values, it is about 13% lower than the highest value of A_{BET} for graphitised Sterling S as measured by Schaeffer et al. It is not surprising that there should be differences in the values of A_{BET} if different batches of Sterling S are used. The value of A_{BET} obtained in this work is as good as any other value for another batch of the same substance and so is used in any calculations requiring knowledge of the surface area. It is interesting to see from the results of Schaeffer, Smith and Polley (1953) that the surface area decreases on graphitisation from 27,000 to 25,000 $\text{m}^2 \text{ kg}^{-1}$. Other results of this group of workers (Polley, Schaeffer and Smith, 1953) with a carbon black designated Sterling R

(a carbon which appears to be similar Sterling S) also shows this effect. The value of A_{BET} decreases from 27,900 to 24,900 m^2kg^{-1} after heat treatment at 2700°C . This is due to various structural changes which lead to an increase in homogeneity or graphitisation (see section 2.9).

It would have been useful if the adsorption isotherm could have been measured directly on the membranes, rather than on the free-powder. This could not be done because of the small quantities of carbon used in the manufacture of the membranes.

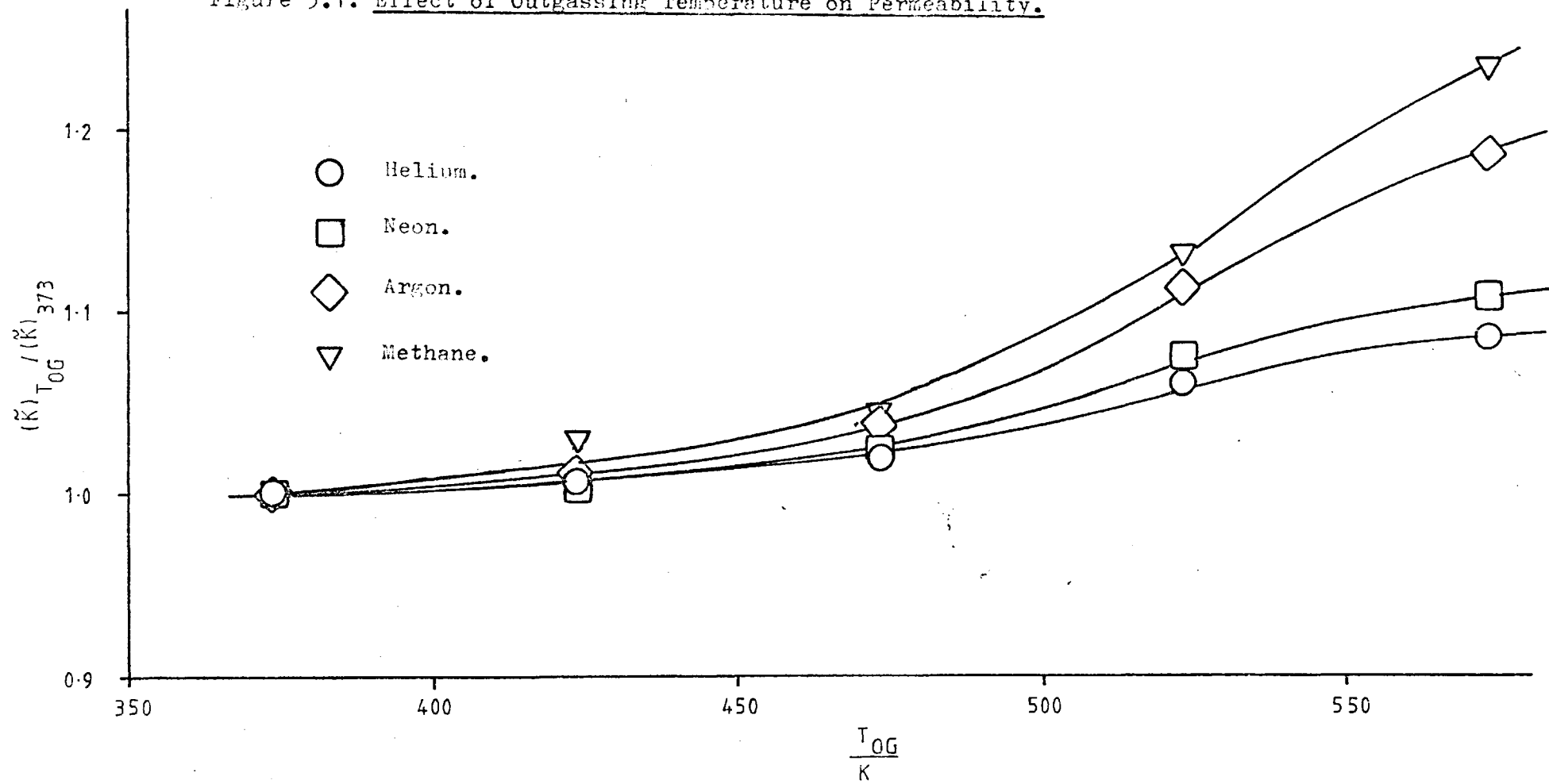
Table 5.2 shows the surface area of various other carbons which have been used in permeability studies.

Table 5.2. Surface Areas of Various Carbons from B.E.T.
 N_2 Isotherms - a_m $1.62 \times 10^{-19} \text{m}^2$

Adsorbent	$\frac{A_{\text{BET}}}{10^4 \text{m}^2\text{kg}^{-1}}$	Reference
Carbolac I	95.0	Ash, Barrer and Lowson (1973)
Black Pearls	21.16	Cabot Technical data sheet (1965)
Graphon	8.97	Cabot Technical data sheet (1965)
Sterling S	2.22	This work

Carbolac I is an ungraphitised carbon black, whereas Black Pearls, Graphon and Sterling S are all graphitised carbons. The high surface area of Carbolac I has been attributed to micropores contained within individual particles (Ash, Barrer and Lowson, 1973). As the surface area decreases the more homogeneous the surface becomes. Sterling S has a surface area which is about a quarter the surface area of Graphon, previously the carbon with the highest degree of homogeneity of those used by the school of Ash and Barrer for flow studies.

Figure 5.1. Effect of Outgassing Temperature on Permeability.



5.2. HELIUM DENSITY MEASUREMENTS.

There is some evidence for the adsorption of helium by some carbons at room temperature (Maggs, Schwabe and Williams, 1960; Kini and Stacy, 1963). Such an effect would lead to a helium density, d_{He} , higher than the true density of the carbon. As Kini and Stacey (1963) point out adsorption would be expected to increase with increasing surface area. The surface area of Sterling S is smaller than other carbon blacks used in flow studies (table 5.2) and so any error in d_{He} should also be smaller. In any case direct measurement of the adsorption of helium on carbon blacks at liquid nitrogen temperature by Steele and Halsey (1954; 1955) showed that even at this temperature adsorption was small.

Another source of inaccuracy which leads to low value of d_{He} is due to the fact that the helium atom is unable to approach closer to the surface of the material than the collision radius (Steele and Halsey, 1954; Kini and Stacy, 1963). For Sterling S the effect of a finite collision radius is small ($< 1\%$).

The mean value for $d_{\text{He}} = 2080 \text{ kg m}^{-3}$ was taken since the 3% variation of the four values of d_{He} was not large enough to show any clear dependence on outgassing temperature. The value obtained in this work is about 4% lower than the value quoted by the Cabot Corporation (1965) of $d_{\text{He}} = 2160 \text{ kg m}^{-3}$. The value from this work was used in any calculation requiring a knowledge of d_{He} .

5.3. FLOW RESULTS FOR MEMBRANE 1

5.3.1. Outgassing Trials

Referring to figure 4.4. and table 4.2 it is clear that the permeability of each of the four gases increases as the outgassing temperature, T_{OG} is increased. Figure 5.1 shows the enhancement of $\tilde{K}$ as a result of increasing the outgassing temperature. The permeability of helium after outgassing at 573K is almost 9% greater than its value after outgassing at 373K. In the case of neon, argon and methane the increases are 11%, 19% and 24% respectively. The effect seems to be

greater as the sorbability of the permeating gas increases. This would seem to imply that the permeability changes are associated with changes in the surface of the carbon black. The enhancement of permeability is also in order of increasing molecule size, suggesting that the passage of the larger molecules through the membrane is restricted by blockage or partial blockage of channels. The blockages being caused by volatile contaminants such as grease, components of which are removed as the outgassing temperature is increased. Removal of impurities will also bring about changes in the nature of the surface. The permeability enhancement is probably brought about by a combination of the two effects.

At outgassing temperatures of 523K or less $\tilde{K}M^{\frac{1}{2}}$ for both argon and methane are less than the corresponding value for helium (table 4.2), implying negative extra flow. This is an unexpected result since if it is assumed that helium is a non adsorbed gas and that argon and methane are adsorbed gases, then on the basis of previous work with other carbons (for example Ash, Barrer, Clint, Dolphin and Murray, 1973) it would be expected that $\tilde{K}M^{\frac{1}{2}}$ for argon and methane to be greater than that of helium at any given temperature. Argon and methane would be expected to show extra flow associated with adsorption.

Ash, Barrer and Pope (1963 (a)) also found that $\tilde{K}$ for helium diffusing through a Carbolac 1 membrane increased with increasing outgassing temperature.

5.3.2. Variation of Helium Permeability with Time.

The consistency in the values of $(\tilde{K}/\tilde{K}_i)$ as demonstrated by figure 4.18 indicates that no significant irreversible ageing of the membrane occurred over the three years of the experimental study. The greatest variation from unity was about 2.6% which occurred for experiment 207. The overall variation which was generally less than 1.5% has been explained by condensation of mercury, on or in the sorbent (Ash, Barrer and Lowson, 1970). This phenomena was minimized by regular outgassing at 573K. The ratio $(\tilde{K}/\tilde{K}_i)_T$ was plotted rather than

$\tilde{K}/T^{\frac{1}{2}}$ (Hamilton, 1980) or $\tilde{K}M^{\frac{1}{2}}/T^{\frac{1}{2}}$ (Ash, Barrer and Lowson, 1970) because of the variation of $\tilde{K}/T^{\frac{1}{2}}$ with temperature, which had not been appreciated at the beginning of the series of helium permeability checks. However all such checks subsequent to experiment 381 were performed at 308.2K, which was also the membrane temperature at which the early experiments had been made. The greatest discerned variation after that experiment was 1.5%.

The Carbolac used by Sharma (Ash, Barrer and Sharma, 1976) showed an increase in helium permeability after experiments involving strong adsorption. This was not the case with the membrane used in this study after flow experiments with hydrocarbons such as propane. Similarly the Graphon and the Black Pearls membranes used by Hamilton (1980) exhibited no variation of helium permeability after flow experiments with propane and iso-butane.

5.3.3. Effect of Pressure.

A commonly accepted criterion for Knudsen flow is that the mean free path, λ , of the flowing gas should be greater than $10d$ (Murray, 1976), where d is an averaged pore diameter based on the hydraulic radius, r_h ($d = 2r_h$) of the membrane. In the case of membrane 1, λ should be more than 9.58×10^{-7} m and for membrane 2, λ should be greater than 4.10×10^{-7} m. Under such conditions it would be expected that the number of molecule-wall collisions would greatly exceed the number of molecule-molecule collisions. It should be stressed that this criterion for Knudsen flow is somewhat arbitrary; there is nothing magic about the factor 10, and for the purposes of this work, $\lambda = \lambda_0$ the mean free path corresponding to the ingoing pressure p_0 of the flowing gas. The mean free path can be calculated using the equation

$$\lambda_0 = \frac{kT}{2^{\frac{1}{2}} \pi (r^*)^2 p_0} \quad (5.1)$$

Where k is the Boltzmann constant and r^* is the equilibrium distance between two interacting molecules or atoms (defined

by equation 2.87). As used in equation 5.1, r^* is better described as the collision diameter of the molecule. The quantity r^* can be obtained from values of r_0 (tabulated by Hirschfelder, Curtiss and Bird, 1964, p.1110) using the equation

$$r^* = 2^{1/6} r_0 \quad (5.2)$$

where r_0 is the separation distance corresponding to zero potential energy (see section 2.7). Table 5.3 gives values of p_0 corresponding to $\lambda_0 = 10d$ for the worst (lowest temperature) case for each gas employed in studies with membrane 1.

Table 5.3. Ingoing Pressures, p_0 , Corresponding to
 $\lambda_0 = 10d$ for Membrane 1.

Gas	$\frac{10^{10} r^*}{\text{m}}$	$\frac{T}{\text{K}}$	$\frac{p_0}{\text{cm Hg}}$
He	2.891	198.9	5.79
Ne	3.131	213.2	5.29
Ar	3.837	213.2	3.52
Kr	4.052	199.0	2.95
Xe	4.552	198.4	2.33
H ₂	3.331	213.2	4.68
D ₂	3.309	213.2	4.74
N ₂	4.132	199.4	2.84
CO ₂	4.485	199.3	2.41
CH ₄	4.290	213.2	2.82
C ₂ H ₆	4.959	233.2	2.31
C ₃ H ₈	5.681	253.2	1.91

Values of p_0 corresponding to $\lambda_0 = d$ are a factor of 10 greater than the values given in table 5.3. The figures in the table emphasize the importance of extrapolating the permeability values to zero pressure so as to be certain of flow occurring

in the Knudsen regime. Outside the Knudsen flow regime some form of pressure dependence would be predicted for the permeability (see for example equation 2.53). Despite the fact that the ingoing pressure of many of the gases studied are of a magnitude where a transition from one flow regime to another would be expected to occur, only xenon, ethane and propane show any clear dependence of the permeability on pressure (figures 4.7 - 4.12). Even these three gases only show the pressure dependence at low temperature (273.2K or less) within the pressure range studied. The remaining gases do not show pressure dependent permeabilities for low pressures (less than 7 cm Hg) at any temperature. At higher pressures there may be some increase in permeability (see the results for the inert gases at 308.2K in Appendix B and figures 4.5 and 4.6). The increases are small (less than 2%) and so should be treated with caution as this is of the same order as the experimental uncertainty.

The pressure dependence of xenon, ethane and propane permeabilities are rather unusual. Looking first at the xenon results. The nature of the pressure dependence at 213.2 K (figures 4.7 and 4.8) is not in itself startling, although the apparent independence at both higher and lower temperatures is unusual. Ash, Baker and Barrer (1967) also observed a diminishing $\tilde{K}$ with increasing pressure for the flow of argon through a Graphon membrane at 153.2 K; at 77.6 K the initial decrease was very great and followed a hyperbolic curve. Decreasing $\tilde{K}$ with increasing pressure has been observed for the flow of various alkane gases through Graphon membranes (Ash, Barrer, Clint, Dolphin and Murray, 1973; Ash, Barrer and Edge, 1976; Ash, Barrer, Chio and Edge, 1979). Hamilton (1980) has recorded permeability minima as a function of pressure. for the flow of propane and iso-butane through a Graphon and a Black Pearls membrane. Such minima have also been observed for the flow of sulphur dioxide (Pope, 1961). A number of other systems also exhibit permeability minima (Monroe and Gaffee, 1956; Lallemand and Eyraud, 1973; Rhim and Hwang, 1975)

although the boundary conditions were at variance with the boundary conditions used in this work. Nicholson and Sing (1979) attribute the initial decrease in permeability to pore blocking by the adsorbed molecules. There is, however, evidence for pore blocking even when $\tilde{K}$ is not pressure dependent (Hamilton, 1981; Ash and Hamilton, to be published). The comparatively open structure suggested by the large hydraulic radius of membrane 1 would indicate that blocking is unlikely to be the cause of the negative $d\tilde{K}/dp_0$ for xenon flowing through that membrane. It is intriguing that in spite of the pressure dependent permeability at 213.2K, the permeability is independent of pressure at 198.4K and 233.2K. On previous evidence the dependence of $\tilde{K}$ on pressure decreases with increasing temperature (Ash, Baker and Barrer, 1967; Ash Barrer, Clint, Dolphin and Murray, 1973). It may be that with this work the pressure dependent behaviour is masked at both the higher and lower temperature by experimental scatter, but even if this were the case the pressure dependence at 213.2K is greater than at 198.4K and 233.2K. There has been no other experimental work with carbon membranes which shows this effect. The phenomena closest to the behaviour observed here is shown in the work of Gilliland, Baddour and Russell, (1959) and Ash, Barrer and Coughlan (1972). For the flow of propene through Vycor porous glass (Gilliland, Baddour and Russell, 1959) the permeability plotted as a function of pressure showed an increase in permeability with pressure at 313.2K, a decrease at 298.2K and a permeability maximum at low pressure at 273.2K. It should be stressed that although the work of Gilliland and his coworkers is a steady-state flow study, the boundary conditions are different to those used in the work (Section 2.1) Ash, Barrer and Coughlan (1972) studied the flow of a number of gases through a compacted membrane made from hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) powder. If the plots of permeability versus pressure are considered (figure 5.2 and figure 4 of the reference) helium shows a minimum in the permeability at 303.2K, 273.2K and 233.2K, but at 77.4K the helium results

appear to show a maximum followed by a minimum. The neon results show a low pressure minimum at 303.2K and 273.2K. At 233.2K the neon permeability seems to show only a small pressure dependence before beginning to increase linearly as a function of pressure. Ash, Barrer and Coughlan (1972) interpret their results in terms of equation 2.53 under conditions where $p_0 \gg p_1$

$$\begin{aligned} \tilde{K} = & \frac{\epsilon^3 \kappa_p}{2 A^2 n} p_0 + \frac{2\pi \epsilon^2 \kappa_c}{3 A} \left(\frac{2 RT}{M\phi} \right)^{\frac{1}{2}} \\ & + \frac{2\epsilon \eta}{3 p_0} \left(\frac{RT}{M\phi} \right) \left(\kappa_k - \frac{\pi}{4} \kappa_c \right) \\ & \cdot \ln \left(1 + \frac{4\epsilon}{A} \frac{1}{\eta} \left(\frac{2 M\phi}{\pi RT} \right)^{\frac{1}{2}} p_0 \right) \end{aligned} \quad (5.3)$$

These results may provide a clue to what is happening in the present work for the flow of xenon. At 198.4K there may be a broad maximum or a plateau occurring in the pressure range studied and if the work were extended to higher pressures this would become apparent. At the present this is speculation however.

The permeability of ethane increases as the ingoing pressure increases at 253.2K and 233.2K, as does the permeability of propane at 273.2K. The permeability of propane at 253.2K shows a pressure maximum. A permeability maximum as a function of pressure, at low pressures, is unusual, but not unknown. The results of Gilliland, Baddour and Russell, (1959) and Ash, Barrer and Coughlan (1972) have already been pointed out. A number of other systems also demonstrate this behaviour; argon and oxygen through porous ceramic (Lallemant and Eyraud, 1973); isobutane through Graphon (Ash, Barrer and Edge, to be published). Ammonia shows a permeability maximum when flowing through a compacted Carbolac membrane (Ash, Barrer and Lowson, 1973). The ammonia results were explained in terms of swelling of the membrane. Ammonia

Figure 5.3. Plot of Equation 5.3 using $K_D = 0$, $K_K = 1.0$
and Data for Propane at 253.2K.

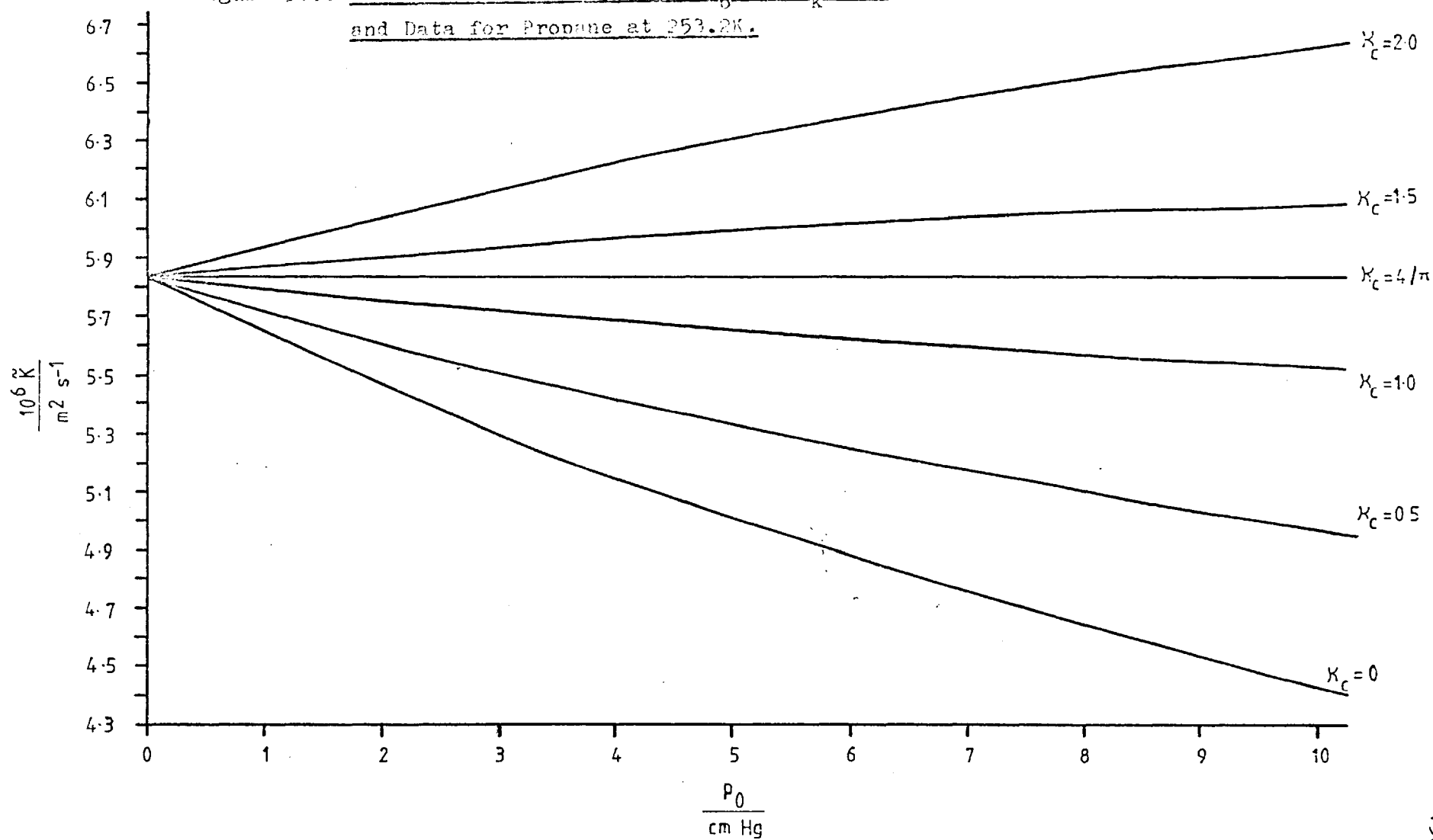


Figure 5.4. Plot of Equation 5.3 using $K_p = 5.0$, $K_k = 1.0$
and Data for Propane at 253.2K.

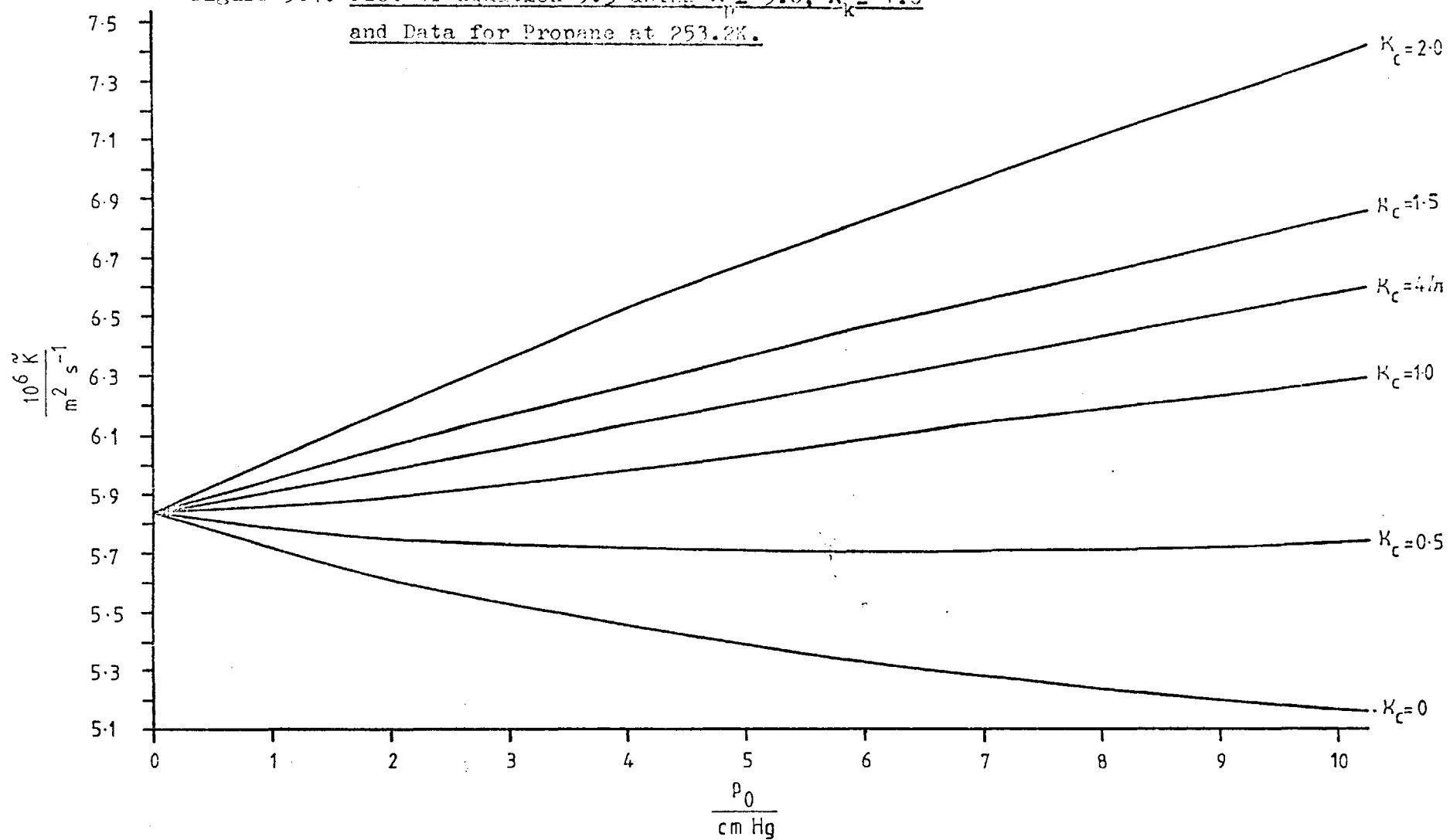
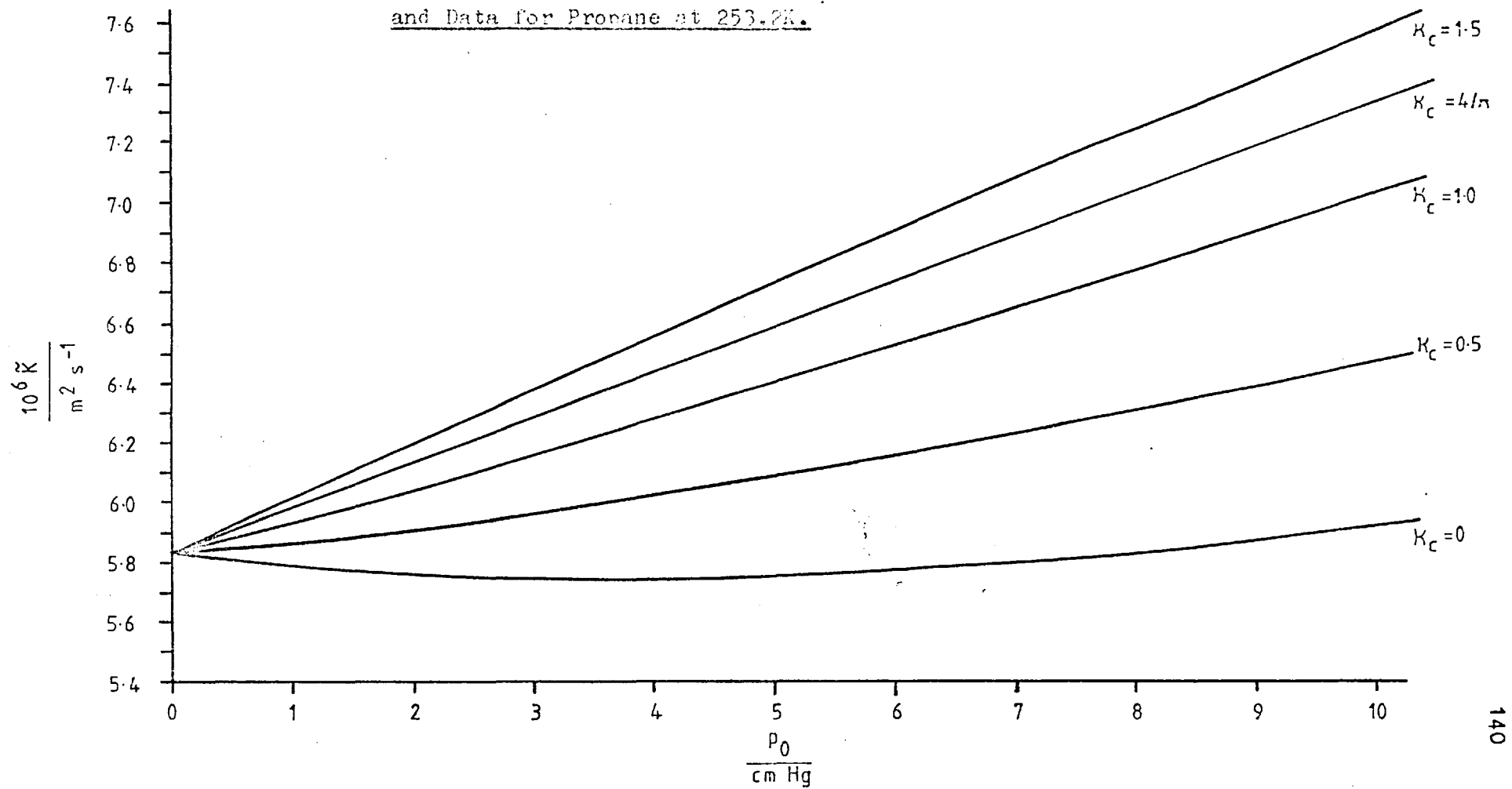


Figure 5.5. Plot of Equation 5.3 using $K_p = 10.0$, $K_v = 1.0$
and Data for Propane at 253.2K.



condensing in the micropores within the Carbolac particles was suggested to swell the particles sufficiently to reduce the flow, by partially choking some of the flow paths. This occurred in the region where capillary condensation was taking place. So the swelling effect is unlikely to be the cause of the permeability maximum for this propane - Sterling S system.

In view of the pressure dependent permeabilities observed in this work it may be instructive to do some calculations using equation 5.3 employing various values for the structure factors; χ_k , χ_p and χ_c and values for the physical constants applicable to propane at 253.2K. A value of 6.7×10^{-6} Pa s was used for the propane viscosity; this quantity was obtained by extrapolating the viscosity data of Kestin, Kholifa and Wakeham (1977). The results of the calculations are given in figures 5.3 - 5.5. It is clear that the equation can be used to predict an initial decrease in permeability with increasing pressure, a permeability minimum or flattening and an increase in permeability with pressure. As pointed out by Ash, Barrer and Coughlan positive values of $(\chi_k - (\pi/4) \chi_c)$ lead to minima or flattening of the $\tilde{K}$ versus p_0 curve, whereas negative values of $(\chi_k - (\pi/4) \chi_c)$ produce a downward curvature. The curves are asymptotic to a line parallel to the line given by $\chi_c = (4/\pi) \chi_k$ (shown by the lines given by $\chi_c = 4/\pi$ in figure 5.3 - 5.5). The intercept of the asymptote is

$$\tilde{K}_c = \frac{2\pi\epsilon^2}{3A} \chi_c \left(\frac{2RT}{\pi M\phi} \right)^{\frac{1}{2}} \quad (5.4)$$

and the gradient is

$$\frac{\tilde{K}_p}{p_0} = \frac{\epsilon^2 \chi_p}{4A^2 \eta} \quad (5.5)$$

Equation 5.3 cannot be used to represent a permeability maximum such as that observed with propane, at least with structure factors which are independent of pressure. The equation also cannot explain the pressure dependence of the xenon permeability,

where there is an apparent reduction in dependence between 213.2K and 198.4K. If it is assumed that the structure factors are independent of temperature a reduction in temperature will lead to a reduction in the gas viscosity and the gradient of the asymptotic line (equation 5.5) will increase.

The similarity of the value of $\tilde{K}_0$ derived by calculations using equation 5.3 ($5.84 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$) with a value of K_k 1 and the experimental value of $\tilde{K}_0$ for propane at 253.2K ($6.07 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$) is a coincidence. Although it is interesting that the two values are of the same order. Calculated values of $\tilde{K}_0$ will be proportional to $T^{\frac{1}{2}}$; the experimental values are not (see figure 4.16).

In summary the pressure dependence of the xenon and propane results cannot be explained by considering gas phase flow described by equation 5.3. The flow is complicated by the fact the flowing gas molecules interact with the pore walls so that molecule trajectories are not necessarily linear, and there are blocking effects due to adsorption of the diffusant.

5.3.4. Effect of Temperature.

The results cover a large number of gases; monatomic, diatomic and polyatomic; over a wide range of temperatures; 200K to 473K. Most previous studies of gas flow through porous carbon membrane deal with either a limited number of gases, or a restricted temperature range. The results presented here, therefore, lend themselves primarily to a study from the point of view of the effect of membrane temperature upon the flow.

Classical theory of gas flow through porous media predicts that $\tilde{K}$ (and hence $\tilde{K}_0$) should be proportional to $T^{\frac{1}{2}}$. From figures 4.13 - 4.16 it is obvious that none of the gases studied exhibit the aforementioned behaviour. Helium, hydrogen, deuterium and neon show decreasing $\tilde{K}_0 \text{ M}^{\frac{1}{2}} T^{-\frac{1}{2}}$ with decreasing temperature, xenon conversely shows increasing $\tilde{K}_0 \text{ M}^{\frac{1}{2}} T^{-\frac{1}{2}}$ with decreasing temperature. The remaining gases all show a minimum when $\tilde{K}_0 \text{ M}^{\frac{1}{2}} T^{-\frac{1}{2}}$ is plotted against T. The decrease in $\tilde{K}_0 \text{ M}^{\frac{1}{2}} T^{-\frac{1}{2}}$ with increasing temperature is well known (Ash, Barrer, Clint, Dolphin and Murray, 1973). $d(\tilde{K}_0 \text{ M}^{\frac{1}{2}} T^{-\frac{1}{2}})/dT$ also

decreases with rising temperature. The effect has even been observed for the flow of helium, through a Graphon and a Black Pearls membrane, at low temperatures (Ash, Baker and Barrer, 1967) and at higher temperatures (Horiguchi, Hudgins and Silveston, 1971). In the past this temperature dependence of $\tilde{K}_0 M^{\frac{1}{2}} T^{-\frac{1}{2}}$ has been interpreted in terms of an activated model for "surface diffusion" (for example: Carman and Raal, 1951; Barrer and Gabor, 1960; Ash, Barrer and Pope, 1963; Ash, Barrer, Clint, Dolphin and Murray, 1973; Gilliland, Baddour, Perkinson and Sladek, 1974). The steady state "surface" diffusion coefficient being given by

$$D_{ss} = D_{0s} \exp \left(- \frac{E_{ss}}{RT} \right) \quad (5.6)$$

where E_{ss} is the activation energy for "surface" diffusion and D_{0s} is a pre-exponential factor. D_{ss} is defined by equation 2.63 (b)

$$\frac{J_s}{A_c} = -D_{ss} \frac{d C_s}{d x} \quad (2.63(b))$$

A differential permeability corresponding to the extra flow can be defined

$$\frac{J_s}{A_c} = -K_s \frac{d C'_g}{d x} \quad (5.7)$$

K_s can be easily related to D_{ss} by equations 2.63 (b) and 5.7.

$$\begin{aligned} K_s &= D_{ss} \left(\frac{\partial C_s}{\partial C'_g} \right)_T \\ &= D_{ss} A \left(\frac{\partial C'_s}{\partial C'_g} \right)_T \end{aligned} \quad (5.8)$$

As the pressure tends to zero

$$K_s \rightarrow K_{s0} \quad \left(\frac{\partial C_s}{\partial C'_g} \right)_T \rightarrow k_s$$

where k_g is the Henry law constant which is related to temperature by an "Arrhenius type" equation

$$k_s = k_{Os} \exp \left(\frac{-\Delta E'}{RT} \right) \quad (5.9)$$

where $\Delta E'$ is an energy of adsorption defined by Ash, Barrer, Clint, Dolphin and Murray (1973). Combining equations 5.6, 5.8 and 5.9 .

$$K_{sO} = A k_{Os} \exp \left(\frac{-\Delta E'}{RT} \right) D_{Os} \exp \left(\frac{-E_{ss}}{RT} \right) \quad (5.10)$$

If $\Delta E' + E_{ss} = E'_{ss}$ and $A k_{Os} D_{Os} = K_{Os}$

$$K_{sO} = K_{Os} \exp \left(\frac{-E'_{ss}}{RT} \right) \quad (5.11)$$

In the work of Ash, Barrer, Clint, Dolphin and Murray (1973) with Carbolac and Graphon membranes $\Delta E'$ is negative E_{ss} is positive and $(-E_{ss}/\Delta E')$ is less than unity, hence E'_{ss} must be a negative quantity and K_{sO} will increase as the temperature decreases

$$\tilde{K}_O = K_O = K_{gO} + K_{sO} \quad (5.12)$$

Substituting for K_{sO}

$$K_O = K_{gO} + K_{Os} \exp \left(\frac{-E'_{ss}}{RT} \right) \quad (5.13)$$

Hence

$$\tilde{K}_O \left(\frac{M}{T} \right)^{\frac{1}{2}} = K_{gO} \left(\frac{M}{T} \right)^{\frac{1}{2}} + K_{Os} \left(\frac{M}{T} \right)^{\frac{1}{2}} \exp \left(\frac{-E'_{ss}}{RT} \right) \quad (5.14)$$

$K_{gO} (M/T)^{\frac{1}{2}}$ is determined by taking the value of $\tilde{K}_O (M/T)^{\frac{1}{2}}$ for helium gas which is taken to be non-adsorbed and hence constant. It is clear from the helium results of this work (figures 4.13 - 4.16) that this quantity is not constant. At some temperatures if the value for helium were subtracted from $\tilde{K}_O (M/T)^{\frac{1}{2}}$ for hydrogen, deuterium, nitrogen, carbon dioxide, ethane or propane at the same temperature a negative value of $K_{sO} (M/T)^{\frac{1}{2}}$

would be obtained which cannot be given by the activated diffusion model since K_{Os} is to be positive. Equation 5.14 also cannot predict a minimum in a plot of $\tilde{K}_0(M/T)^{\frac{1}{2}}$ versus T . The activated diffusion model is hence not applicable for this work. Ash, Barrer, Clint, Dolphin and Murray (1973) have split the extra flow into two parts: that part which through any cross-section normal to x is entirely in the surface and that part in which molecules are in the gas phase (some gas molecules make evaporative flights). They have defined two corresponding diffusion coefficients obeying an equation similar to equation 5.6. The modified equation still cannot be used to explain all the features of the experimental results.

There are few other experimental studies which show a permeability minimum with temperature as observed in this work. The most important work is perhaps that of Hwang and Kammermeyer (1966 (a,b); 1967) whose results show minima for a number of gases, including helium. Also, as with this work, the helium calibration method will lead to negative extra permeabilities for some of the gases. $\tilde{K} (M/T)^{\frac{1}{2}}$ versus temperature for carbon dioxide through magnesium chromite membrane shows a minimum (Ciosmak-Galland and Delafosse, 1977); indeed, as the temperature decreases the value of $\tilde{K} (M/T)^{\frac{1}{2}}$ increases to a maximum, then drops to a minimum and then rises steadily with decreasing temperature. This latter group of workers also observed a decrease in $\tilde{K} (M/T)^{\frac{1}{2}}$ with decreasing temperature as has been observed with the present study. Ash, Barrer and Lowson (1970) looking at the flow of helium through a Graphon compacted membrane noted a 3% decrease of $\tilde{K} (M/T)^{\frac{1}{2}}$ between 573K and 78K. In this work the decrease between 473K and 199K is 8% of the value at 473K.

Hwang and Kammermeyer (1966 (a)) interpreted their results using equation 2.69 derived using transition state theory. It is interesting to apply equation 2.69 to the results of this present work. Writing equation 2.69 in the form

$$\tilde{K}_0 \left(\frac{M}{T} \right)^{\frac{1}{2}} = A + BT \exp \left(\frac{\Delta}{T} \right) \quad (5.15)$$

where A is a geometry constant for a given porous membrane and B and Δ are constants for a particular combination of gas and porous medium. Following the method of Hwang and Kammermeyer (1966 (a)) the calculation procedure was carried out using a CDC 6500 computer. A value of A was assumed and after rearrangement of equation 5.15 to give

$$\ln \left(\frac{\tilde{K}_0 (M/T)^{\frac{1}{2}} - A}{T} \right) = \ln B + \frac{\Delta}{T} \quad (5.16)$$

values of B and Δ were determined by the method of least mean squares for each of the gases in turn. The sum of squared errors for all the gases was calculated for the set of constants. A further value of A was assumed and the procedure was repeated until the sum of squared errors for all the gases was minimized. The results are summarized in table 5.4 together with the standard deviation, σ of $\tilde{K}_0 (M/T)^{\frac{1}{2}}$ for the various gases. Figures 5.6 to 5.8 show the fit of the experimental data to the lines calculated from the coefficients obtained from the computer programme. Hwang and Kammermeyer (1966 (a), (b), 1967) found a good correlation for the flow of a wide range of gases through Vycor porous glass and an equation of the form of equation 5.16. With this work although there appears to be a reasonable fit to equation 5.16 for the Noble gases (figure 5.6) and hydrogen and deuterium (figure 5.7). The correlations for the remaining gases are not so good, especially for carbon dioxide (figure 5.7) and ethane (figure 5.8). Both carbon dioxide and ethane show sharp minima when $\tilde{K}_0 (M/T)^{\frac{1}{2}}$ is plotted against temperature. The results emphasise the assertion made by Nicholson and Petropoulos (1973) that the validity of equations 2.69 and 5.15 is in doubt in the region of the minimum.

The flow behaviour of hydrogen and deuterium gases, when corrections have been made for differences in molecular mass, are similar. This has also been observed by Hwang and Kammermeyer (1966 (b)). It is also interesting to see that the Δ values for these two gases are negative. This would

Table 5.4. Values of A, B and Δ for Various Gases
Flowing through Sterling S Membrane 1.

$$A = 1.10_5 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} \text{ g}^{\frac{1}{2}} \text{ mol}^{-\frac{1}{2}} \text{ K}^{-\frac{1}{2}}$$

Gas	$10^{10} B$ $\text{m}^2 \text{ s}^{-1} \text{ g}^{\frac{1}{2}} \text{ mol}^{-\frac{1}{2}} \text{ K}^{-\frac{1}{2}}$	Δ $\bar{K}$	$10^6 \sigma$ $\text{m}^2 \text{ s}^{-1} \text{ g}^{\frac{1}{2}} \text{ mol}^{-\frac{1}{2}} \text{ K}^{-\frac{1}{2}}$
He	4.97	110	0.007
Ne	5.55	142	0.009
Ar	4.70	215	0.02
Kr	2.04	588	0.07
Xe	1.21	925	0.10
H ₂	7.79	-142	0.006
D ₂	9.18	-184	0.005
N ₂	5.31	119	0.02
CO ₂	0.89	537	0.05
CH ₄	3.25	340	0.04
C ₂ H ₆	0.38	948	0.07
C ₃ H ₈	0.11	1565	0.09

Figure 5.6. Correlation of Experimental Results for
the Noble Gases with Equation 5.16.

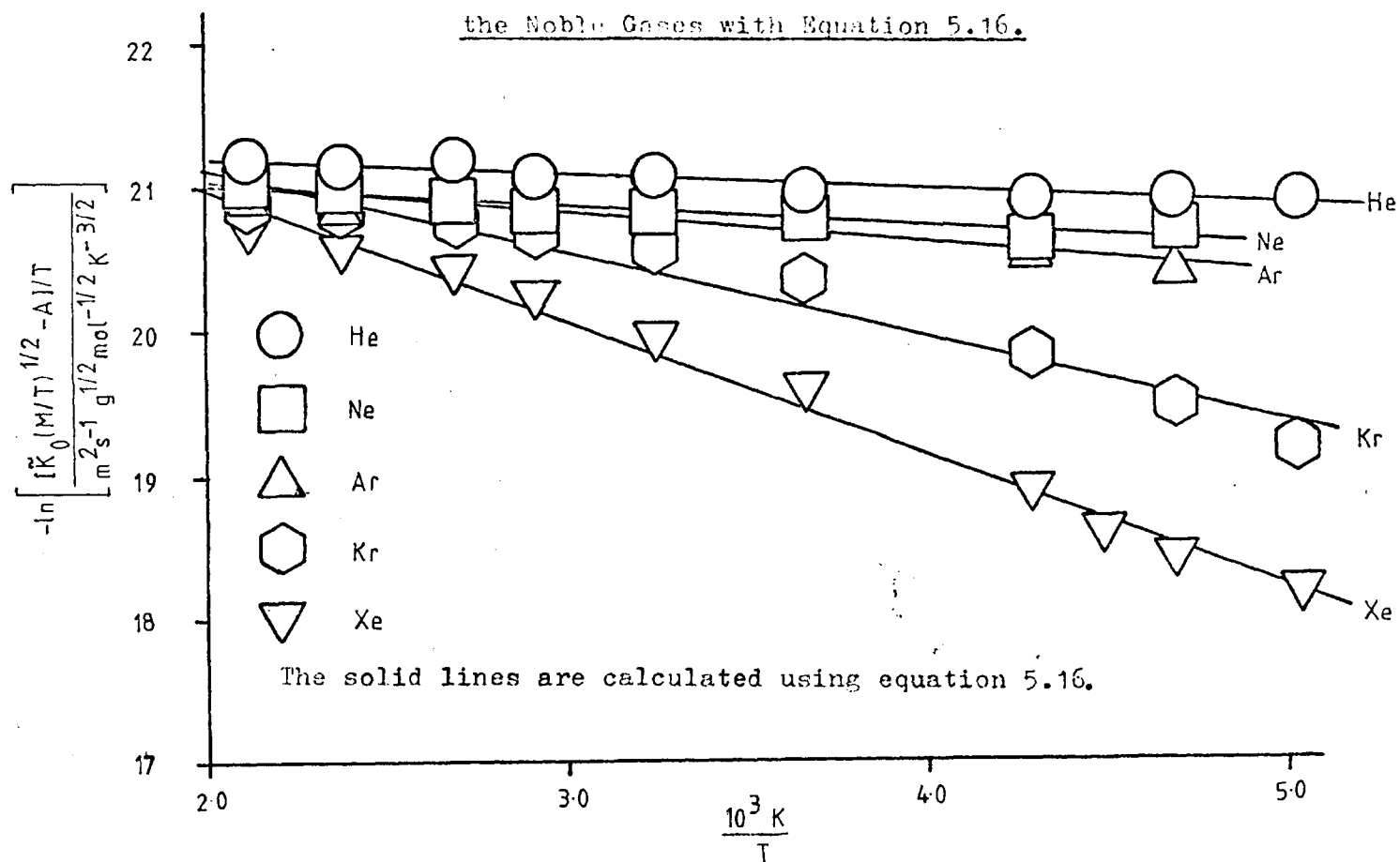
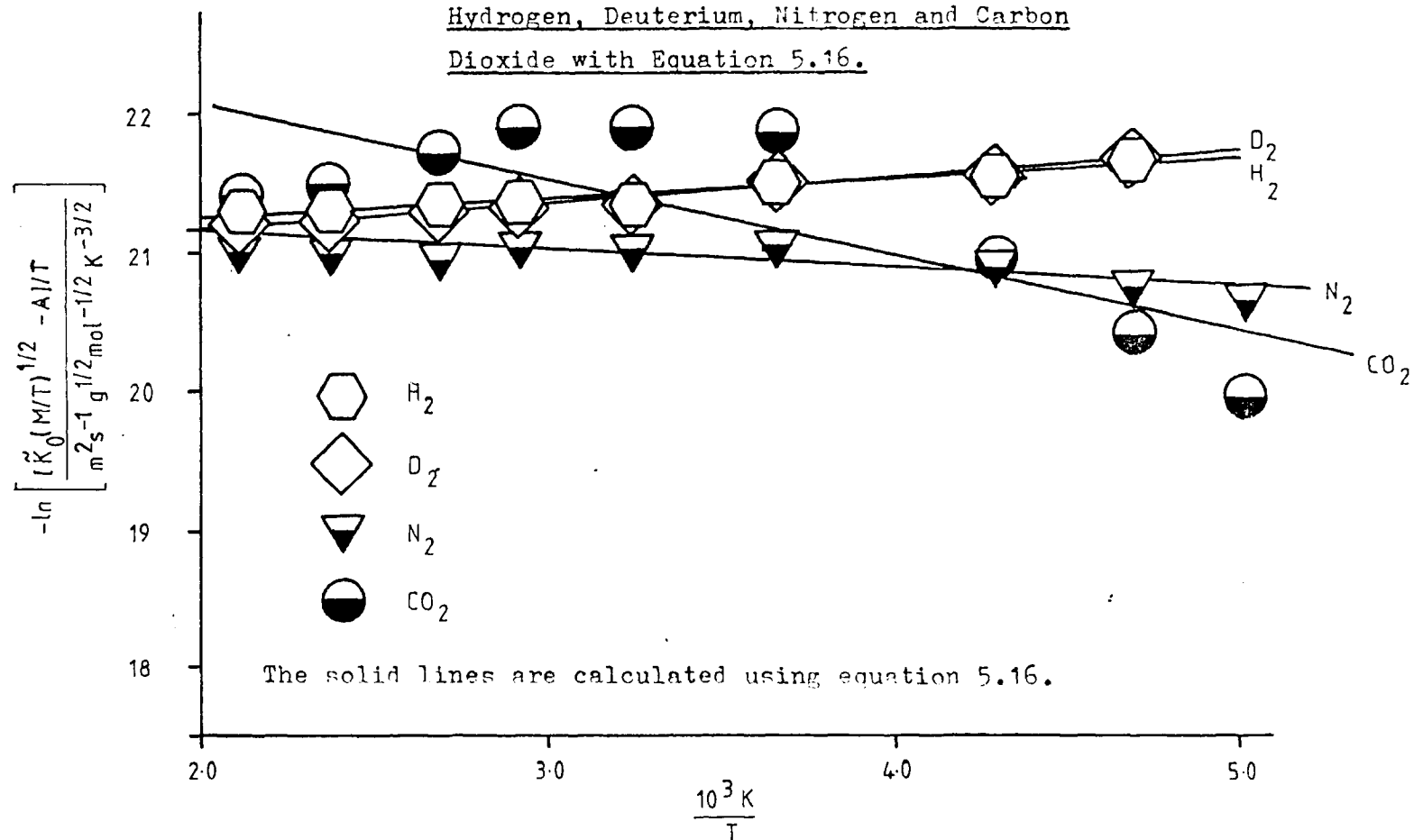
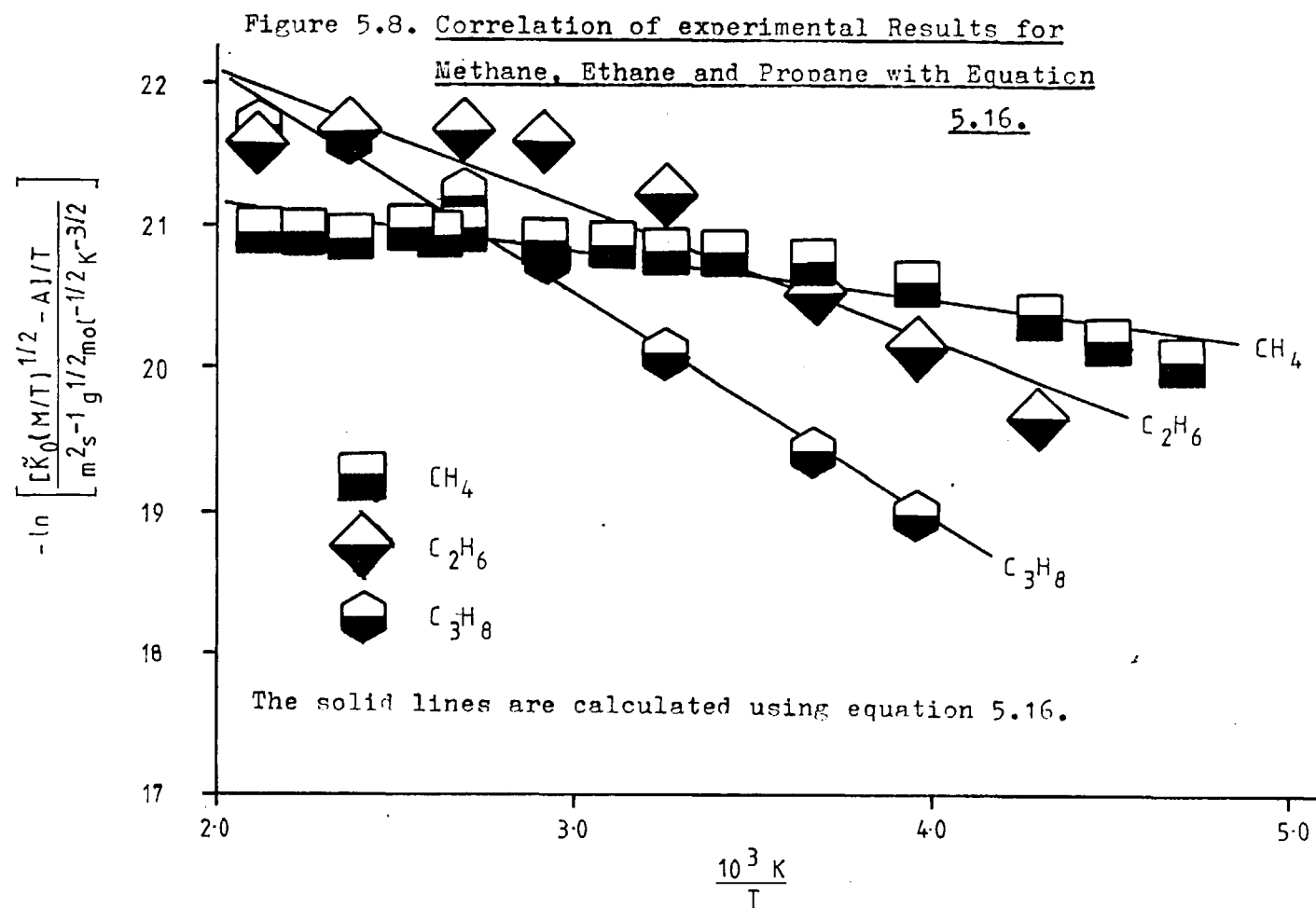


Figure 5.7. Correlation of Experimental Results for
Hydrogen, Deuterium, Nitrogen and Carbon
Dioxide with Equation 5.16.





imply that hydrogen and deuterium will not show a $\tilde{K}_0 (M/T)^{\frac{1}{2}}$ minimum when plotted against temperature, since Δ is equal to the value of T at the minimum. On previous evidence this is surprising since $\tilde{K}_0 (M/T)^{\frac{1}{2}}$ normally shows a sharp upturn at low temperatures.

With porous glass (Hwang and Kammermeyer, 1966 (a)) it was found that $1/B$ was approximately proportional to Δ . When $1/B$ is plotted against Δ for this work (figure 5.9) there is no useful correlation. This again is an indication that the analysis of Hwang and Kammermeyer is not applicable to the flow of gases through a Sterling S carbon membrane.

In the procedure used above A was fixed so that it was a geometrical constant characteristic of the membrane. As an alternative method the values of $\tilde{K}_0 (M/T)^{\frac{1}{2}}$ for each of the gases can be fitted separately to an equation of the form of equation 5.15.

$$\tilde{K}_0 \left(\frac{M}{T} \right)^{\frac{1}{2}} = A' + B' T \exp \left(\frac{\Delta'}{T} \right) \quad (5.17)$$

A second set of parameters A' , B' and Δ' can be obtained where all three may be dependent upon both the membrane and the gas. For each gas in turn a value of A' was assumed and values of B' and Δ' were obtained using the least mean square method, after rearranging equation 5.17.

$$\ln \left(\frac{\tilde{K}_0 (M/T)^{\frac{1}{2}} - A'}{T} \right) = \ln B' + \frac{\Delta'}{T} \quad (5.18)$$

Further choices of A' were made until the sum of squared errors for the gas under consideration was minimised. As previously the calculations were performed using a CDC 6500 computer. The results are given table 5.5. Figures 5.10 to 5.12 show plots of $\ln ([\tilde{K}_0 (M/T)^{\frac{1}{2}} - A']/T)$ against $1/T$ together with the lines of best fit. It is most apparent that there are widely ranging values of A' , from $1.180 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} \text{ g}^{\frac{1}{2}} \text{ mol}^{-\frac{1}{2}} \text{ K}^{-\frac{1}{2}}$ for helium to $-6.135 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} \text{ g}^{\frac{1}{2}} \text{ mol}^{-\frac{1}{2}} \text{ K}^{-\frac{1}{2}}$ for propane. This is in direct contradiction to Hwang and Kammermeyer's theory according to which A' is a geometric constant and hence independent of the diffusing gas. The improved treatment of Nicholson and Petropoulos

Figure 5.9. Plot of $1/B$ against Δ .

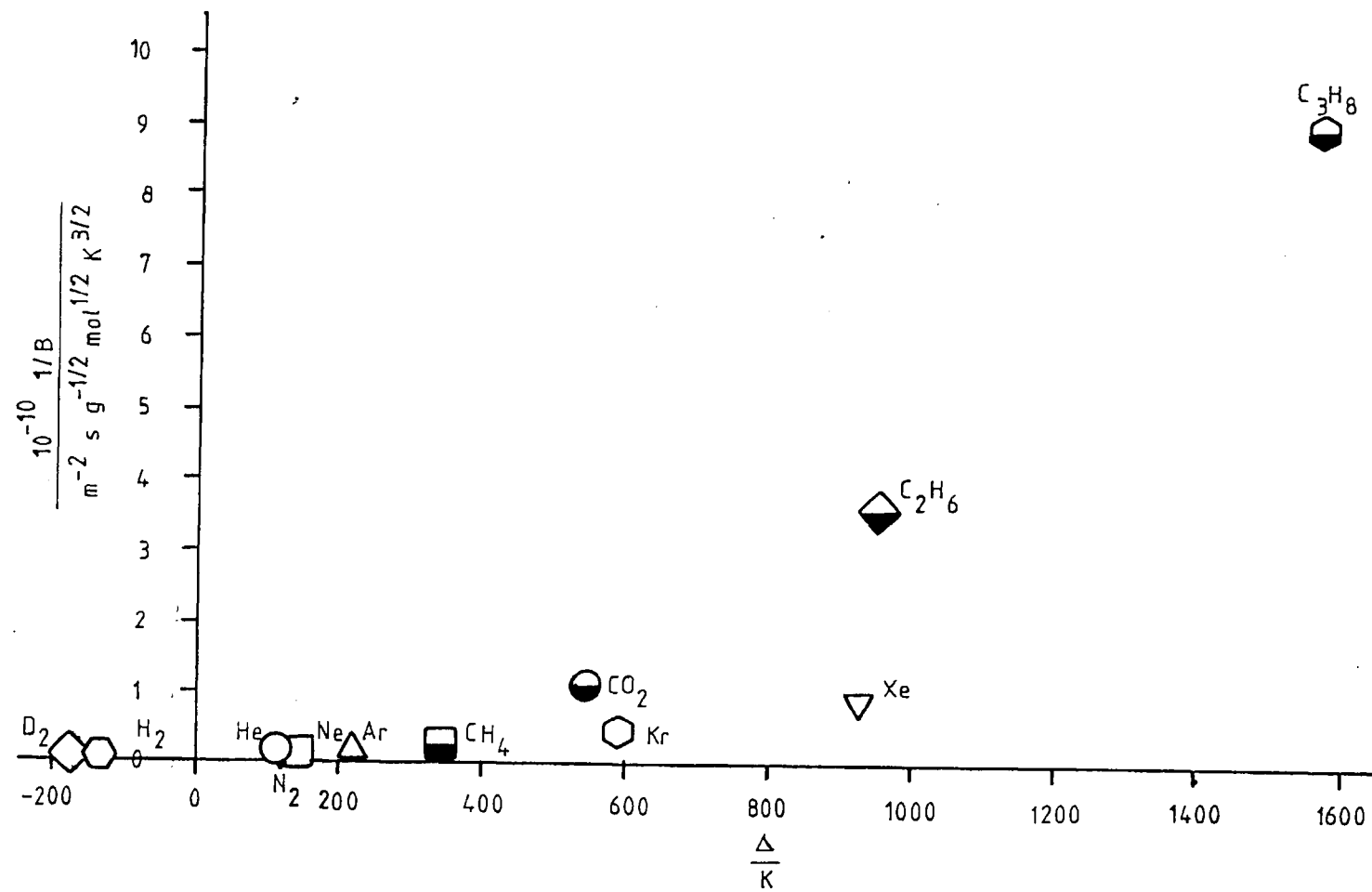
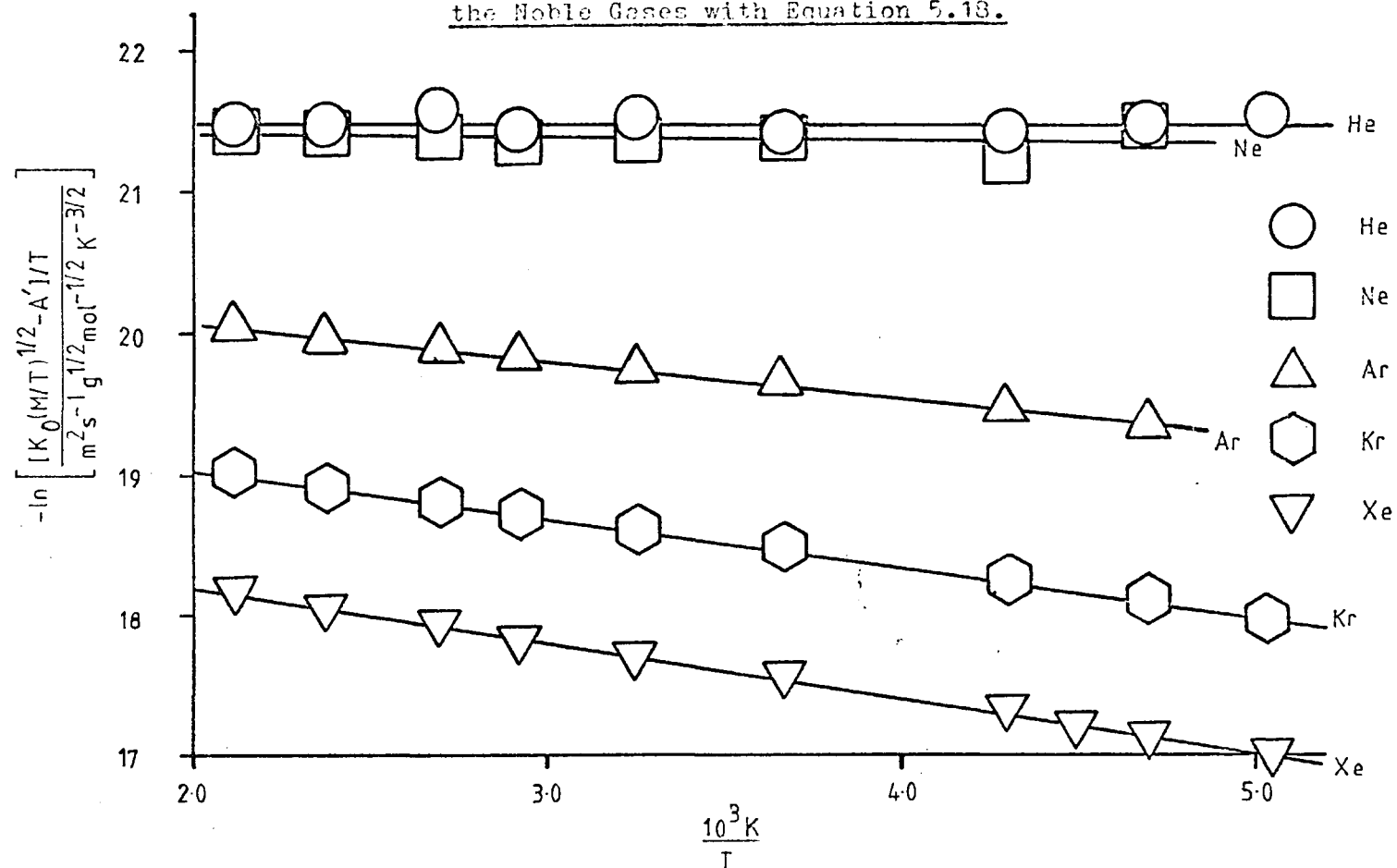


Table 5.5 Values of A' , B' and Δ' for Various Gases
Flowing through Sterling S Membrane 1.

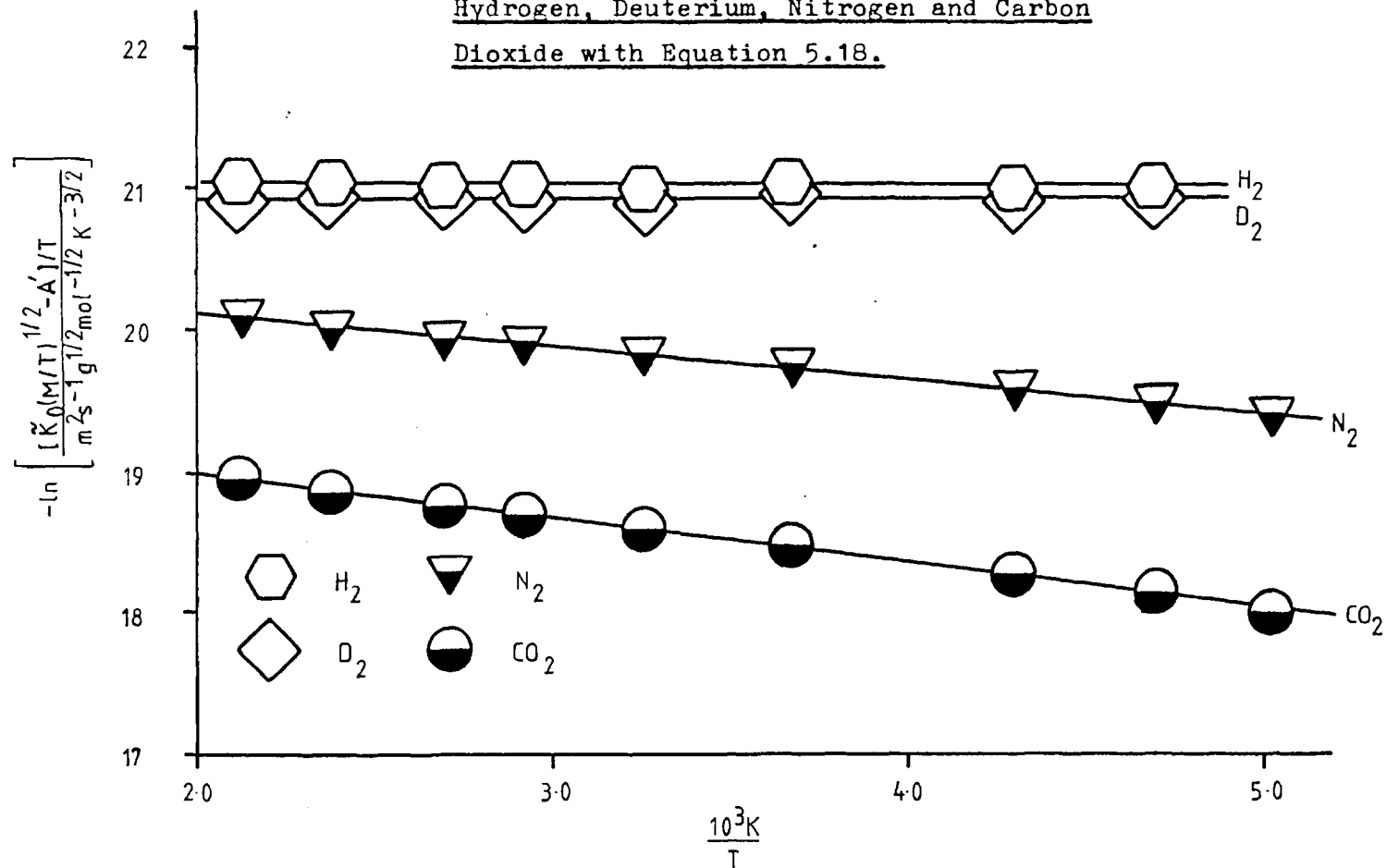
Gas	$10^6 A'$ $\text{m}^2 \text{s}^{-1} \text{g}^{\frac{1}{2}} \text{mol}^{-\frac{1}{2}} \text{K}^{-\frac{1}{2}}$	$10^{10} B'$ $\text{m}^2 \text{s}^{-1} \text{g}^{\frac{1}{2}} \text{mol}^{-\frac{1}{2}} \text{K}^{-\frac{1}{2}}$	Δ' K	$10^6 \sigma$ $\text{m}^2 \text{s}^{-1} \text{g}^{\frac{1}{2}} \text{mol}^{-\frac{1}{2}} \text{K}^{-\frac{1}{2}}$
He	1.18 ₀	4.54	10.8	0.007
Ne	1.21 ₈	4.80	24.5	0.008
Ar	0.55 ₂	11.09	272	0.006
Kr	-1.10 ₆	26.58	352	0.02
Xe	-4.53 ₉	56.61	396	0.06
H ₂	1.03 ₄	7.14	4.9	0.005
D ₂	1.01 ₄	8.03	1.5	0.004
N ₂	0.58 ₃	11.28	235	0.008
CO ₂	-1.34 ₅	29.44	316	0.03
CH ₄	-0.13 ₆	17.64	314	0.01
C ₂ H ₆	-2.44 ₇	36.14	374	0.02
C ₃ H ₈	-6.13 ₅	64.40	422	0.01

Figure 5.10. Correlation of Experimental Results for
the Noble Gases with Equation 5.18.



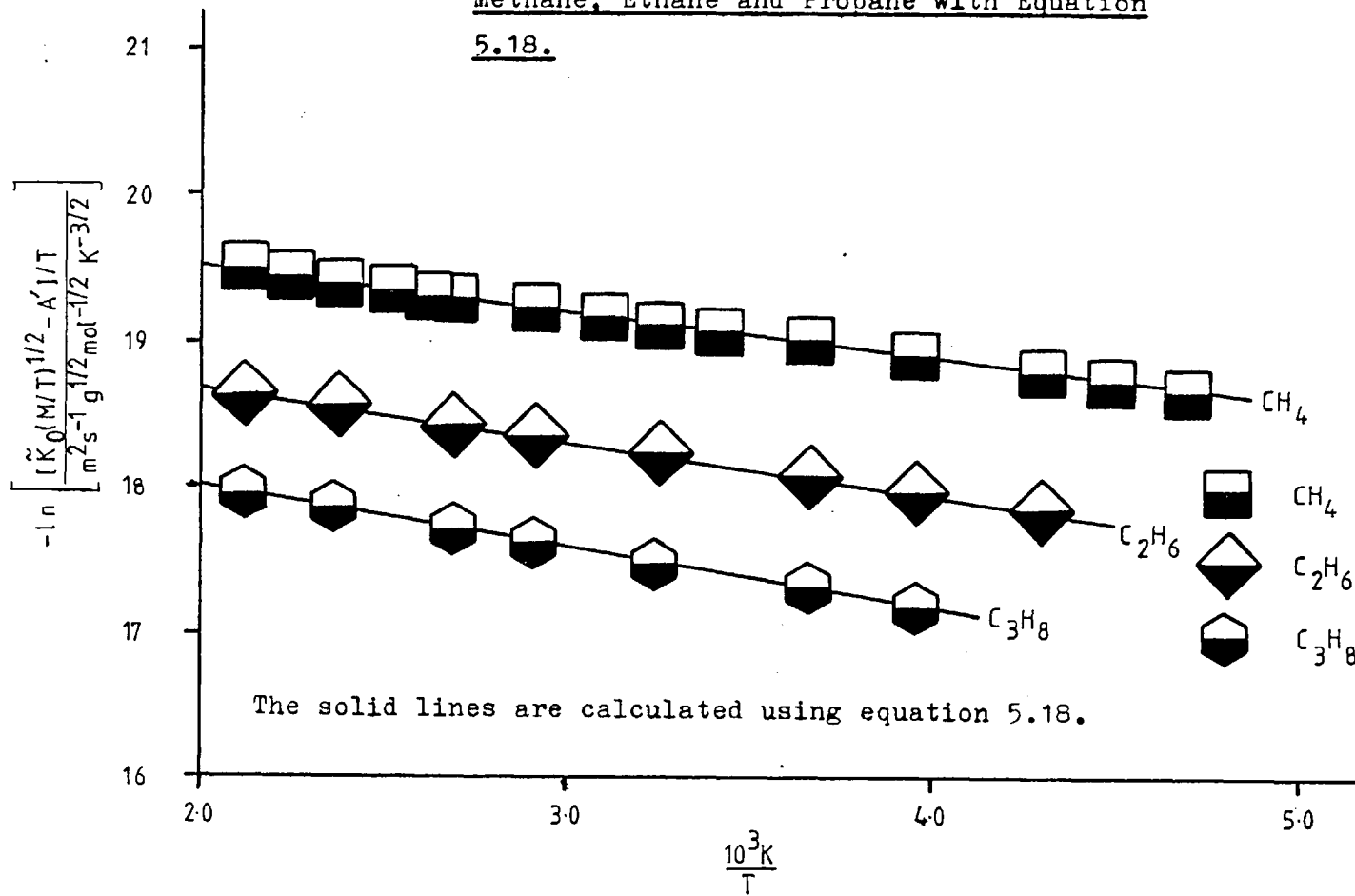
The solid lines are calculated using equation 5.18.

Figure 5.11. Correlation of Experimental Results for
Hydrogen, Deuterium, Nitrogen and Carbon
Dioxide with Equation 5.18.



The solid lines are calculated using equation 5.18.

Figure 5.12. Correlation of Experimental Results for
Methane, Ethane and Propane with Equation
5.18.



(1973) predicts a temperature dependent gas phase component, in which case the meaning of A' , B' and Δ' are questionable. Negative values of A' are difficult to explain since at high temperature $\tilde{K}_0(M/T)^{1/2} \rightarrow A'$ in order to preserve the correct limit that $K_{SO}(M/T)^{1/2} \rightarrow 0$ (Kammermeyer, 1968; Nicholson and Petropoulos, 1973; Hwang and Kammermeyer, 1975). Agreement between the values of A and B obtained from equation 5.16 and the values of A' and B' derived using equation 5.18 is closest for weakly adsorbed gases, such as helium, neon, hydrogen and deuterium. Differences between values of Δ and Δ' are very marked for all gases. Despite its lack of theoretical justification equation 5.17 can be used empirically to fit experimental results.

An alternative approach is that of Sandler (1972) who introduced wall forces into the "dusty-gas" model. The permeability is given by the equation

$$\tilde{K}_0 = C_{n,m} \left(\frac{T^{(4+3n-2m)/2n}}{S_{n,m} + T^{(n-m)/n}} \right) \quad (5.19)$$

n and m are respectively the indices of the repulsive and attractive components of the interaction energy, $C_{n,m}$ and $S_{n,m}$ constants depending on both the gas and membrane, (see section 2.6). Rearranging equation 5.19

$$\frac{T^{(4+3n-2m)/2n}}{\tilde{K}_0} = \frac{S_{n,m}}{C_{n,m}} + \frac{T^{(n-m)/n}}{C_{n,m}} \quad (5.20)$$

A plot of $T^{(4+3n-2m)/2n}/\tilde{K}_0$ against $T^{(n-m)/n}$ should give a straight line of intercept $S_{n,m}/C_{n,m}$ and of gradient $1/C_{n,m}$. The temperature, $T_{\min}$, corresponding to the minimum of a plot of $\tilde{K}_0(M/T)^{1/2}$ versus T is given by

$$T_{\min} = \left(\frac{-(2+n-m) S_{n,m}}{2} \right)^{n/(n-m)} \quad (5.21)$$

An equation commonly used to represent the interaction between two molecules is equation 2.87 with $n = 12$ and $m = 6$. Whilst this equation is not over-appropriate for the interaction between a gas molecule and a solid surface, in the "dusty-gas"

model the solid is treated as one component of a gas mixture (Deryagin and Bakanov, 1957; Evans, Watson and Mason, 1962) and so the experimental results can be treated in terms of Sandler's analysis with the above Lennard-Jones 6 - 12 potential. When $n=12$ and $m=6$ equation 5.20 becomes

$$\frac{T^{7/6}}{\tilde{K}_0} = \frac{S_{12,6}}{C_{12,6}} + \frac{T^{1/2}}{C_{12,6}} \quad (5.22)$$

and $T_{\min}$ is given by

$$T_{\min} = 16 S_{12,6}^2 \quad (5.23)$$

Figures 5.13 to 5.15 show plots of $T^{7/6}/\tilde{K}_0$ versus $T^{1/2}$, the line is the line of best fit obtained by the method of least squares. The values of the constants, $C_{12,6}$ and $S_{12,6}$, are given in table 5.6 together with $T_{\min}$ and $\sigma(\tilde{K}_0)$ the standard deviation of $\tilde{K}_0$ and $\sigma(\tilde{K}_0(M/T)^{1/2})$ the standard deviation of $\tilde{K}_0(M/T)^{1/2}$. Again deviations from linearity increase as the sorbability of the diffusing gas increases. Values of $\sigma(\tilde{K}_0(M/T)^{1/2})$ are of the same order as the values quoted in table 5.4 for equation 5.16, but are higher than the values quoted in table 5.5 for equation 5.18, particularly for the more strongly sorbed gases such as krypton, xenon, ethane, propane and carbon dioxide. Table 5.7 shows the values of $T_{\min}$ estimated from the experimental results where the minimum of a plot of $\tilde{K}_0(M/T)^{1/2}$ against T occurs within the temperature range studied. Only the calculated value of $T_{\min}$ for methane bears any relation to the experimental value of $T_{\min}$. This is in contrast to the values of Δ' obtained from equation 5.18 which are generally in close agreement with the values of $T_{\min}$ estimated from the results. Generally large negative values of $S_{12,6}$ corresponds to small values of $C_{12,6}$ and strongly adsorbed gases. Small negative and positive values of $S_{12,6}$ occur for weakly adsorbed gases and large values of $C_{12,6}$.

Figure 5.13. Correlation of Experimental Results for
the Noble Gases with Equation 5.22.

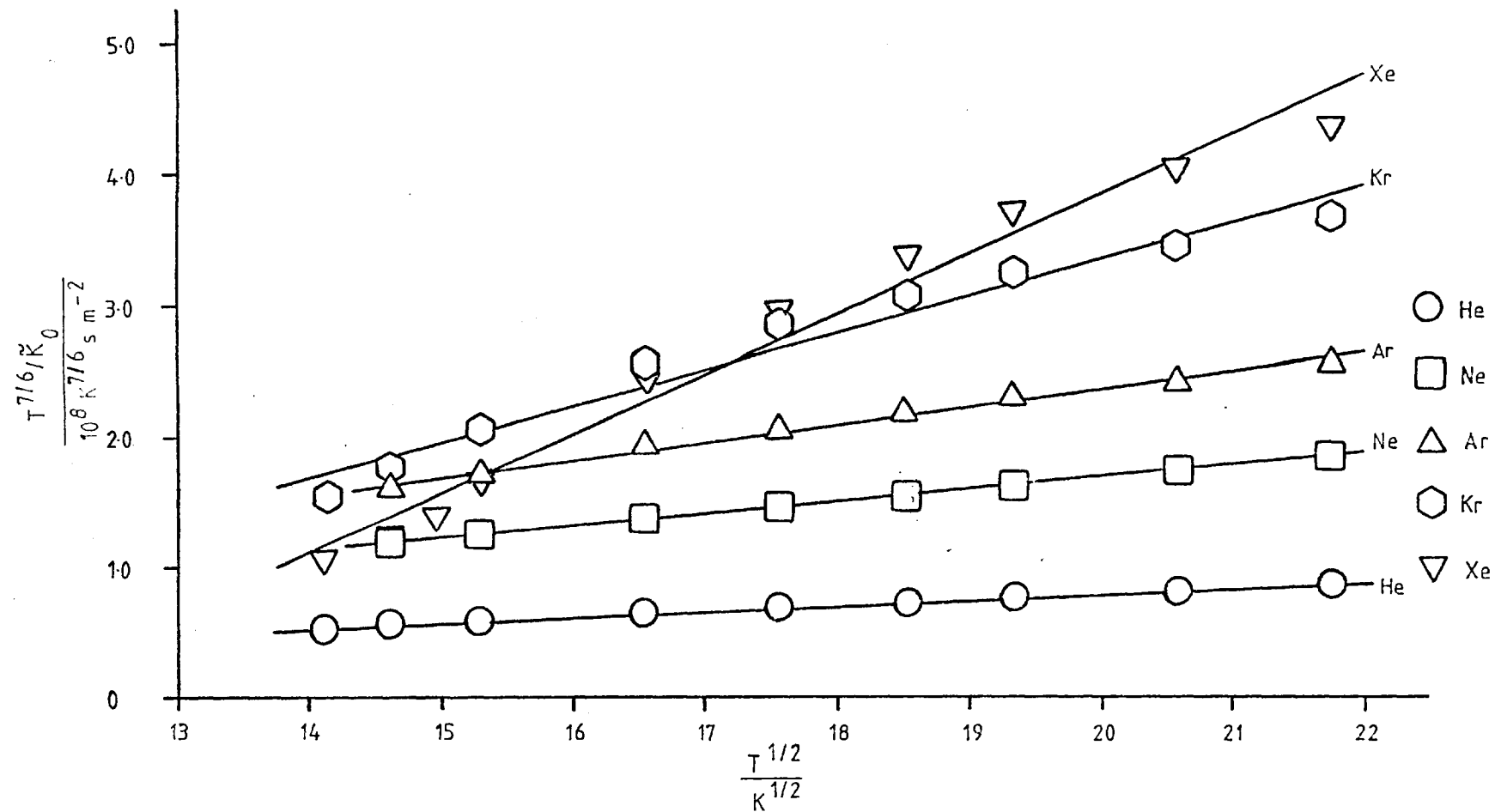


Figure 5.14. Correlation of Experimental Results for
Hydrogen, Deuterium, Nitrogen and Carbon
Dioxide with Equation 5.22.

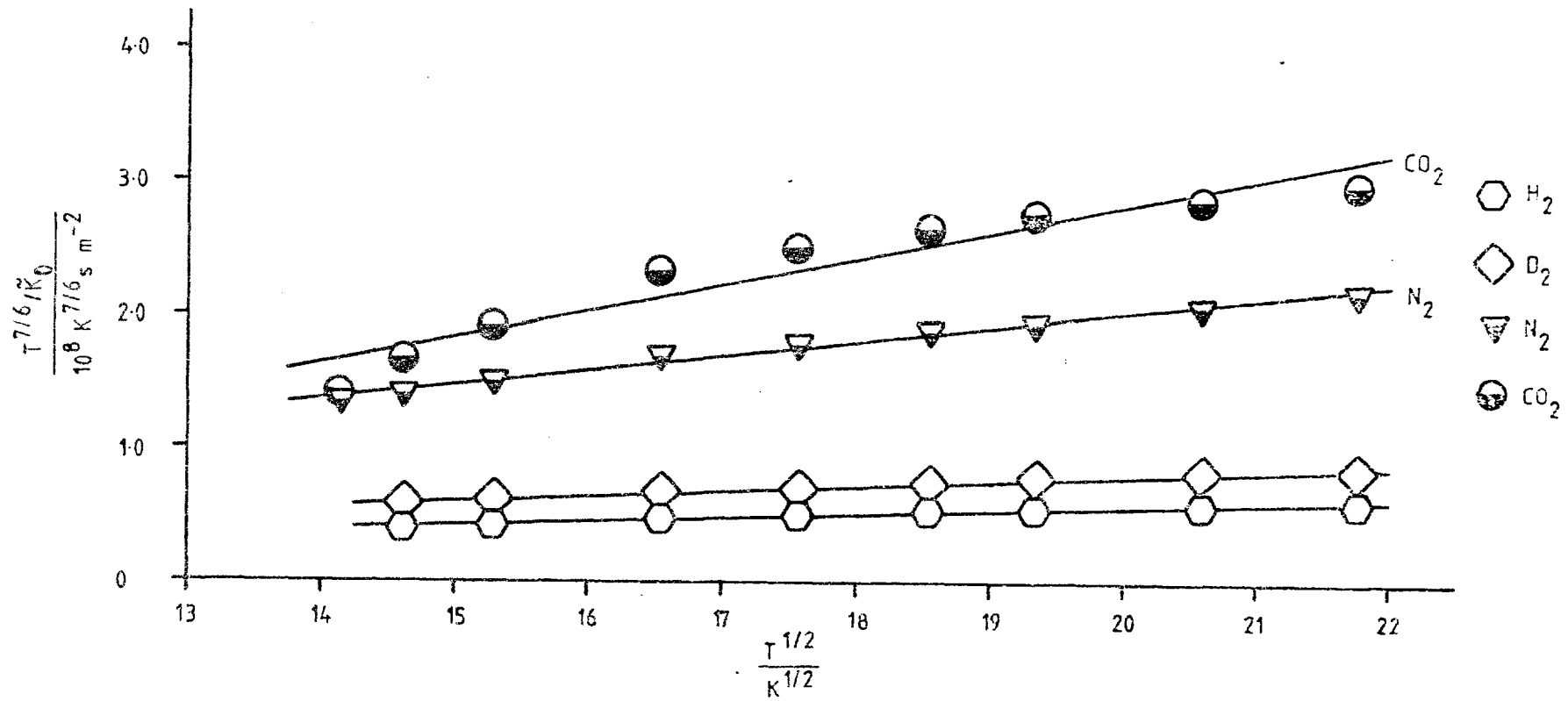


Figure 5.15. Correlation of Experimental Results for
Methane, Ethane and Propane with Equation 5.22.

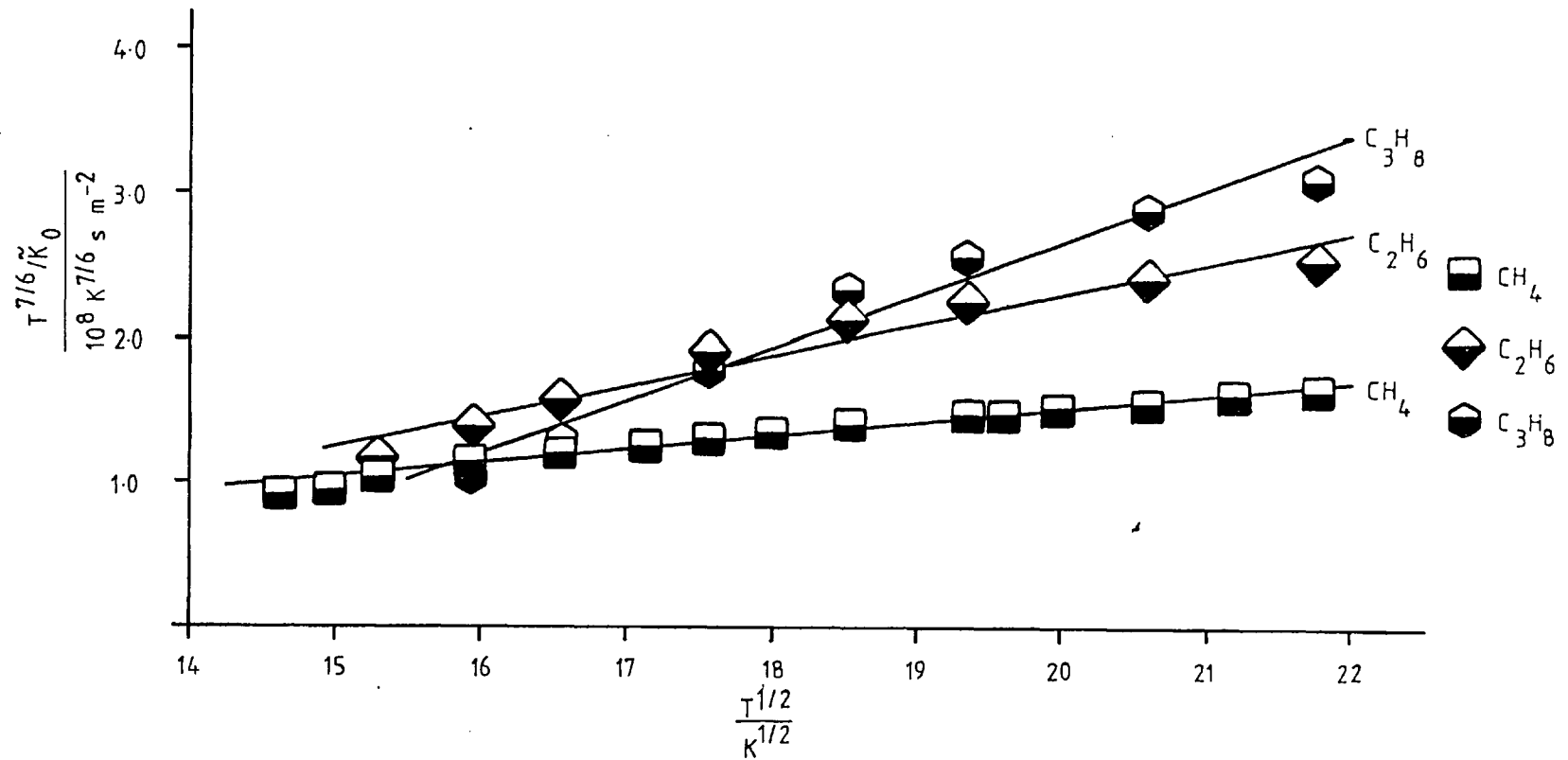


Table 5.6. Values of $C_{12,6}$, $S_{12,6}$ and $T_{\min}$ for Various Gases Flowing through Sterling S Membrane 1.

Gas	$\frac{10^8 C_{12,6}}{m^2 s^{-1} K^{-2/3}}$	$\frac{S_{12,6}}{K^{1/2}}$	$\frac{T_{\min}}{K}$	$\frac{\sigma(\tilde{K}_0)}{m^2 s^{-1}}$	$\frac{\sigma(\tilde{K}_0 (M/T)^{1/2})}{m^2 s^{-1} g^{1/2} mol^{-1/2} K^{-1/2}}$
He	22.76	-1.91	58	0.07	0.008
Ne	10.52	-1.95	61	0.02	0.008
Ar	7.32	-2.49	99	0.06	0.02
Kr	3.60	-7.87	990	0.2	0.1
Xe	2.19	-11.55	2133	0.3	0.2
H ₂	35.07	0.42	3	0.06	0.005
D ₂	26.27	1.38	30	0.06	0.007
N ₂	9.09	-1.32	28	0.08	0.02
CO ₂	5.05	-5.62	505	0.2	0.1
CH ₄	10.26	-4.27	291	0.2	0.04
C ₂ H ₆	4.72	-9.03	1306	0.3	0.09
C ₃ H ₈	2.72	-12.70	2581	0.3	0.1

Table 5.7.

Experimental Values of $T_{\min}$

Gas	$T_{\min}$ K
Ar	272
Kr	326
N ₂	248
CO ₂	308
CH ₄	293
C ₂ H ₆	365
C ₃ H ₈	423

A 3-9 potential as represented by equation 2.98 is often used to describe the interaction between a gas molecule and a solid surface. When $n = 9$ and $m = 3$ equation 5.20 becomes

$$\frac{T^{25/18}}{\tilde{K}_0} = \frac{S_{9,3}}{C_{9,3}} + \frac{T^{2/3}}{C_{9,3}} \quad (5.24)$$

and $T_{\min}$ becomes

$$T_{\min} = (-4 S_{9,3})^{3/2} \quad (5.25)$$

Plots of $T^{25/18}/\tilde{K}_0$ against $T^{2/3}$ are given in figures 5.16 to 5.18 together with the lines of best fit. Table 5.8 shows the values of $C_{9,3}$ and $S_{9,3}$ obtained from the intercept and gradient of the line. Calculated values of $T_{\min}$, $\sigma(\tilde{K}_0)$ and $\sigma(\tilde{K}_0(M/T)^{1/2})$ are also given in the table. The results show trends similar to the trends for the 6-12 potential. Deviations from linearity increase with the adsorbability of the diffusing gas. Large negative values of $S_{9,3}$ occur where

Figure 5.16. Correlation of Experimental Results for the Noble Gases with Equation 5.24.

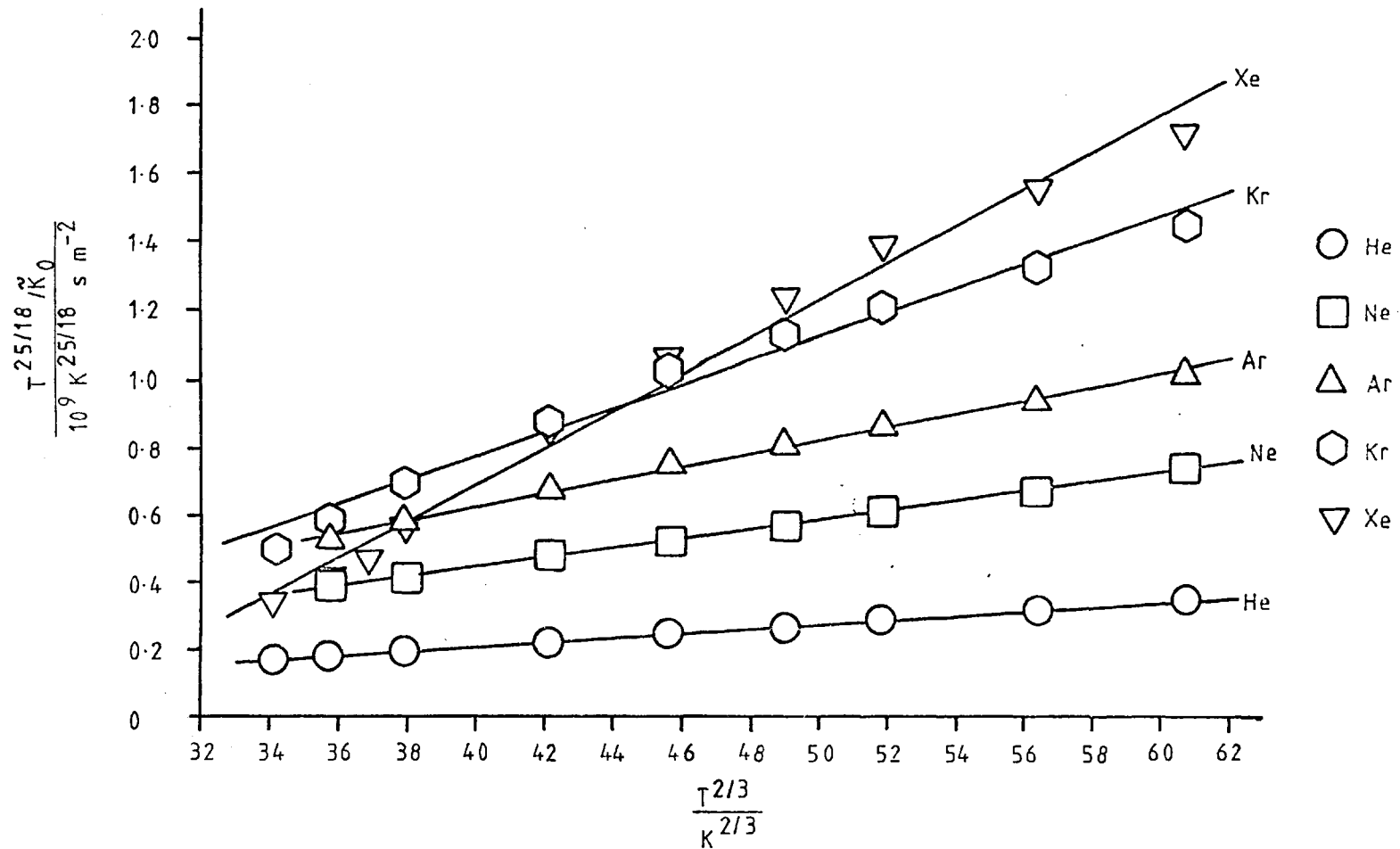


Figure 5.17. Correlation of Experimental Results for Hydrogen, Deuterium, Nitrogen and Carbon Dioxide with Equation 5.24.

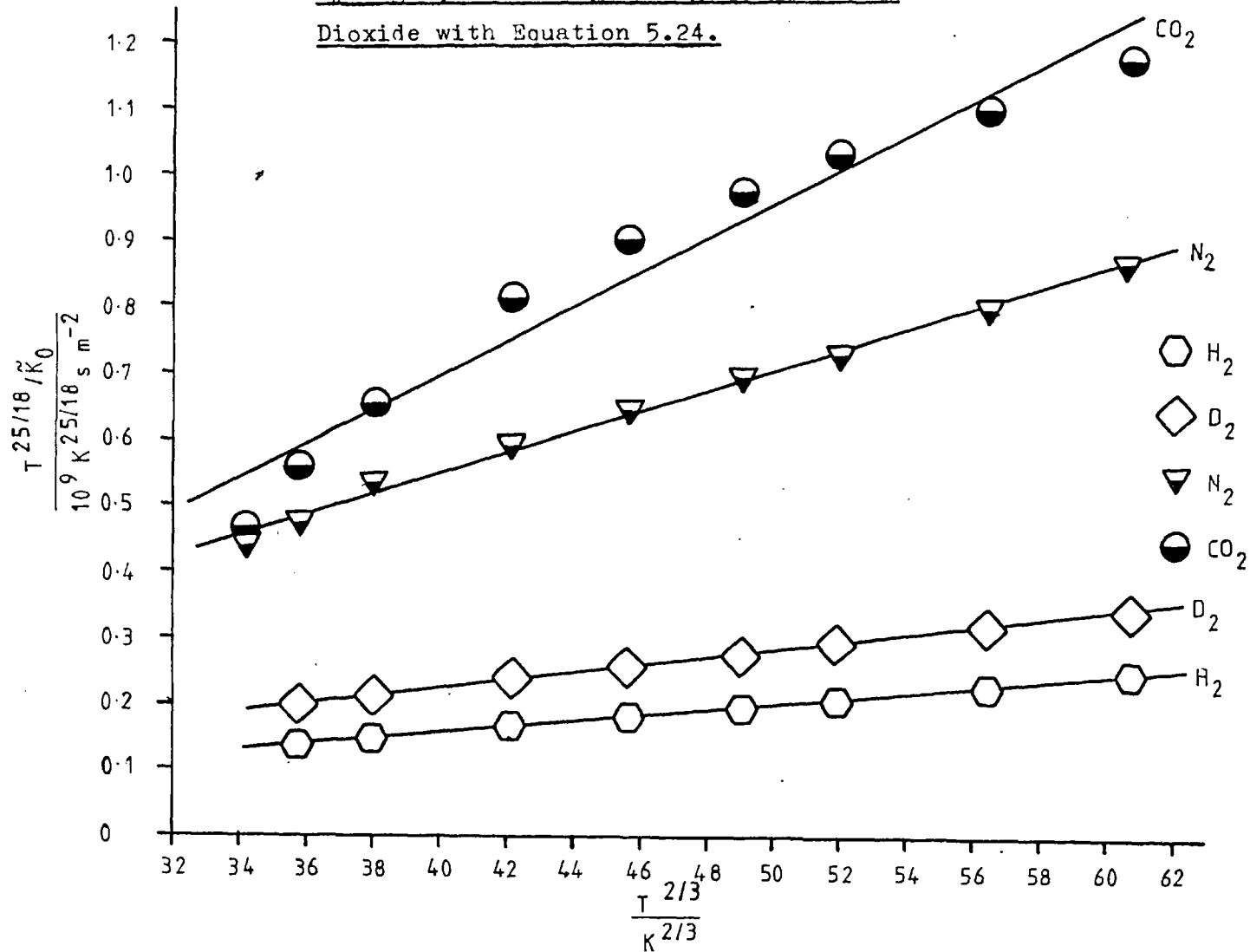


Figure 5.18. Correlation of Experimental Results for
Methane, Ethane and Propane with Equation 5.24.

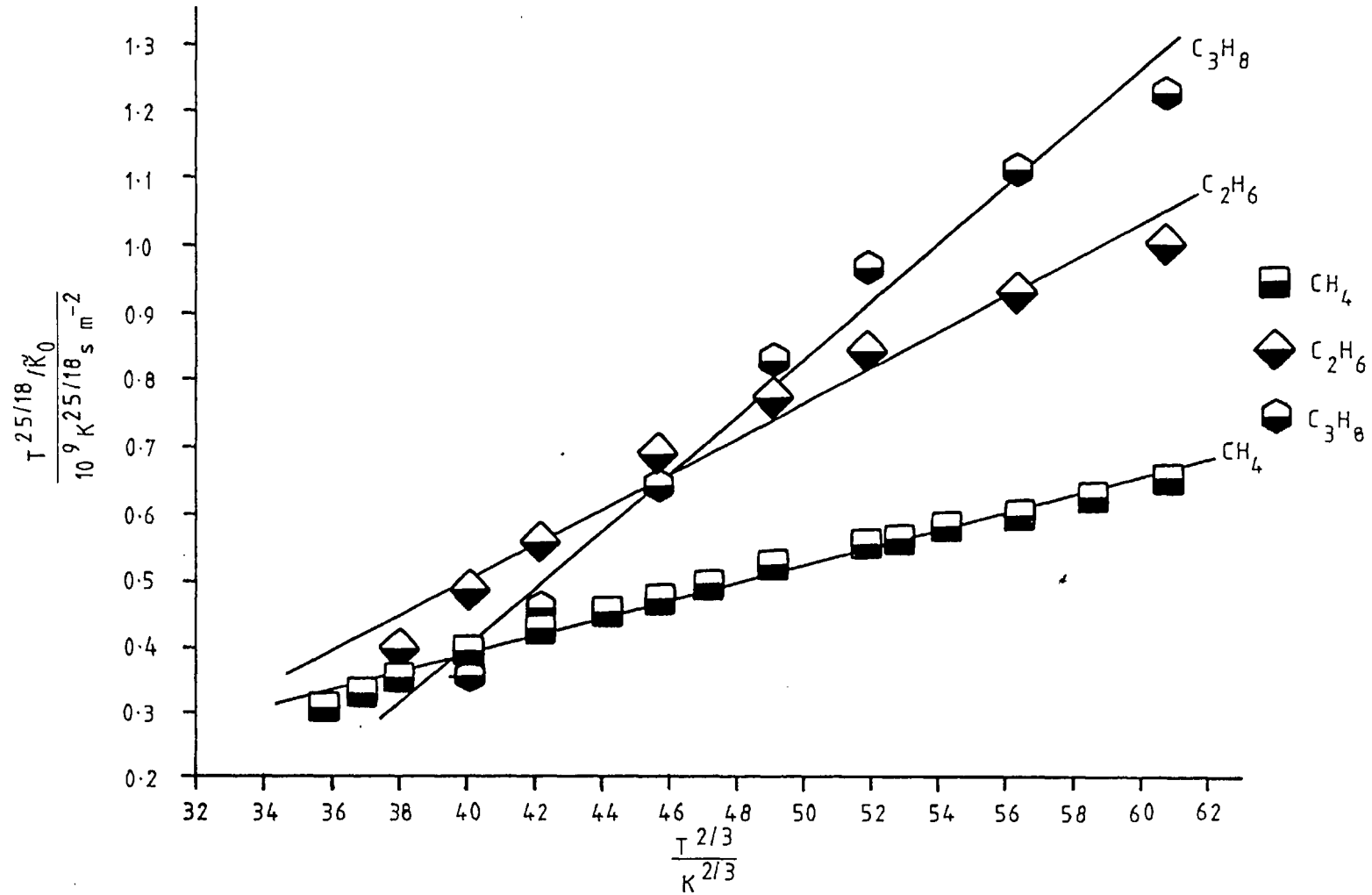


Table 5.8 Values of $C_{9,3}$, $S_{9,3}$ and $T_{\min}$ for Various
Gases Flowing through Sterling S Membrane 1.

Gas	$\frac{10^8 C_{9,3}}{\text{m}^2 \text{s}^{-1} \text{K}^{-1}}$	$\frac{S_{9,3}}{\text{K}^{2/3}}$	$\frac{T_{\min}}{\text{K}}$	$\frac{\sigma(\tilde{K}_0)}{\text{m}^2 \text{s}^{-1}}$	$\frac{\sigma(\tilde{K}_0 (\text{M/T})^{1/2})}{\text{m}^2 \text{s}^{-1} \text{g}^{1/2} \text{mol}^{-1/2} \text{K}^{-1/2}}$
He	15.80	-6.72	139	0.07	0.007
Ne	7.28	-6.96	147	0.03	0.009
Ar	5.14	-7.75	173	0.05	0.02
Kr	2.83	-18.24	623	0.2	0.09
Xe	1.85	-27.20	1135	0.2	0.2
H ₂	23.34	-2.82	38	0.05	0.004
D ₂	17.21	-1.24	11	0.05	0.006
N ₂	6.35	-4.86	86	0.08	0.02
CO ₂	3.82	-13.24	385	0.2	0.1
CH ₄	7.48	-10.92	289	0.2	0.04
C ₂ H ₆	3.76	-21.22	782	0.3	0.09
C ₃ H ₈	2.31	-30.87	1372	0.3	0.1

$C_{9,3}$ is small and for strongly adsorbed gases. The standard deviations are of the same order to those for the 6-12 potential, perhaps a little lower but not significantly so. Again, with the exception of methane and in this case carbon dioxide, the calculated values of $T_{\min}$ bear little relation to the experimental values.

In summary it is difficult to assess whether the analysis of Hwang and Kammermeyer (1966(a)) or the treatment of Sandler (1972) is better used to interpret the experimental results. The values of $\sigma(\tilde{K}_0(M/T)^{\frac{1}{2}})$ are a little lower for equation 5.16, for some gases, than for equations 5.22 and 5.24. For most gases, however, there is little to choose between the two interpretations. Sandler (1972) considering only the flow of helium through porous glass came to the same conclusion. The standard deviations from the experimental values of $\tilde{K}_0(M/T)^{\frac{1}{2}}$, in the worst cases were less than 10% for both Hwang and Kammermeyer's equation and Sandler's equation. The predicted values of $T_{\min}$ (or Δ) generally bear little relation to the experimental values. The empirical equation 5.18 (related to Hwang and Kammermeyer's equation) fits the experimental results better than with Hwang and Kammermeyer's derived equation or Sandler's equation (with either a 6-12 potential or a 3-9 potential). The standard deviation is less than 3% for xenon, the worst case. The values of Δ' are in close agreement with the experimental values of $T_{\min}$.

Berman and Lund investigated the flow of gases through porous media (Berman and Lund, 1958; Lund and Berman, 1958) and capillaries (Lund and Berman, 1966 (a,b)). A dimensionless transport parameter w was defined by equation

$$w = \frac{4 G}{\Delta p A_c \bar{c}} \quad (5.26)$$

Where G is the total transport in pressure-volume units per unit time, $\bar{c}$ is the mean molecular speed (see equation 2.21) through the porous sample or capillary. The transmission probability w_0 is the value of w in the limit of vanishing

pressures

$$w_0 = \lim_{\bar{p} \rightarrow 0} w \quad (5.27)$$

It was found (Berman and Lund, 1958; Lund and Berman, 1958) for various porous media with pore radii ranging from $1 \times 10^{-6} \text{ m}$ to $2.36 \times 10^{-4} \text{ m}$ that w_0 was dependent on the flowing gas. When $w_0/w_0 \text{ Ar298K}$ ($w_0 \text{ Ar298K}$ being the transmission probability for argon gas at 298.2K) was plotted against $\bar{\epsilon}^*/kT$ it was found that for helium the w_0 ratio increased with decreasing temperature, whereas for neon, argon, krypton and xenon the w_0 ratio decreased with temperature. Various metal and ionic crystal capillaries have been considered in this way (Lund and Berman, 1966 (b)). It is interesting to make a similar analysis of the data obtained in this work

$$G = \frac{d(p_1 V_1)}{dt} \frac{T}{T_R} \quad (5.28)$$

where V_1 is the volume on the outgoing side in which the pressure is p_1 at time t . Assuming gas ideality

$$G = R T J_{\infty} \quad (5.29)$$

recalling equation 2.10, the definition of $\tilde{K}$

$$\tilde{K} = \frac{G \cdot l}{A_c \Delta p} \quad (5.30)$$

Rearranging and substituting for G in equation 5.26

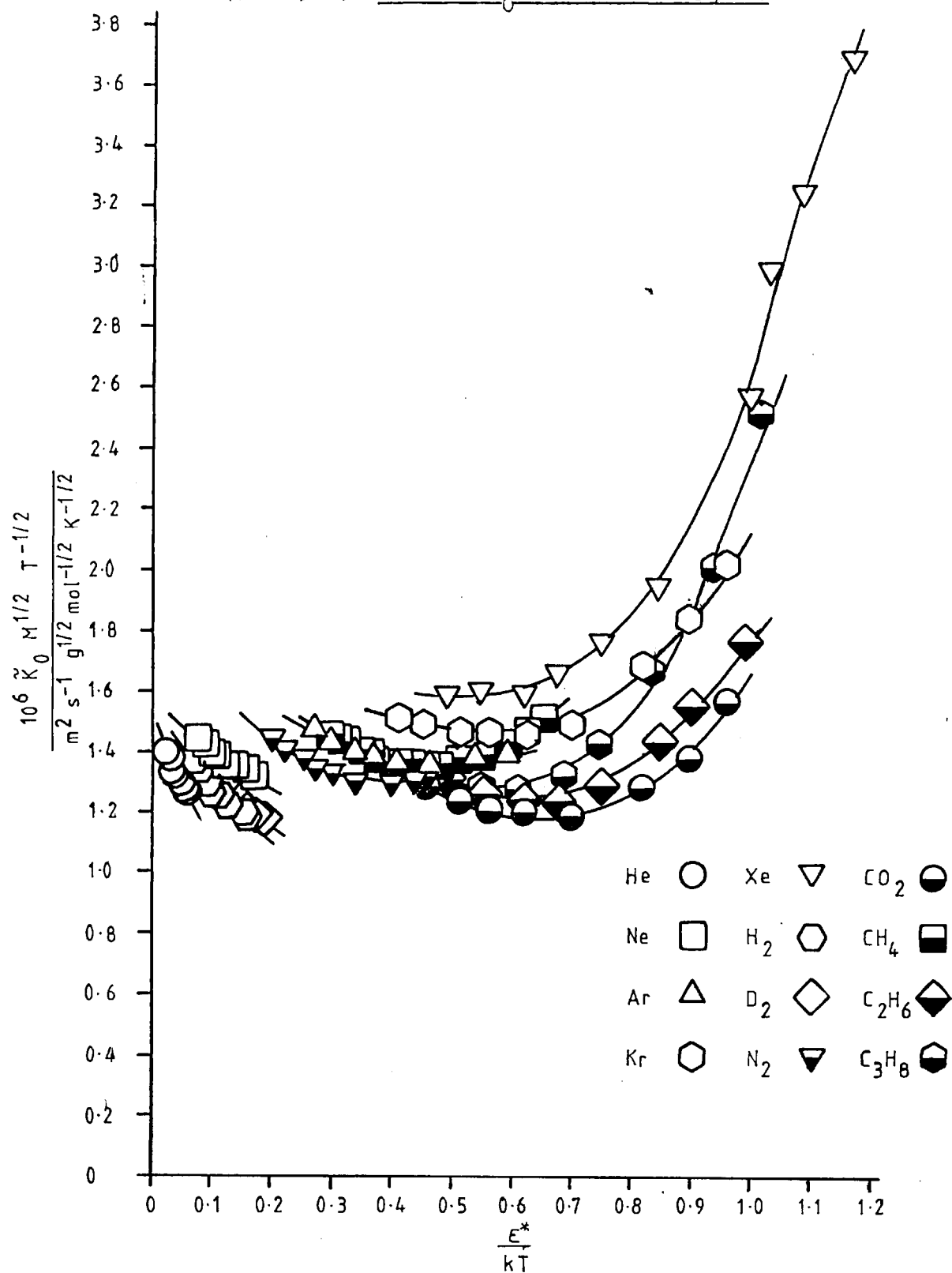
$$w = \frac{4 \tilde{K}}{l \bar{c}} \quad (5.31)$$

substituting for $\bar{c}$ from equation 2.21

$$w = \left(\frac{2\pi \phi}{R l} \right)^{\frac{1}{2}} \tilde{K} \left(\frac{M}{T} \right)^{\frac{1}{2}} \quad (5.32)$$

hence w is proportional to $K(\tilde{M}/T)^{\frac{1}{2}}$, and in the same way w_0 is proportional to $\tilde{K}_0(M/T)^{\frac{1}{2}}$ as is $w_0/w_0 \text{ Ar298K}$. Figure 5.19 shows a plot of $\tilde{K}_0 (M/T)^{\frac{1}{2}}$ against $\bar{\epsilon}^*/kT$. Table 5.9

Figure 5.19. Plot of $\tilde{K}_0 M^{1/2} T^{-1/2}$ versus ϵ^*/kT .



show the values of ϵ^*/k used (from Hirschfelder, Curtis and Bird, 1964 p. 1110). From figure 5.19 it is clear that $\tilde{K}_0(M/T)^{1/2}$ as a function of ϵ^*/kT does not form a common curve for different gases, as the results of Berman and Lund (1958) seem to indicate. This difference is probably due to interactions with the pore walls being more important in the Sterling S system than in systems studied by Berman and Lund. The pore size of the Sterling S membrane is considerably smaller than the porous media studied by Berman and Lund.

For the flow of gases through porous media, it is more appropriate to plot $\tilde{K}_0(M/T)^{1/2}$ against gas-solid interaction parameters rather than gas interaction parameters. There have been no experimental determinations of the minimum energy of interaction $E_g(z^*)$ of gases with Sterling S. Determinations have however been made for a graphitised carbon black, P.33 (also known as Sterling FT) assuming various functional forms for the gas-solid interaction potential (Sams, Constabaris and Halsey, 1960; Constabaris, Sams and Halsey, 1961; Rybolt and Pierotti, 1979). The carbon P.33 has a smaller surface area than Sterling S, so the values of $E_g(z^*)$ obtained are not strictly comparable with the values for Sterling S, but carbon black P.33 is a graphitised carbon prepared by a similar process to the method used for Sterling S. In the absence of any more appropriate values of $E_g(z^*)$ those obtained by Halsey and his coworkers are useful for correlation purposes.

Theoretical values of $E_g(z^*)$ can be calculated using equation 2.100.

$$E_g(z^*) = - \frac{\pi B \bar{n}}{9 z^{*3}} \quad (2.100)$$

There exists three expressions for B due respectively to London, Slater and Kirkwood and Kirkwood and Müller (equations 2.92 to 2.94 respectively). For this work $E_g(z^*)$ has been calculated using the Kirkwood-Müller expression, frequently used in calculations for a variety of adsorbate-adsorbent

Table 5.9. Values of ϵ^*/k used in Plotting
Figure 5.19

Gas	$\frac{\epsilon^*}{k}$ K
He	10.22
Ne	35.7
Ar	124
Kr	190
Xe	229
H ₂	33.3
D ₂	39.3
N ₂	91.5
CO ₂	190
CH ₄	137
C ₂ H ₆	230
C ₃ H ₈	254

Values taken from Hirschfelder, Curtiss and Bird 1964 (p.1110)

systems (Steele, 1974 p.32). Table 5.10 shows the values of the physical constants used in the calculation of $E_g(z^*)$

$$z^* = (1/5)^{1/6} \quad r^* = (1/5)^{1/6} (r_1 + r_2) \quad (5.33)$$

where r_1 is half the interplanar spacing of a graphite lattice and r_2 is half the equilibrium separation of the gas molecule (table 5.3). Table 5.11 gives values of $-E(z^*)/R$ calculated using

$$E(z^*) = \frac{\bar{n} m c^2}{24\pi \epsilon_0 N_A z^{*3}} \frac{\alpha_1 \alpha_2}{(\alpha_1/\chi_1) + (\alpha_2/\chi_2)} \quad (5.34)$$

in comparison with the values for carbon black P.33 obtained by Halsey and his coworkers obtained using a 3-9 potential and the Kirkwood-Müller expression. The calculated values of $-E(z^*)/R$ are of the same order as the values obtained for graphitised carbon P.33. Differences in order (i.e. the calculated values of $E(z^*)/R$ for H_2 and D_2 are less than the value for Ne, whereas the experimental values of $-E(z^*)/R$ show a lower value for Ne than for either H_2 or D_2) may be accounted for by differences in the physical constants used in calculation. Figures 5.20 and 5.21 show the plots of $\tilde{K}_0(M/T)^{1/2}$ against the calculated values and the literature values of $-E_g(z^*)/RT$ respectively. The resulting curves are qualitatively similar in shape to curves predicted by Nicholson and Petropoulos (1975 (b), 1979, to be published) by both their molecular path tracing approach and their Monte-Carlo calculations. Nicholson and Petropoulos plot J_∞/J_g against $-E(z^*)/RT$ and obtain a temperature minimum, where J_g is the flux of a non-adsorbed gas. J_g is proportional to $(T/M)^{1/2}(\Delta C'_g/l)$ hence at the limit of zero pressure J_∞/J_g is proportional to $\tilde{K}_0(M/T)^{1/2}$. The permeability minimum is thus a consequence of the adsorbent force field within the pores. Without complex numerical computation it is difficult to compare directly Nicholson and Petropoulos molecular path tracing approach with the experimental results. The model

Table 5.10 Physical Constants Used in Evaluation
of $E_g(z^*)$ and B.

Atom or Molecule	$\frac{10^{16}\alpha}{\text{cm}^2\text{V}^{-1}\text{mol}^{-1}}$	$\frac{-10^{10}\chi}{\text{m}^3\text{mol}^{-1}}$	$\frac{10^{10}z^*}{\text{m}}$
He	0.136	0.24	2.386
Ne	0.263	0.85	2.478
Ar	1.090	2.45	2.748
Kr	1.647	3.52	2.830
Xe	2.681	5.41	3.021
H ₂	0.538	0.50	2.554
D ₂	0.519	0.50	2.546
N ₂	1.162	1.51	2.861
CO ₂	1.739	2.64	2.996
CH ₄	1.73	2.19	2.921
C ₂ H ₆	2.900	3.44	3.177
C ₃ H ₈	4.34	5.09	3.453
C	0.684	2.87	-

$r_1 = 1.675 \times 10^{-10} \text{ m}$ (Lipson and Stokes, 1942)

$\bar{n} = 1.04 \times 10^{29}$ molecules (calculated from the Helium density of Sterling S).

The α values for He, D₂ and C₃H₈ were taken from values tabulated by Moelwyn-Hughes (1961); Hirschfelder, Curtiss and Bird (1964, p. 947), Ross and Olivier, (1964) respectively. The remaining values were from Ash, Barrer, Clint, Dolphin and Murray (1973).

χ values for He, D₂ and C₃H₈ were calculated from values tabulated by Foex (1957). The remaining values come from Ash, Barrer, Clint, Dolphin and Murray (1973)

Table 5.11

Values of $E_g(z^*)/R$

Gas	$\frac{-E_g(z^*)}{K}$	
	Calculated using equation 5.34	For graphitised carbon P.33
He	217	-
Ne	550	382 (a)
Ar	1340	1107 (a)
Kr	1793	1460 (a)
Xe	2309	1919 (a)
H ₂	428	574 (b)
D ₂	429	579 (b)
N ₂	858	-
CO ₂	1256	-
CH ₄	1176	1483 (b)
C ₂ H ₆	1457	-
C ₃ H ₈	1684	-

(a) Sams, Constabaris and Halsey (1960)

(b) Constabaris, Sams and Halsey (1961)

Figure 5.20. Plot of $\tilde{K}_0 M^{1/2} T^{-1/2}$ versus $-E_s(z^*)/RT$.

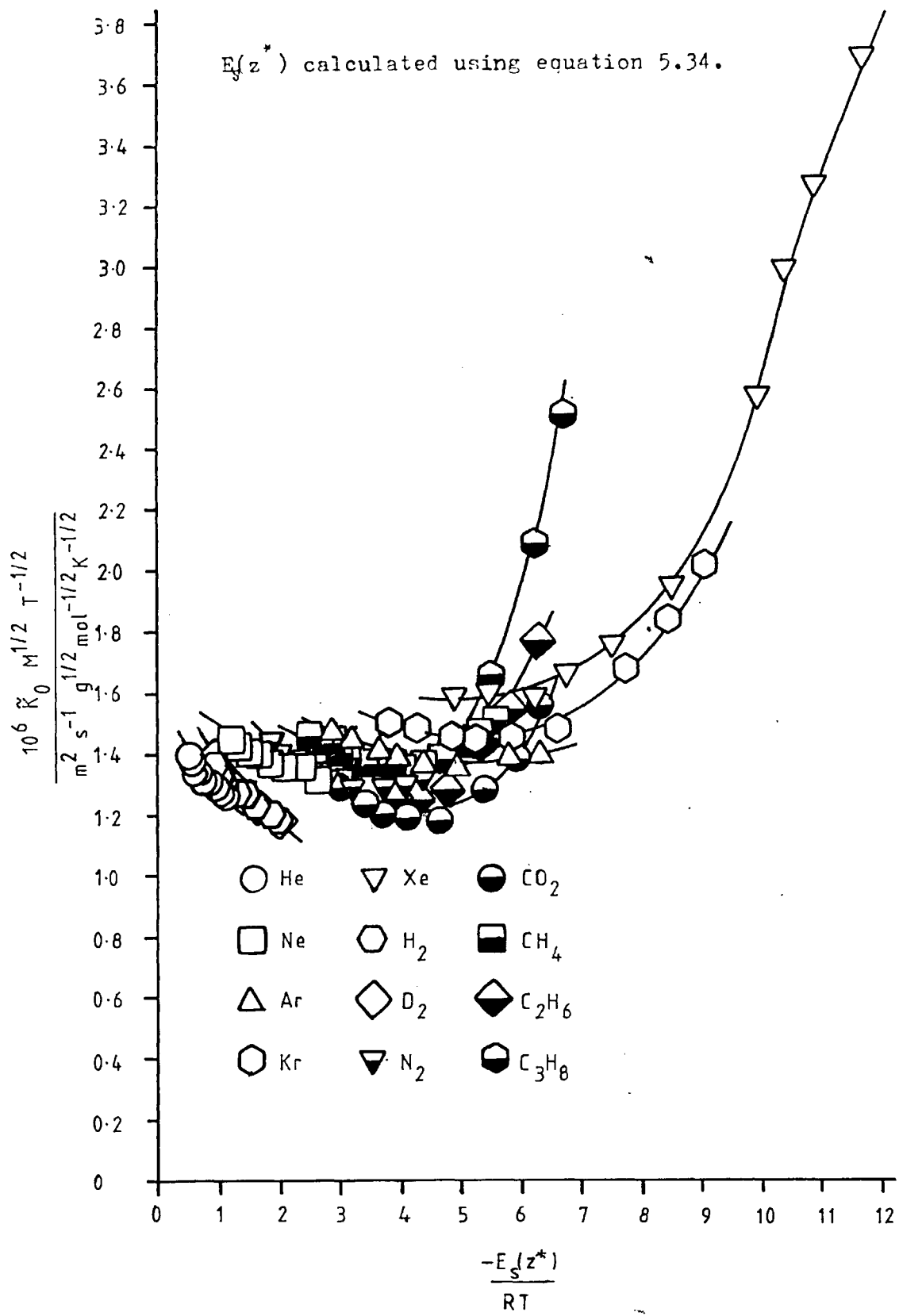
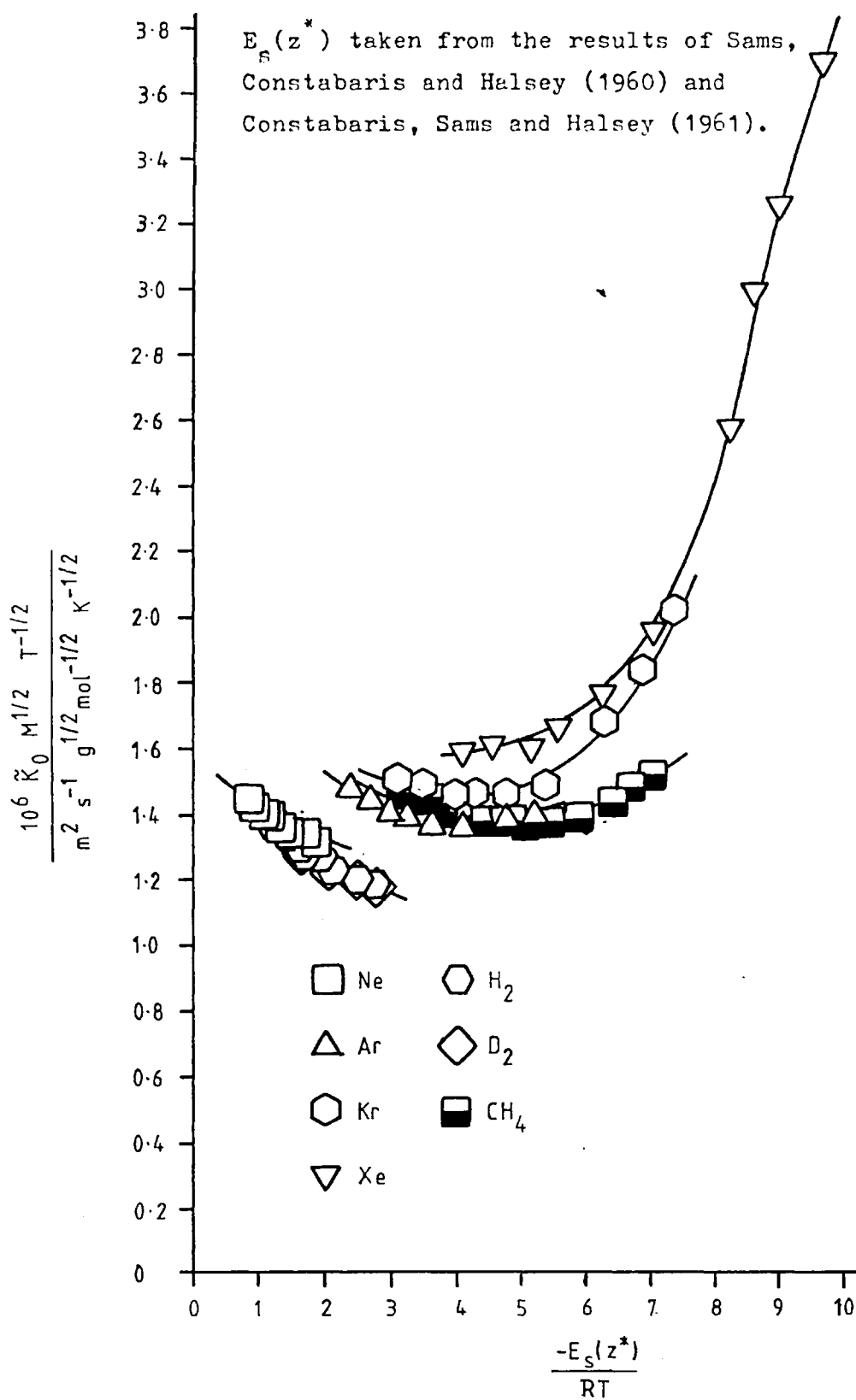


Figure 5.21. Plot of $\tilde{K}_0 M^{1/2} T^{-1/2}$ versus $-E_s(z^*)/RT$.



as has been pointed out by Nicholson and Petropoulos themselves, is simplistic (Nicholson and Petropoulos, to be published), but can lead to a more effective consideration of diffusion in relation to pore structure, surface heterogeneity and concentration dependence. There are nevertheless a number of inconsistencies between theoretical predictions and the experimental results still to be explained. According to Nicholson and Petropoulos (to be published) increasing r/z_0 (r is capillary radius and z_0 is the separation between adsorbate and adsorbent corresponding to zero potential) causes the minimum to broaden continuously, getting deeper at first, but then becoming shallower. The lowest value of the minimum J_∞/J_g occurring at $2r/z_0 \approx 10$ for the 9-3 potential. With the experimental results the hydrocarbons show as predicted a broadening of the minimum as z_0 gets smaller, the results for the noble gases also are not inconsistent with this trend (figures 5.20). It is difficult to find any trend for the depth of the minimum considering the gases as a whole. The hydrocarbons show the well depth increasing with decreasing z_0 , as do the results for the noble gases. However, such an effect is only predicted for $2r/z_0 \lesssim 10$ and for this work $2r/z_0 > 250$ (taking $r = 2\epsilon/A = 4.79 \times 10^{-8} \text{ m}$). This is difficult to explain, but no calculations have been made at such high values of $2r/z_0$. Also for a real porous medium the pores will not be cylindrical with a circular cross-section and consideration of a network would be an improvement on the simple model. Such calculations are, however, complex and require considerable computer time.

The model can be used to explain why negative extra flow can be obtained when the helium calibration procedure is used (Nicholson and Petropoulos, to be published). This is shown with the results of hydrogen, deuterium, carbon dioxide, nitrogen, ethane and propane. The change of gas from helium corresponds chiefly to an increase in $-E_s(z^*)$ (and only secondarily to a decrease r/z_0). Hence on the high temperature side of its minimum $\tilde{K}_0 (M/T)^{1/2}$ for helium can

exceed the value for other molecules.

There are problems in interpretation but the similarity between the shapes of the experimental curves and theoretical plots of Nicholson and Petropoulos is very marked.

5.4. COMPARISON BETWEEN RESULTS FOR MEMBRANE 1 AND MEMBRANE 2- THE EFFECT OF INCREASED COMPRESSION.

There are only a limited number of temperatures studied for membrane 2 with consideration being given to only two gases: helium and carbon dioxide. The results should, therefore, be interpreted with a degree of caution. Nevertheless each value of $\tilde{K}_0(M/T)^{\frac{1}{2}}$ is obtained from between 9 and 17 permeability measurements over an ingoing pressure range of 0.2 to 18 cm Hg.

The pressure dependence of the permeability of both helium and carbon dioxide is small. This is clear from the results tabulated in appendices C1 and C2, also from the linearity of the J_∞ versus p_0 plots in figures 4.20 and 4.21.

According to classical theory (see equation 2.55 for example) in the Knudsen flow regime.

$$\tilde{K}_0 \left(\frac{M}{T} \right)^{\frac{1}{2}} = K_k \frac{8}{3} \frac{\epsilon^2}{A} \left(\frac{2R}{\pi \phi} \right)^{\frac{1}{2}} \quad (5.35)$$

hence $\tilde{K}_0(M/T)^{\frac{1}{2}}$ is proportional to $K_k \epsilon^2/A$. If R_K is given by

$$R_K = \frac{[\tilde{K}_0 (M/T)^{\frac{1}{2}}]_{\text{Membrane 1}}}{[\tilde{K}_0 (M/T)^{\frac{1}{2}}]_{\text{Membrane 2}}} \quad (5.36)$$

in the Knudsen flow regime

$$R_K = \frac{K_{k1} \epsilon_1^2}{K_{k2} A_1} \frac{A_2}{\epsilon_2^2} \quad (5.37)$$

The subscripts 1 and 2 refer to membrane 1 and 2 respectively. If the structure factor is assumed to be the same for both membranes R_K is equal to 3.81. It would be expected that R_K would approach the classical limit as $T \rightarrow \infty$, but at 473.2K, the highest temperature studied R_K for helium equals 5.09. The difference between the two values of R_K is partly accounted for by K_k being different for the two membranes and partly by

deviations from the classical theory.

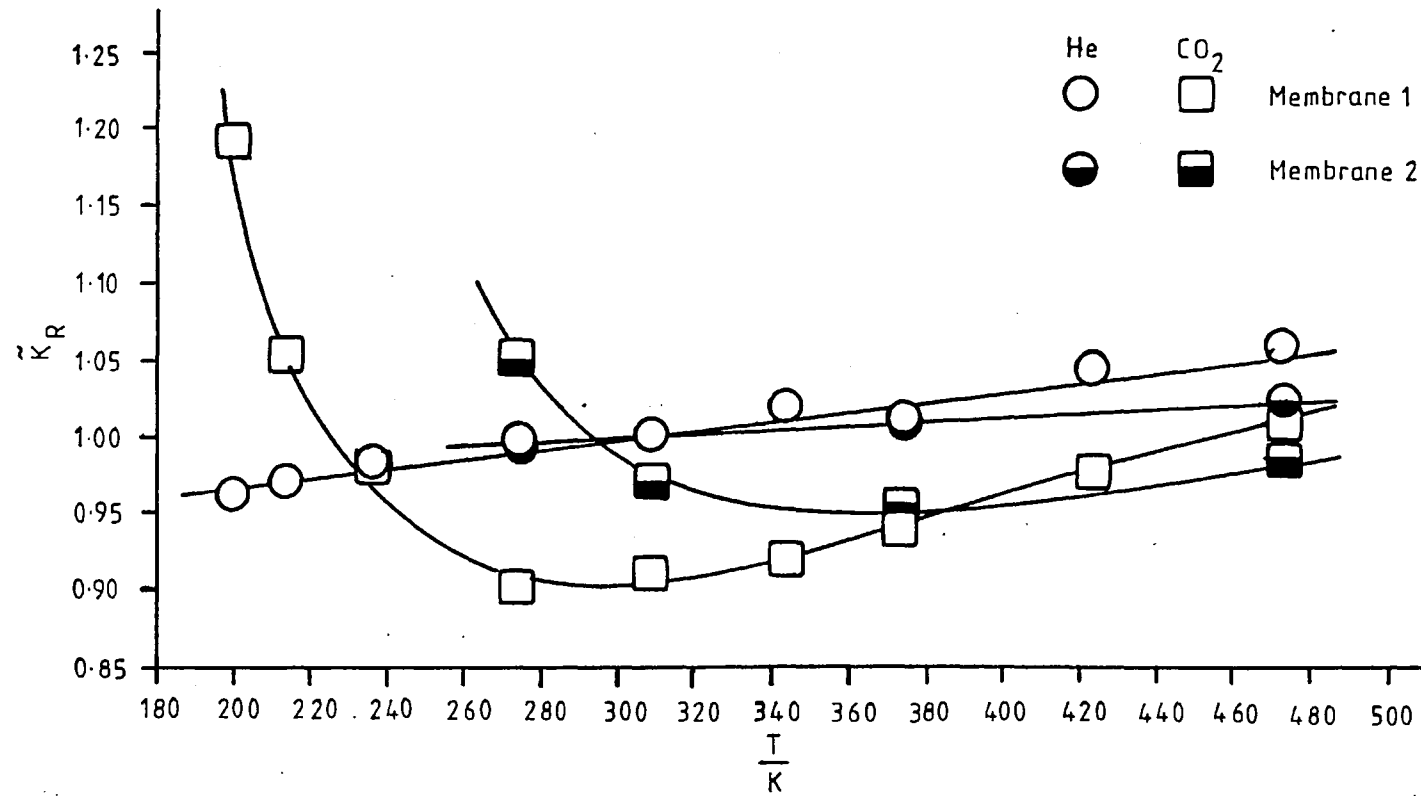
As with membrane 1 the flow results for membrane 2 show $\tilde{K}_O(M/T)^{\frac{1}{2}}$ for helium decreasing with temperature and carbon dioxide shows a temperature minimum. Figure 5.22 is a comparison of the results for membrane 1 and the results for membrane 2. The ratio $\tilde{K}_R$ is given by

$$\tilde{K}_R = \frac{\tilde{K}_O (M/T)^{\frac{1}{2}}}{[\tilde{K}_O (M/T)^{\frac{1}{2}}]_{\text{He, 308.2K}}} \quad (5.38)$$

When the two membranes are compared the $\tilde{K}_R$ values for helium lie very close together. The results for carbon dioxide fall in with the theoretical predictions of Nicholson and Petropoulos (1975 (b), 1979, to be published) in that the minimum shifts to higher temperatures (lower values of $-E_s(z^*)/RT$ as the pore radius decreases. The value of $\tilde{K}_O(M/T)^{\frac{1}{2}}/(\tilde{K}_O(M/T)^{\frac{1}{2}})_{T \rightarrow \infty}$ at the minimum would also be expected to decrease for a smaller pore radius. It is difficult to come to any conclusions on that point since the limit of $\tilde{K}_O(M/T)^{\frac{1}{2}}$ at infinite temperature is not available.

The shifting of the minimum to higher temperatures with decreasing radius may also explain the apparent anomaly between the results for Sterling S and the results for other carbon black membranes such as Graphon, Black Pearls and Carbolac. These latter three carbons have a higher surface area than Sterling S. For a constant porosity the hydraulic radius would be smaller so it would be expected that the effect of adsorption forces would be greater. The anomaly which is apparent at first sight is that flow results for Graphon, Black Pearls and Carbolac do not show temperature minima or decreasing values of $\tilde{K}_O(M/T)^{\frac{1}{2}}$ for helium with temperature (see for example Ash, Barrer and Lowson, 1970; Ash, Barrer, Clint, Dolphin and Murray, 1973; Hamilton, 1980). This "apparent anomaly" can be explained if the minimum is shifted to higher temperatures with decreasing radius. With the Sterling S membranes (large hydraulic radii compared with other

Figure 5.22. Comparison between Results for Membrane 1
and Results for Membrane 2.



carbon membranes) either the descending region of the $\tilde{K}_O(M/T)^{\frac{1}{2}}$ curve is observed or the region of the minimum. On the other hand for the other carbon blacks, due to the shifting of the minimum to higher temperatures (lower $-E_g(z^*)/RT$), a broad flat helium minimum or for other gases the region where $\tilde{K}_O(M/T)^{\frac{1}{2}}$ is ascending with decreasing temperature is being observed.

5.5. IMPLICATIONS FOR GAS SEPARATION

The enrichment (or separation) factor, η_{AB} for component A in a binary gas mixture A and B is defined (Ash, Barrer and Foley, 1976)

$$\eta_{AB} \equiv \left(\frac{C'_g A}{C'_g B} \right)_{x=1} \left(\frac{C'_g B}{C'_g A} \right)_{x=0} \quad (5.39)$$

where $C'_g A$ and $C'_g B$ are the gas phase concentrations of components A and B respectively. For steady state isothermal flow the enrichment factor becomes (Ash, Barrer and Lowson, 1973)

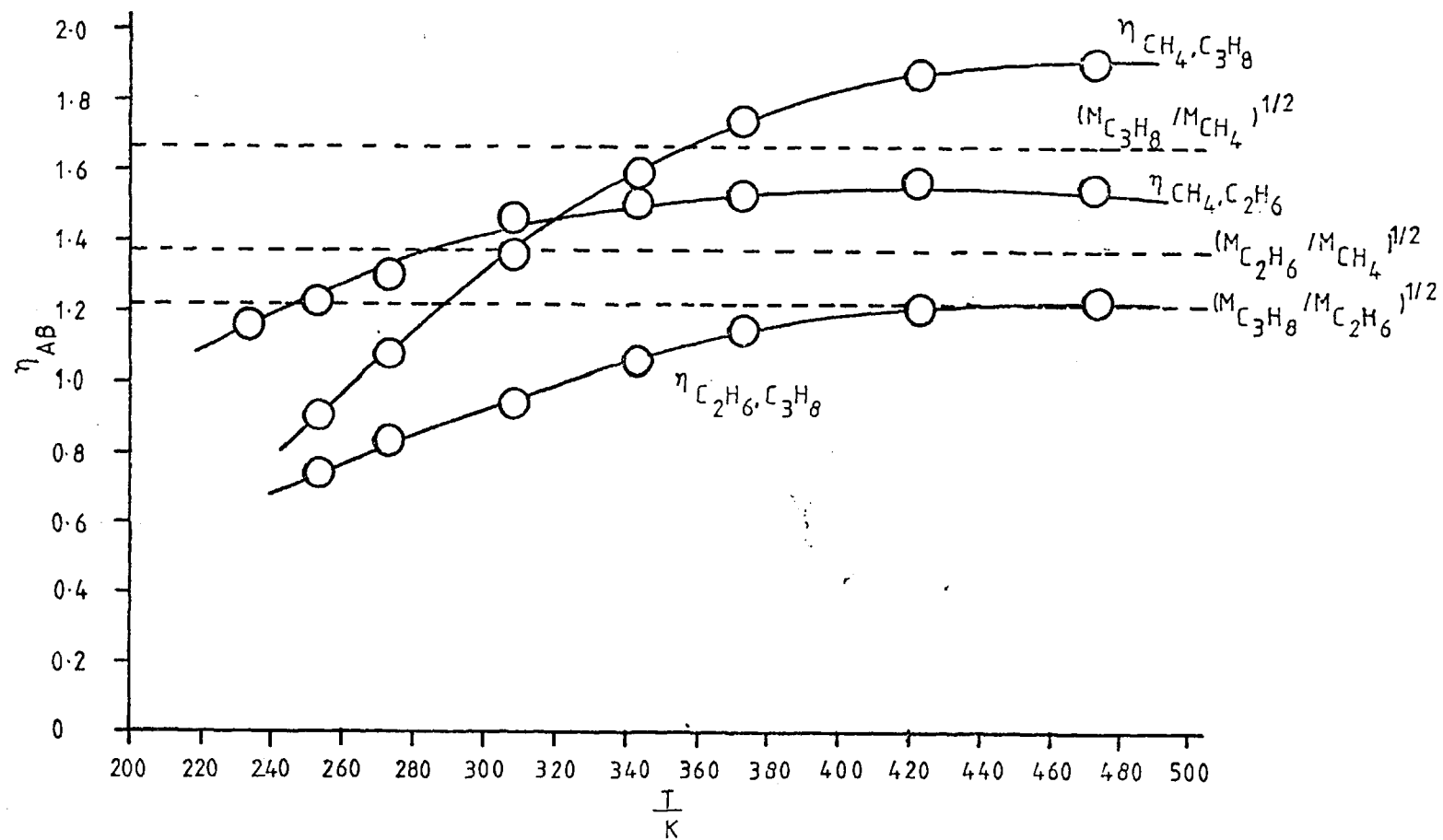
$$\eta_{AB} = \frac{\tilde{K}_A}{\tilde{K}_B} \quad (5.40)$$

For pure Knudsen flow conditions

$$\eta_{AB} = \left(\frac{M_B}{M_A} \right)^{\frac{1}{2}} \quad (5.41)$$

Figure 4.17 shows a plot of $\tilde{K}_O/T^{\frac{1}{2}}$ against temperature of the three hydrocarbons studies. As has been pointed out (section 4.3.4) $\tilde{K}_O/T^{\frac{1}{2}}$ for propane lies below that of both methane and ethane at high temperatures whereas at low temperatures $\tilde{K}_O/T^{\frac{1}{2}}$ for propane is greater than for the other two gases. This implies that in any gas mixture of propane and one of the other hydrocarbons at low temperatures the mixture will be enriched with propane after permeation through a Sterling S membrane. At high temperatures the concentration of propane will be reduced. This effect is clearly shown in figure 5.23

Figure 5.23. Enrichment Factors for Various Binary Hydrocarbon Gas Mixtures as Functions of Temperature.



where the enrichment factors (as calculated from equation 5.40) for three hydrocarbon mixtures: methane and ethane; methane and propane; ethane and propane, are plotted as functions of the membrane temperature. The Knudsen enrichment factors are also shown for comparison. For the methane-ethane mixture and for the methane-propane mixture at low temperatures the heavier gas is enriched on the outgoing side of the membrane to a greater extent than is predicted for Knudsen flow conditions (without an adsorbent potential field), whereas at high temperatures the lighter gas is enriched. An enhanced enrichment of the heavier gas at lower temperatures is well known and has been recorded or predicted for a number of binary gas systems flowing through porous media such as: benzene-methanol vapours; benzene-ethanol vapours (Hagerbaumer and Kammermeyer, 1954); oxygen-carbon dioxide (Hwang and Kammermeyer, 1966 (a)); methane-propane (Hwang and Kammermeyer, 1966 (b)); hydrogen-sulphur dioxide (Ash, Barrer and Pope, 1963 (b)). These are the first systems where enhanced enrichment can be predicted for both the lighter gas and the heavier gas of the mixture depending on the temperature of the membrane. The temperature at which the enrichment factor is equal to unity has been described as the "azeotropic point" by Hwang and Kammermeyer (1966 (b)), it is the temperature at which there is no separation.

The above analysis assumes that there is no interaction between the two permeating gases constituting the mixture. Various experimental studies have shown that the flow is indeed the same for gases in mixtures as it is for a single gas where both of the gases are weakly adsorbed (Aylmore and Barrer, 1968; Ash, Barrer and Lowson, 1973). For more strongly adsorbed gases blockage effects occur (Ash, Barrer and Lowson, 1973; Ash, Barrer and Sharma, 1976; Hamilton 1980), blockage even occurring in the Henry Law region (Hamilton, 1980). Experimental determinations of the flow of binary hydrocarbon gas mixtures through Sterling S should be carried out before it can be assumed that no interaction between the gas components

is occurring.

The separation of hydrocarbon gas is of interest in the purification of natural gas.

5.6. APPLICATION OF THE HELIUM CALIBRATION METHOD

The helium calibration method is the method of using helium as a non-adsorbed gas to assess the extra flow of adsorbed gases. But as has already been pointed out for membrane 1 (section 5.3.4) some gases (hydrogen, deuterium, carbon dioxide, nitrogen, ethane and propane) have values of $\tilde{K}_0(M/T)^{\frac{1}{2}}$ less than the corresponding value for helium over all or part of the temperature range studied. This is also shown by the results for membrane 2. If the helium calibration method were used as it has come to be used in the literature negative values for the extra flow would be obtained. In addition there is the problem that $\tilde{K}_0(M/T)^{\frac{1}{2}}$ for helium also varies with temperature so that either the value at a standard temperature would have to be used in the helium calibration method or a different value would have to be taken, a value which would depend on the temperature under consideration. There are also a number of other problems with the helium calibration method referred to in section 2.6.

(a) Not all the extra or "surface" flow can be attributed to the adsorbed phase, because there are some evaporative flights.

(b) There is a blocking effect which leads to a reduction of the gas phase flow.

The division of the flow into a "gas-phase" flow and an extra flow should thus be avoided.

CHAPTER 6

SUMMARY AND RECOMMENDATIONS FOR FURTHER WORK

The isothermal flow of a large number of gases through a membrane (membrane 1) made to a porosity of 0.524 from graphitised carbon black called Sterling S has been studied. The boundary conditions were chosen so that the permeabilities were measured by a steady-state flow technique.

The membrane was conditioned by increasing the outgassing temperature in 50K intervals from 373K to 573K. It was found that the permeabilities increased with increasing outgassing temperature.

The flow was studied over the membrane temperature range of 198K to 473K. Only the most strongly adsorbed gases (xenon, ethane and propane) exhibited permeabilities which were significantly pressure dependent. At 213.2K the permeability of xenon diminished with increasing pressure. For ethane (at 253.2K and 233.2K) and propane (at 273.2K) the permeability in contrast increased with increasing pressure. At 253.2K the propane permeabilities showed a pressure maximum.

The main thrust of the work was in consideration of the temperature dependence of the permeabilities of the various gases studied. Permeability in this case refers to the value of the permeability extrapolated to zero pressure ($\tilde{K}_0$). All the gases studied exhibited a temperature dependent $\tilde{K}_0(M/T)^{\frac{1}{2}}$ in contrast to what is predicted by classical equations obtained by Knudsen and others. For helium, neon, hydrogen and deuterium $\tilde{K}_0(M/T)^{\frac{1}{2}}$ decreased with decreasing temperature, for xenon $\tilde{K}_0(M/T)^{\frac{1}{2}}$ increased with decreasing temperature. All the remaining gases (argon, krypton, nitrogen, carbon dioxide, methane, ethane and propane) showed a temperature minimum for $\tilde{K}_0(M/T)^{\frac{1}{2}}$. Equations derived by Hwang and Kammermeyer (1966(a)), who assumed an activated surface diffusion model, and Sandler (1972), who introduced forces of interaction into a dusty gas model, were found to be inadequate. The results showed a qualitative similarity to predicted

permeability curves obtained by Nicholson and Petropoulos (1975 (b), 1979) using a molecular path tracing analysis.

A second more highly compressed Sterling S membrane (membrane 2) made to a porosity of 0.321 was used to study the isothermal steady-state flow of helium and carbon dioxide. The temperature dependence of $\tilde{K}_O(M/T)^{\frac{1}{2}}$ was similar to that of membrane 1. The results were again consistent with predictions of Nicholson and Petropoulos.

The temperature dependence of the permeabilities has a number of consequences. From the point of view of gas separation there is a possibility that at low temperatures the gas mixture can be enriched (that is enriched to a greater extent than then enrichment if flow was in the Knudsen regime) with the heavier gas after permeation through the porous medium. Whereas at higher temperatures the mixture can be enriched with the lighter gas on the upstream side of the membrane.

For some gases over all or part of the temperature range studied the value for $\tilde{K}_O(M/T)^{\frac{1}{2}}$ was less than the corresponding value for helium. This and the temperature dependence of $\tilde{K}_O(M/T)^{\frac{1}{2}}$ for helium means that the helium calibration method is unsuitable for assessing the extra flow.

The helium density and the B.E.T. surface area of Sterling S have been determined.

There are a number of directions in which further work can proceed. It would be interesting if theoretical calculations could be made along the lines of the molecular path tracing method proposed by Nicholson and Petropoulos (1975; 1979; to be published; Nicholson, Petrou and Petropoulos, 1979). Computations should be made using a pore radius and interaction potentials consistent with Sterling S. Initial calculation could be made for a single capillary and then perhaps extended to a network of capillaries. Further experimental work could be carried out on Membrane 2 by studying the flow of other gases and extending the temperature range. Other Sterling S membranes could be

prepared of different porosities. Adsorption measurements could be carried out on Sterling S employing the gases used in the flow studies at various temperatures; within the temperature range at which the permeation measurements were made. Ideally adsorption isotherms should be measured on the membrane used for the flow studies.

Sterling S has a surface area lower than other graphitised carbons previously used in transport studies, but there are other carbon blacks such as Sterling FT and Sterling MT which have still lower surface areas. These latter two carbons could be used in a similar study programme to this work.

There is much scope for the study of the flow of binary gas mixtures through carbon membranes, from the point of view of separation of gas mixtures.

The temperature dependence of $\tilde{K}_0(M/T)^{\frac{1}{2}}$ for gases flowing through Sterling S, would make it an interesting material for parallel studies of isothermal and non-isothermal flow. The results could be analysed in terms of the theoretical work of Nicholson and Petropoulos (1981) and the work of Ash, Barrer and Foley; Ash and Rizvi (to be published).

APPENDIX A: NITROGEN ADSORPTION ISOTHERM DATA.

All pressures quoted have been corrected to be consistent with the density of mercury at 273.2K.

A.1: Adsorption Isotherm 1.

T — K	P_0 — cm Hg	p — cm Hg	$\frac{p}{P_0}$	v — $\text{cm}^3_{\text{stp}} \text{g}^{-1}$
77.4	76.000	0.008	0.0001	0.445
		0.011	0.0001	0.814
		0.018	0.0002	1.862
		0.050	0.0007	3.467
		0.480	0.0063	4.763
		1.660	0.0218	5.189
		2.928	0.0385	5.304
		3.884	0.0511	5.383
		5.498	0.0723	5.500
		6.304	0.0829	5.556
		7.178	0.0944	5.614
		8.354	0.1099	5.697
		9.938	0.1308	5.820
		11.646	0.1532	5.990
		13.102	0.1724	6.150
		14.551	0.1915	6.315
		15.290	0.2012	6.413

A.2: Adsorption Isotherm 2.

T — K	P_0 — cm Hg	p — cm Hg	$\frac{p}{P_0}$	v — $\text{cm}^3_{\text{stp}} \text{g}^{-1}$
77.4	76.000	0.023	0.0003	1.116
		0.022	0.0003	2.415
		0.051	0.0003	3.666
		0.673	0.0089	4.931
		0.706	0.0093	4.923
		3.492	0.0459	5.364
		4.145	0.0545	5.417
		4.954	0.0650	5.472
		5.690	0.0749	5.524
		6.469	0.0851	5.579
		7.337	0.0972	5.655
		8.813	0.1160	5.757
		10.415	0.1370	5.893
		11.820	0.1555	6.021
		13.097	0.1723	6.170
		14.272	0.1878	6.311
		15.861	0.2087	6.539
		17.286	0.2274	6.780
		17.988	0.2367	6.931
		19.636	0.2584	7.266
		21.091	0.2775	7.600
		22.436	0.2952	7.915
		24.292	0.3196	8.360
		26.070	0.3430	8.777
		27.993	0.3683	9.191
		30.767	0.4048	9.692

APPENDIX B: FLOW DATA FOR MEMBRANE 1.

1. Outgassing trials.
2. Helium flow results.
3. Neon flow results.
4. Argon flow results.
5. Krypton flow results.
6. Xenon flow results.
7. Nitrogen flow results.
8. Hydrogen flow results.
9. Deuterium flow results.
10. Methane flow results.
11. Ethane flow results.
12. Propane flow results.
13. Carbon Dioxide flow results.
14. Helium permeability checks.

B.1: Outgassing Trials

The plug temperature for all measurements is 308.15K.

T_{OG} is the outgassing temperature, p_0 is the mean ingoing pressure corrected to the mercury density at 273 K.

T_{OG} K	Gas	Experiment number	p_0 cm Hg	$10^6 \frac{\tilde{K}}{m^2 s^{-1}}$
373	Helium	2	1.362	10.73
		1	6.613	10.70
		3	8.124	10.75
		8	9.020	10.76
		Mean		10.74
	Neon	12	1.386	4.84
		4	5.272	4.89
		5	14.201	4.87
		Mean		4.87
	Argon	14	1.453	3.21
		10	2.178	3.25
		9	8.834	3.26
		11	20.965	3.25
		Mean		3.24
	Methane	13	1.245	4.89
		6	10.958	4.82
		7	14.235	4.92
		Mean		4.88
423	Helium	15	2.031	10.82
		16	3.463	10.75
		27	10.402	10.84
		Mean		10.80
	Neon	17	1.685	4.88
		18	3.334	4.91
		19	5.086	4.86
		Mean		4.88
	Argon	20	1.469	3.29
		21	4.016	3.29
		22	7.502	3.27
		Mean		3.28
	Methane	26	1.275	5.11
		23	1.407	5.02
		24	4.303	4.99
		25	12.602	4.99
		Mean		5.03
473	Helium	28	1.093	10.97
		29	9.721	10.94
		30	14.012	10.96
		Mean		10.96
	Neon	31	1.847	5.00
		32	8.191	4.99
		33	15.318	4.98
		Mean		4.99

B.1 (continued).

$\frac{T_{OG}}{K}$	Gas	Experiment number	$\frac{p_0}{\text{cm Hg}}$	$\frac{10^6 \tilde{\kappa}}{\text{m}^2 \text{ s}^{-1}}$
473	Argon	34	1.236	3.37
		35	7.263	3.36
		36	13.328	3.35
		Mean		3.36
	Methane	37	1.685	5.11
		38	7.778	5.04
		39	12.798	5.13
		Mean		5.09
523	Helium	40	1.224	11.35
		55 (a)	3.621	11.35
		55 (b)	3.625	11.50
		55 (c)	3.615	11.39
		42	3.166	11.39
		41	9.703	11.36
		Mean		11.39
	Neon	43	0.802	5.20
		44	4.498	5.30
		54 (a)	5.527	5.24
		54 (b)	5.527	5.25
		54 (c)	5.529	5.29
		45	8.166	5.20
		46	9.708	5.23
		Mean		5.24
	Argon	47	0.939	3.55
		48	6.423	3.60
		49 (a)	9.704	3.62
		49 (b)	9.704	3.63
		49 (c)	9.702	3.60
		Mean		3.60
	Methane	50	2.990	5.49
		53 (a)	4.727	5.55
		53 (b)	4.726	5.53
		53 (c)	4.728	5.54
		51	9.543	5.50
		52	11.195	5.52
		Mean		5.52

B. 1. (continued)

For the results after outgassing at 573K, see tables, B.2, B.3, B.4, and B.10 for helium, neon, argon and methane respectively. The mean permeabilities have been extracted and are given below.

Gas	$10^6 \frac{\bar{K}}{\text{m}^2 \text{ s}^{-1}}$
Helium	11.68
Neon	5.40
Argon	3.84
Methane	6.15

H.2: Helium Flow Results.

T — K	Experiment number	p_0 — cm Hg	$10^6 \tilde{\kappa}$ — $m^2 s^{-1}$	$10^3 J_\infty$ — $mol s^{-1}$
198.9	390	1.725	8.80	0.924
	389	3.455	8.91	1.874
	388	5.347	8.97	2.924
	387	6.624	9.05	3.650
213.2	257	1.318	9.42	0.974
	256	3.094	9.31	1.637
	255	4.730	9.32	2.506
	254	6.787	9.40	3.625
233.2	148	1.292	9.94	0.667
	147	2.000	10.05	1.045
	149	4.280	9.81	2.183
	144	6.574	9.94	3.395
273.2	120	1.111	10.93	0.539
	119	1.737	10.92	0.841
	118	3.609	10.85	1.736
	121	5.772	10.83	2.771
	117	8.712	10.95	4.231
	116	14.404	10.88	6.949
	115	19.531	10.92	9.458
	114	28.643	10.97	13.93
308.2	60	1.798	11.60	0.819
	56	2.564	11.59	1.168
	61	4.032	11.60	1.839
	62	5.344	11.56	2.428
	57	7.538	11.71	3.469
	63	11.121	11.59	5.065
	59	14.798	11.76	6.839
	58	18.620	11.77	8.618
	66	23.049	11.78	10.67
	65	27.165	11.71	12.51
	64	32.924	11.78	15.25
343.2	171	1.052	12.55	0.469
	168	2.430	12.47	1.069
	170	4.360	12.55	1.932
	169	6.409	12.46	2.819

B.2 (Continued)

T — K	Experiment number	n_0 — cm Hg	$10^6 \frac{\eta}{\eta^2}$ — s ⁻¹	$10^3 J_\infty$ — mol s ⁻¹
373.2	124	1.320	13.04	0.559
	111	2.068	12.90	0.886
	123	3.570	13.01	1.507
	122	4.820	12.97	2.029
	110	7.935	12.90	3.323
	109	13.963	12.99	5.883
	112	20.131	13.05	8.526
	113	27.825	13.06	11.88
423.2	217	1.856	14.27	0.758
	216	3.427	14.22	1.395
	215	5.192	14.12	2.098
	214	6.844	14.21	2.863
473.2	229	1.813	15.11	0.701
	228	2.770	15.29	1.085
	227	4.486	15.23	1.749
	226	6.756	15.25	2.639

B.3: Neon Flow Results.

T — K	Experiment number	p_0 — cm Hg	$10^6 \frac{\eta}{K}$ — $\frac{m^2}{s^{-1}}$	$10^8 \frac{J_\infty}{mol. s^{-1}}$
213.2	261	1.612	4.34	0.447
	260	3.141	4.26	0.761
	259	5.073	4.26	1.229
	258	6.802	4.29	1.660
233.2	155	1.672	4.67	0.405
	154	3.053	4.62	0.735
	153	4.748	4.63	1.142
	152	6.461	4.61	1.547
273.2	125	1.863	4.99	0.413
	131	2.448	5.01	0.544
	130	3.761	5.07	0.645
	129	5.397	5.01	1.200
	128	9.185	4.97	2.024
	127	13.214	5.01	2.936
	126	19.086	5.06	4.29
308.2	79	1.525	5.37	0.322
	78	3.326	5.36	0.701
	87	4.779	5.42	1.018
	77	6.239	5.37	1.318
	86	9.500	5.38	2.010
	85	11.015	5.40	2.336
	82	15.562	5.41	3.31
	84	17.030	5.44	3.64
	81	20.151	5.44	4.31
	83	21.127	5.42	4.50
	80	26.020	5.43	5.55
343.2	175	1.287	5.86	0.266
	174	2.827	5.80	0.579
	173	4.360	5.78	0.882
	172	5.811	5.78	1.186
373.2	179	1.531	6.21	0.309
	178	3.216	6.01	0.628
	177	4.549	6.04	0.892
	176	6.435	6.03	1.270
423.2	221	1.905	6.53	0.356
	220	3.873	6.56	0.729

B. 3 (continued)

T — K	Experiment number	p_0 — cm Hg	$10^6 \tilde{\kappa}$ — $m^2 s^{-1}$	$10^3 J_\infty$ — $mol s^{-1}$
423.2	219	5.269	6.50	0.931
	218	6.871	6.59	1.296
473.2	225	1.663	7.01	0.293
	224	3.462	7.01	0.627
	223	4.659	7.00	0.836
	222	6.536	7.03	1.185

T — K	Experiment number	p_0 — cm Hg	$10^5 \bar{K}$ — $m^2 s^{-1}$	$10^8 J_\infty$ — $mol s^{-1}$
213.2	265	1.750	3.20	0.320
	264	3.481	3.22	0.637
	263	4.911	3.25	0.907
	262	6.510	3.24	1.200
233.2	159	1.569	3.37	0.275
	158	3.066	3.37	0.538
	157	4.676	3.37	0.819
	156	6.259	3.35	1.090
273.2	135	1.634	3.55	0.237
	134	2.473	3.53	0.387
	133	4.069	3.56	0.642
	132	6.681	3.55	1.052
308.2	76	1.494	3.82	0.224
	75	2.847	3.86	0.433
	74	5.123	3.81	0.767
	73	7.032	3.81	1.054
	72	8.886	3.85	1.346
	71	11.475	3.76	1.696
	70	15.061	3.83	2.27
	69	20.212	3.87	3.07
	68	25.479	3.90	3.91
	67	27.760	3.89	4.25
343.2	187	1.250	4.09	0.181
	186	3.189	4.11	0.462
	185	4.808	4.11	0.697
	184	6.312	4.11	0.917
373.2	183	1.866	4.29	0.260
	182	2.668	4.33	0.375
	181	4.231	4.32	0.593
	180	6.583	4.30	0.919
423.2	245	1.893	4.71	0.255
	244	3.937	4.74	0.534
	243	5.040	4.74	0.683
	242	6.511	4.77	0.889
473.2	233	2.143	5.09	0.279
	232	3.579	5.09	0.466
	231	5.234	5.10	0.690
	230	6.413	5.10	0.837

T — K	Experiment number	p_0 — cm Hg	$10^6 \tilde{\kappa}$ — $m^2 s^{-1}$	$10^8 J_\infty$ — mol.s ⁻¹
199.0	593	1.537	3.04	0.285
	595	2.160	3.00	0.394
	596	3.662	3.16	0.702
	599	4.335	3.15	0.831
	597	5.301	3.11	1.004
	600	6.804	3.15	1.310
213.2	269	1.795	2.83	0.294
	268	3.365	2.97	0.568
	267	5.278	2.90	0.870
	266	6.385	2.93	1.063
233.2	160	1.069	2.80	0.155
	161	3.280	2.79	0.475
	162	4.172	2.78	0.604
	163	6.134	2.79	0.839
273.2	136	1.584	2.72	0.191
	137	3.594	2.68	0.427
	139	4.191	2.71	0.504
	138	6.145	2.70	0.736
308.2	91	1.303	2.82	0.144
	92	2.231	2.82	0.252
	89	3.174	2.77	0.346
	93	5.293	2.79	0.580
	94	9.208	2.81	1.024
	95	10.976	2.83	1.220
	96	14.761	2.82	1.637
	97	18.551	2.84	2.06
	98	22.071	2.83	2.46
	90	27.051	2.85	3.04
343.2	188	1.869	2.96	0.195
	189	2.874	2.96	0.300
	190	3.745	2.96	0.391
	191	5.443	2.97	0.571
	195	5.102	3.05	0.506
373.2	193	1.739	3.10	0.175
	194	3.239	3.07	0.322

B.5: (Continued)

T — K	Experiment number	p_0 — cm Hg	$10^6 \tilde{\kappa}$ — $\text{m}^2 \text{s}^{-1}$	$10^8 J_\infty$ — mol s^{-1}
373.2	195	5.102	3.05	0.506
	196	6.183	3.08	0.619
423.2	239	1.815	3.35	0.174
	240	4.027	3.35	0.387
	241	5.164	3.35	0.495
	238	6.699	3.35	0.643
473.2	234	2.099	3.59	0.193
	236	3.533	3.61	0.327
	235	4.675	3.62	0.434
	237	6.795	3.57	0.621

B. 6: Xenon Flow Results.

T — K	Experiment number	p_0 — cm Hg	$10^6 \frac{\dot{W}}{K}$ — $m^2 s^{-1}$	$10^8 \frac{J_{\infty}}{K}$ — $mol s^{-1}$
198.4	601	0.764	4.56	0.213
	602	1.576	4.63	0.447
	603	2.561	4.55	0.712
	604	3.983	4.49	1.091
	605	5.428	4.51	1.495
	606	6.756	4.53	1.866
213.2	287	0.870	4.17	0.206
	280	1.266	4.10	0.295
	286	1.667	4.09	0.389
	285	2.062	4.06	0.478
	607	2.366	4.13	0.555
	281	3.034	4.06	0.701
	282	4.968	3.98	1.124
	608	5.810	4.00	1.320
	284	6.694	3.95	1.501
223.2	609	1.393	3.96	0.299
	611	2.754	3.90	0.583
	612	4.086	3.90	0.864
	613	4.837	3.85	1.011
	610	6.573	3.88	1.384
	614	6.772	3.91	1.438
233.2	164	1.757	3.46	0.315
	165	3.400	3.45	0.610
	166	4.528	3.38	0.795
	167	6.246	3.41	1.106
273.2	140	1.457	2.80	0.181
	143	2.839	2.80	0.353
	141	3.653	2.82	0.456
	142	5.578	2.81	0.696
308.2	99	1.192	2.68	0.127
	100	2.277	2.71	0.243
	101	3.553	2.72	0.378
	102	6.140	2.71	0.655
	104	8.628	2.70	0.914
	105	11.423	2.71	1.216
	106	15.368	2.71	1.644
	107	19.008	2.71	2.03

B.6. (Continued)

T — K	Experiment number	p_0 — cm Hg	$10^6 \tilde{\kappa}$ — $m^2 s^{-1}$	$10^8 J_\infty$ — $mol s^{-1}$
308.2	108	23.162	2.72	2.47
	103	27.456	2.72	2.93
343.2	201	1.300	2.70	0.124
	202	2.421	2.70	0.231
	203	4.249	2.69	0.403
	204	6.018	2.68	0.570
373.2	197	1.478	2.72	0.131
	198	2.620	2.66	0.227
	199	4.002	2.68	0.348
	200	5.906	2.71	0.519
423.2	246	1.251	2.89	0.174
	247	2.428	2.90	0.387
	248	4.701	2.89	0.495
	249	6.517	2.87	0.643
473.2	253	1.253	3.00	0.096
	252	2.655	3.00	0.205
	251	5.220	3.03	0.403
	250	6.561	3.04	0.511

B. 7: Hydrogen Flow Results.

T — K	Experiment Number	p_0 — cm Hg	$10^6 \tilde{\kappa}$ — $m^2 s^{-1}$	$10^8 J_\infty$ — mol s^{-1}
213.2	291	1.526	12.14	1.053
	290	3.261	12.20	2.262
	289	4.747	12.24	3.302
	288	6.241	12.27	4.351
233.2	303	1.613	12.88	1.079
	302	3.884	12.85	2.593
	301	5.185	13.02	3.507
	300	7.124	13.14	7.124
273.2	277	1.437	14.25	0.908
	276	3.562	14.30	2.259
	275	5.386	14.26	3.407
	274	6.976	14.32	4.431
308.2	356	1.483	15.57	0.908
	355	3.195	15.76	1.980
	354	4.709	15.30	2.926
	353	5.765	15.67	3.552
343.2	357	1.645	16.89	0.981
	358	3.004	16.73	1.774
	359	4.618	16.68	2.719
	360	6.458	16.72	3.811
373.2	342	1.488	17.71	0.856
	341	2.824	17.83	1.635
	344	5.017	17.62	2.871
	343	6.552	17.84	3.795
423.2	349	2.245	19.43	1.249
	350	3.501	19.37	1.941
	351	4.961	19.42	2.758
	352	6.235	19.34	3.451
473.2	348	1.910	20.97	1.025
	347	3.766	20.94	2.019
	346	5.455	20.90	2.919
	345	6.518	21.08	3.518

B. 8: Deuterium Flow Results.

T — K	Experiment number	p_0 — cm Hg	$10^6 \frac{\dot{V}}{K}$ — $\frac{m^3}{m^2 s}^{-1}$	$10^8 \frac{J_m}{\dot{V}}$ — $\frac{mol}{mol s}^{-1}$
213.2	295	1.750	8.56	0.351
	294	3.329	8.67	1.641
	293	4.926	8.62	2.414
	292	6.810	8.61	3.334
233.2	299	1.224	9.17	0.584
	298	3.231	9.12	1.530
	297	4.866	9.16	2.315
	296	6.483	9.30	3.133
273.2	319	1.644	10.08	0.735
	318	3.917	10.07	1.749
	317	5.647	10.08	2.525
	316	7.093	10.18	3.202
308.2	340	1.595	11.10	0.695
	339	3.360	11.09	1.464
	338	4.696	11.15	2.058
	337	6.597	11.09	2.877
343.2	320	2.205	11.97	0.932
	321	3.267	11.89	1.371
	322	4.984	11.96	2.105
	323	5.910	11.95	2.492
373.2	333	1.995	12.58	0.815
	334	3.176	12.71	1.311
	335	5.586	12.65	2.293
	336	6.959	12.70	2.868
423.2	327	1.539	13.74	0.605
	326	3.110	13.92	1.239
	325	4.960	13.86	1.968
	324	6.216	13.94	2.480
473.2	328	1.815	15.18	0.705
	329	3.272	15.26	1.278
	330	5.378	14.99	2.064
	331	6.584	15.10	2.546

B. 9: Nitrogen Flow Results.

T — K	Experiment number	p_0 — cm Hg	$10^6 \frac{\eta}{m^2 s^{-1}}$	$10^8 \frac{J_s}{mol s^{-1}}$
199.4	386	1.882	3.53	0.404
	385	4.675	3.49	0.992
	384	5.662	3.53	1.222
	383	6.766	3.53	1.449
213.2	311	1.995	3.65	0.414
	310	3.983	3.59	0.813
	309	5.429	3.55	1.096
	308	6.528	3.67	1.360
233.2	307	1.476	3.71	0.285
	306	3.333	3.74	0.647
	305	5.158	3.76	1.008
	304	6.297	3.76	1.230
273.2	270	1.833	4.08	0.331
	271	3.726	4.03	0.666
	272	5.848	4.08	1.059
	273	6.416	4.05	1.153
308.2	377	2.039	4.46	0.357
	378	3.187	4.39	0.550
	379	4.542	4.39	0.733
	380	5.817	4.46	1.021
343.2	361	1.842	4.62	0.300
	362	3.560	4.75	0.598
	363	4.759	4.74	0.797
	364	6.403	4.81	1.086
373.2	359	1.845	5.08	0.304
	370	3.472	5.02	0.566
	371	4.959	5.07	0.817
	372	6.437	5.08	1.062
423.2	368	1.619	5.41	0.251
	367	3.471	5.50	0.546
	366	5.146	5.52	0.814
	365	6.210	5.52	0.918

B.9. (Continued)

T — K	Experiment number.	p_0 — cm Hg	$10^6 \kappa$ — $m^2 s^{-1}$	$10^3 J_\infty$ — $mol s^{-1}$
473.2	376	2.103	5.94	0.320
	375	3.547	6.03	0.547
	374	5.106	5.93	0.775
	373	6.216	5.96	0.949

B. 10: Carbon Dioxide Flow Results.

T — K	Experiment number.	p_0 — cm Hg	$10^6 \frac{\dot{V}}{K}$ — m ³ s ⁻¹	$10^3 J_{\infty}$ — mol s ⁻¹
199.3	591	1.689	3.29	0.339
	592	2.863	3.31	0.576
	593	5.111	3.32	1.031
	594	6.567	3.39	1.355
213.2	587	1.406	2.96	0.237
	590	1.527	3.06	0.265
	588	2.684	3.05	0.465
	589	4.039	3.08	0.707
233.2	583	1.567	2.88	0.235
	584	2.779	2.95	0.427
	585	4.335	2.94	0.662
	586	6.712	3.00	1.045
273.2	579	1.321	2.87	0.168
	580	2.820	2.93	0.366
	581	3.993	2.95	0.522
	582	6.355	2.98	0.840
308.2	558	1.153	3.26	0.148
	559	2.467	3.15	0.305
	560	4.740	3.18	0.592
	561	6.119	3.16	0.761
343.2	562	1.299	3.37	0.154
	563	2.583	3.35	0.306
	564	4.178	3.44	0.507
	565	6.050	3.39	0.723
373.2	566	1.469	3.45	0.165
	567	2.573	3.59	0.300
	568	4.350	3.64	0.515
	569	5.690	3.63	0.671
423.2	570	1.643	4.03	0.190
	571	2.926	4.00	0.335
	572	4.439	4.03	0.517
	573	6.300	4.04	0.728

T — K	Experiment number	p_0 — cm Hg	$10^6 \tilde{\kappa}$ — $m^2 s^{-1}$	$10^3 J_\infty$ — mol s^{-1}
473.2	574	1.486	4.31	0.164
	575	2.474	4.46	0.292
	578	3.757	4.40	0.423
	576	4.176	4.46	0.477
	579	6.445	4.40	0.727

3.11: Methane Flow Results.

T — K	Experiment Number	p_0 — cm Hg	$10^6 \frac{\eta}{K}$ — $\frac{m^2}{s^{-1}}$	$10^3 J_\infty$ — $\frac{mol}{s^{-1}}$
213.2	442	1.840	5.51	0.576
	440	2.736	5.55	0.359
	441	4.208	5.56	1.322
	443	5.359	5.56	1.843
223.2	444	1.620	5.45	0.480
	445	2.885	5.53	0.866
	446	4.391	5.55	1.322
	447	5.151	5.55	1.552
233.2	448	1.965	5.49	0.561
	438	3.075	5.44	0.869
	439	5.130	5.51	1.469
	449	6.602	5.54	1.902
253.2	450	2.357	5.44	0.613
	451	3.281	5.46	0.856
	452	5.368	5.54	1.424
	453	6.282	5.55	1.668
273.2	454	1.712	5.64	0.428
	436	2.521	5.55	0.621
	437	4.668	5.55	1.150
	455	7.033	5.74	1.791
293.2	456	1.758	5.82	0.423
	457	2.893	5.78	0.691
	458	5.435	5.83	1.309
	459	6.770	5.90	1.649
308.2	434	1.469	5.97	0.345
	460	2.872	6.01	0.678
	435	5.451	5.95	1.276
	461	7.403	6.09	1.772
323.2	462	1.589	6.11	0.364
	463	3.843	6.23	0.998
	464	5.908	6.16	1.365
	465	7.200	6.15	1.660

B.11 (continued)

T — K	Experiment number	$\frac{v_0}{\text{cm Hg}}$	$\frac{10^6 \tilde{\kappa}}{\text{m}^2 \text{ s}^{-1}}$	$\frac{10^3 J_\infty}{\text{mol s}^{-1}}$
343.2	432	1.643	5.36	0.367
	466	2.535	6.46	0.579
	433	5.138	6.25	1.134
	467	6.654	6.44	1.512
373.2	430	1.723	6.79	0.380
	468	3.535	6.79	0.780
	431	4.623	6.71	1.008
	469	6.426	6.70	1.399
383.2	428	2.079	6.88	0.452
	429	3.379	6.82	0.729
	470	4.655	6.92	1.018
	471	6.868	6.90	1.499
396.2	472	1.855	7.06	0.399
	426	3.672	6.93	0.774
	427	4.961	7.02	1.059
	473	6.969	7.09	1.503
423.2	424	2.177	7.41	0.462
	474	2.252	7.52	0.485
	425	4.051	7.32	0.849
	475	6.414	7.44	1.366
448.2	476	1.900	7.66	0.394
	477	3.678	7.61	0.757
	478	5.619	7.68	1.167
	479	7.290	7.70	1.517
473.2	422	1.998	7.97	0.408
	480	3.365	8.03	0.692
	423	4.622	7.90	0.935
	431	6.640	8.04	1.367

B.12: Ethane Flow Results.

T — K	Experiment number	p_0 — cm Hg	$10^6 \tilde{\kappa}$ — m ² s ⁻¹	$10^3 J_\infty$ — mol s ⁻¹
233.2	514	0.567	4.99	0.147
	513	0.860	4.96	0.222
	508	2.255	5.07	0.594
	509	3.336	5.19	1.048
	511	4.595	5.19	1.239
	510	5.919	5.31	1.633
	512	10.027	5.40	2.31
253.2	515	1.302	4.52	0.282
	516	2.232	4.57	0.483
	517	3.957	4.60	0.871
	518	6.652	4.70	1.495
273.2	504	2.136	4.31	0.409
	505	3.580	4.40	0.699
	506	5.529	4.34	1.064
	507	7.229	4.36	1.398
308.2	484	1.613	4.13	0.261
	485	2.796	4.20	0.461
	486	4.400	4.19	0.724
	487	5.811	4.12	0.942
343.2	488	2.101	4.30	0.319
	489	3.814	4.24	0.570
	490	4.703	4.27	0.703
	491	5.799	4.24	0.867
373.2	492	1.829	4.36	0.259
	493	2.836	4.37	0.402
	494	4.399	4.40	0.628
	495	5.962	4.45	0.861
423.2	496	1.387	4.86	0.193
	497	3.349	4.78	0.458
	498	4.367	4.77	0.596
	499	5.512	4.77	0.752
473.2	500	2.261	5.12	0.297
	501	3.238	5.15	0.427
	502	5.229	5.18	0.694
	503	6.201	5.20	0.825

B. 13: Propane Flow Results.

T — K	Experiment number	p_0 — cm Hg	$10^6 \tilde{\kappa}$ — $\text{m}^2 \text{s}^{-1}$	$10^3 J_\infty$ — mol s^{-1}
253.2	549	0.527	6.21	0.157
	547	1.160	6.39	0.354
	543	1.551	6.48	0.481
	550	2.154	6.61	0.682
	548	2.597	6.78	0.842
	544	3.540	6.77	1.146
	545	4.518	6.71	1.450
	546	5.627	6.61	1.780
273.2	555	0.902	5.27	0.211
	539	1.533	5.25	0.357
	540	2.549	5.31	0.600
	553	3.117	5.49	0.759
	552	3.389	5.54	0.830
	551	3.738	5.44	0.902
	541	4.297	5.45	1.040
	554	5.571	5.54	1.369
	542	6.520	5.47	1.582
308.2	535	1.503	4.45	0.263
	536	2.575	4.33	0.438
	537	4.412	4.43	0.768
	538	6.733	4.43	1.171
343.2	531	1.366	4.05	0.195
	532	2.798	3.99	0.394
	533	4.402	3.94	0.612
	534	6.165	4.02	0.876
373.2	527	1.998	3.83	0.248
	528	4.051	3.82	0.502
	529	5.189	3.85	0.648
	530	6.260	3.93	0.799
423.2	523	1.370	4.06	0.159
	524	2.492	3.91	0.279
	525	4.000	4.03	0.461
	526	6.064	3.97	0.689
473.2	519	1.418	4.27	0.155
	520	3.415	4.21	0.368
	521	4.908	4.23	0.531
	522	6.570	4.22	0.710

B.14: Helium Permeability Checks.

Experiment number	T — K	p_0 — cm Hg	$10^6 \tilde{K}$ — $m^2 s^{-1}$	$10^8 J_3$ — $mol s^{-1}$	$\tilde{K}$ — $\tilde{K}_i$
145	273.2	2.817	10.90	1.361	1.001
146	273.2	2.391	10.95	1.161	1.006
150	273.2	3.305	10.89	1.597	1.000
151	273.2	2.786	10.93	1.351	1.004
205	343.2	5.493	12.34	2.393	0.989
206	343.2	3.773	12.19	1.623	0.977
207	343.2	3.449	12.15	1.479	0.974
211	343.2	4.676	12.35	2.038	0.990
212	343.2	4.561	12.44	2.003	0.997
213	343.2	4.126	12.47	1.816	0.999
278	273.2	5.506	10.82	2.642	0.994
279	273.2	5.173	10.84	2.487	0.995
312	233.2	4.986	9.86	2.555	0.996
313	233.2	4.639	9.90	2.386	1.000
314	213.2	4.350	9.33	2.306	0.998
315	213.2	4.071	9.42	2.180	1.007
381	308.2	4.534	11.70	2.086	1.009
382	308.2	4.305	11.66	1.974	1.006
407	308.2	6.598	11.70	3.034	1.009
408	308.2	6.213	11.63	2.840	1.003
409	308.2	4.618	11.76	2.134	1.015
410	308.2	4.358	11.70	2.004	1.009
482	308.2	3.027	11.73	1.395	1.012
483	308.2	2.988	11.76	1.381	1.015
556	308.2	3.180	11.74	1.467	1.013
557	308.2	4.815	11.74	2.222	1.013

The $\tilde{K}_i$ values are equal to the values of $\tilde{K}_0$ for helium tabulated in table 4.3, but for convenience the relevant values are also given below:

T — K	$10^6 \tilde{K}_i$ — $m^2 s^{-1}$
213.2	9.35
233.2	9.90
273.2	10.89
308.2	11.59
343.2	12.48

APPENDIX C: FLOW DATA FOR MEMBRANE 2

1. Helium flow results.
2. Carbon Dioxide flow results.

C.1: Helium Flow Results.

T — K	Experiment number	p_0 — cm Hg	$10^7 \frac{\bar{K}}{m^2 s^{-1}}$	$10^9 \frac{J_\infty}{mol s^{-1}}$
273.2	54 (2)	0.343	22.20	0.307
	55 (2)	2.054	22.20	1.840
	56 (2)	3.843	22.08	3.424
	57 (2)	6.461	21.93	5.729
	58 (2)	8.174	21.95	7.239
	59 (2)	10.174	21.87	8.981
	60 (2)	11.440	22.15	10.22
308.2	11 (2)	0.778	23.35	0.651
	10 (2)	1.175	23.68	0.995
	9 (2)	1.737	23.43	1.498
	8 (2)	2.476	23.44	2.076
	7 (2)	3.332	23.50	2.801
	6 (2)	4.065	23.44	3.408
	5 (2)	4.830	23.74	4.101
	2 (2)	5.648	23.66	4.780
	1 (2)	6.523	23.57	5.500
	14 (2)	7.796	23.59	6.579
	13 (2)	9.236	23.43	7.757
	4 (2)	10.577	23.54	8.907
	3 (2)	10.782	23.68	9.133
	12 (2)	11.903	23.53	10.02
373.2	27 (2)	0.205	26.11	0.158
	22 (2)	1.659	26.30	1.289
	19 (2)	2.240	26.16	1.731
	21 (2)	2.397	25.92	2.219
	20 (2)	3.773	25.93	2.394
	64 (2)	4.815	26.54	3.775
	63 (2)	6.686	26.42	5.217
	62 (2)	8.900	26.40	6.941
	61 (2)	11.422	26.38	8.901
473.2	95 (2)	1.265	30.07	0.886
	18 (2)	2.321	29.69	1.605
	17 (2)	3.881	29.37	2.655
	94 (2)	5.624	30.07	0.886
	16 (2)	5.917	29.13	4.015

C.1:(continued)

T — K	Experiment number	p_0 — cm lig	$10^7 \tilde{\kappa}$ — m ² s ⁻¹	$10^9 J_\infty$ — mol s ⁻¹
473.2 (cont,)	17 (2)	7.592	29.46	5.210
	93 (2)	8.061	30.59	5.745
	92 (2)	10.345	30.45	7.338
	91 (2)	11.764	30.41	8.333

C. 2: Carbon Dioxide Flow Results.

T — K	Experiment number	p_0 — cm Hg	$10^7 \tilde{\kappa}$ — m ² s ⁻¹	$10^9 J_w$ — mol s ⁻¹
273.2	65 (2)	0.557	7.05	0.158
	66 (2)	0.929	6.93	0.259
	73 (2)	1.526	6.88	0.424
	72 (2)	1.603	7.13	0.461
	67 (2)	1.928	6.88	0.535
	71 (2)	2.603	7.09	0.745
	68 (2)	3.196	7.06	0.910
	69 (2)	4.122	7.05	1.173
	70 (2)	6.170	7.02	1.747
	79 (2)	7.412	7.03	2.102
	74 (2)	9.842	7.01	2.630
	75 (2)	11.230	7.03	3.186
	78 (2)	13.671	7.04	3.826
	77 (2)	15.422	7.05	4.39
	76 (2)	17.523	7.04	4.98
303.2	41 (2)	0.616	7.02	0.155
	53 (2)	0.853	6.89	0.210
	46 (2)	0.872	6.86	0.214
	37 (2)	1.106	6.86	0.271
	42 (2)	1.576	6.37	0.387
	38 (2)	2.328	6.82	0.568
	43 (2)	3.626	6.81	0.883
	44 (2)	4.905	6.81	1.194
	45 (2)	6.028	6.85	1.477
	47 (2)	7.027	6.85	1.721
	40 (2)	8.334	6.93	2.066
	48 (2)	9.431	6.93	2.337
	49 (2)	10.685	6.93	2.649
	39 (2)	12.074	6.94	2.995
	52 (2)	13.429	6.93	3.326
	51 (2)	15.461	6.93	3.83
	50 (2)	17.848	6.94	4.43
373.2	34 (2)	0.278	7.66	0.063
	28 (2)	0.562	7.57	0.126
	33 (2)	0.745	7.67	0.169
	29 (2)	1.126	7.44	0.247
	36 (2)	1.188	7.49	0.263
	24 (2)	1.739	7.60	0.390
	35 (2)	2.399	7.32	0.519
	25 (2)	3.305	7.48	0.730
	26 (2)	4.754	7.46	1.047
	23 (2)	6.548	7.39	1.430
	32 (2)	8.406	7.39	1.836
	31 (2)	10.147	7.40	2.217
	30 (2)	12.228	7.39	2.669

C. 2 (continued)

T — K	Experiment number	p_0 — cm Hg	$10^7 \frac{\eta}{K}$ — $m^2 s^{-1}$	$10^9 \frac{J_\infty}{\eta}$ — mol s^{-1}
473.2	90 (2)	0.764	8.92	0.159
	80 (2)	1.404	8.75	0.286
	81 (2)	2.553	8.68	0.516
	82 (2)	3.939	8.59	0.788
	83 (2)	5.226	8.60	1.043
	84 (2)	6.834	8.58	1.366
	85 (2)	8.110	8.56	1.618
	86 (2)	9.829	8.59	1.967
	89 (2)	12.338	8.71	2.605
	88 (2)	15.045	8.71	3.054
	87 (2)	17.898	8.70	3.628

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