STUDIES IN GASEOUS THERMAL DIFFUSION

A THESIS

presented for the

DIPLOMA of IMPERIAL COLLEGE

by

A.N. DAVENPORT

May 1952

ACKNOWLEDGMENT

The author's thanks are due to Professor H.V.A. Briscoe for putting at his disposal the research facilities of the Department of Inorganic and Physical Chemistry, Imperial College.

The author is particularly indebted to Dr. E.R.S. Winter for advice, encouragement, constructive criticism and practical help throughout the course of the work.

Of others who gave valuable assistance, special mention must be made of J.A. Barnard Esq., who carried out the many isotopic abundance measurements resulting from the oxygen exchange experiments, and of Dr. E. Pitts whose mathematical advice eased the theoretical investigation described in Chapter 8.

Finally, the author wishes to record his sincere thanks for financial support during his stay at Imperial College so willingly given by his father.

A. N. Davenport.

ABSTRACT

The simpler formulae that have been proposed for representing the forces between spherical non-polar molecules in the gaseous state are outlined. Certain expressions derived with their use from the results of the detailed kinetic theory for calculating the properties of pure gases and their mixtures, and required in the later treatment are then given.

Thermal diffusion constants have been measured for the separation of isotopic species in pure carbon monoxide, nitrogen and methane using a two-bulb apparatus: the results are compared with the corresponding theoretical values, obtained using the Lennard-Jones 13:7 intermolecular force model, and in the cases of nitrogen and methane, with those found by previous experimenters. Reasonable agreement between the theoretical and the new experimental values was found for all three gases studied, thus providing further evidence for the suitability of this force law as a means for predicting the thermal diffusion effect in isotopic gas mixtures.

The Furry-Jones theory of the thermal diffusion separating column and the semi-empirical modifications thereof proposed subsequently are described. In particular, the equations of Drickamer and co-workers used for treating the results obtained with rare-gas mixtures in precisely constructed columns are criticised, it being shown that their data may be explained

almost exactly in terms of the unmodified theory.

The construction, operation and performance of a concentric-tube separating column are described and discussed in the light of the theory. Both carbon monoxide and nitrogen were studied and fairly good agreement with theory found in each case. The transport coefficients used by Furry and Jones to describe the processes occurring in separating columns have been evaluated for the present apparatus by a new method based on the Lennard-Jones 13:7 model as well as with the usual formulae derived for the less realistic Maxwellian case. The similarity found between the results of the two methods provides the first theoretical justification for the use of the approximate equations when considering real gases.

The exchange between oxygen gas and magnesium and zinc oxides at high temperatures has been studied in an attempt to obtain values for the diffusion coefficient of oxygen ions in the solid phase. It was found that the surface of the silica reaction vessels employed became active and exchanged freely with the gas thereby vitiating the results.

CONTENTS

	PAGE
ACKNOWLEDGMENT	i
ABSTRACT	ii
CONTENTS	iv
LIST OF SYMBOLS	vii
" " TABLES and DIAGRAMS	ix
CHAPTER 1. INTRODUCTION	1
CHAPTER 2. DIFFUSION IN GASES - THEORY	
1. INTRODUCTION	5
2. INTERMOLECULAR FORCE LAWS	
a) The elastic sphere model	7
b) The inverse power model	8
c) The Sutherland model	9
d) The Lennard-Jones model	10
3. THE LENNARD-JONES 13:7 FORCE LAW	10
a) Diffusion	12
b) Viscosity	13
c) Thermal conductivity	13
d) Thermal diffusion	14
CHAPTER 3. DIFFUSION IN GASES - EXPERIMENTAL METHODS AND RESULTS	
1. SUMMARY OF AVAILABLE METHODS FOR DETERMINING THERMAL DIFFUSION CONSTANTS.	
a) The two bulb apparatus	16
b) The separating column	16
c) The diffusion thermo-effect	16
2. THEORY OF THE TWO-BULB APPARATUS	17
3. CALCULATION OF α FROM EXPERIMENTAL DATA	21
4. TEMPERATURE ALLOCATION OF EXPERIMENTAL THERMAL DIFFUSION CONSTANTS	22
5. PREVIOUS EXPERIMENTS WITH THE TWO-BULB APPARATUS	
a) Methane	27
b) Helium	30
c) Other gas mixtures	30

CHAPTER 4. THERMAL DIFFUSION CONSTANT MEASUREMENTS

1. APPARATUS AND METHOD 32
2. PREPARATION OF THE GASES
   a) Carbon monoxide 36
   b) Nitrogen 38
   c) Methane 39
3. COMBUSTION OF METHANE SAMPLES 41
4. MASS SPECTROMETER ANALYSIS 42
5. ALTERNATIVE METHODS OF EMPLOYING ANALYTICAL RESULTS 44
6. EXPERIMENTAL RESULTS 46
7. DISCUSSION OF RESULTS
   a) Carbon monoxide 49
   b) Nitrogen 50
   c) Methane 51
8. CONCLUSIONS 51

CHAPTER 5. THE THERMAL DIFFUSION COLUMN - THEORY

1. INTRODUCTION 54
2. THEORY OF THE SEPARATING COLUMN 55
3. EXPLICIT EQUATIONS FOR THE TRANSPORT COEFFICIENTS
   a) Solution for a small temperature difference 59
   b) Solution for Maxwellian molecules 60
   c) Other solutions 61
   d) The cylindrical case 61
4. CONSEQUENCES OF THE TRANSPORT EQUATION 62
5. EQUILIBRIUM TIME FOR A COLUMN 65
6. TURBULENCE 66

CHAPTER 6. SOME EXPERIMENTS WITH THERMAL DIFFUSION COLUMNS AND PROPOSED MODIFICATIONS OF THE FURRY-JONES THEORY

1. THE METHANE COLUMN OF NIER 68
2. THE SEMI-EMPIRICAL TREATMENT OF SIMON 71
3. THE WORK OF DRICKAMER AND COLLABORATORS
   a) The modified theory 73
   b) A new comparison with theory 77
   c) Discussion 80

CHAPTER 7. THE THERMAL DIFFUSION COLUMN - EXPERIMENTAL

1. DESCRIPTION OF THE COLUMN 83
2. AUXILIARY APPARATUS
   a) Carbon monoxide 84
   b) Nitrogen 85

3. EXPERIMENTAL PROCEDURE 85
4. RESULTS 86
5. A QUANTITATIVE TREATMENT OF THE COLUMN OPERATING CONDITIONS
a) Electrical heating and power consumption 87
b) Equilibrium time 91
c) Turbulence 92
6. CALCULATION OF THE TRANSPORT COEFFICIENTS AND COMPARISON BETWEEN THEORY AND EXPERIMENT 92

CHAPTER 8. A NEW METHOD OF EVALUATING THE TRANSPORT COEFFICIENTS

1. INTRODUCTION 96
2. TEMPERATURE VARIATION OF THE GAS PROPERTIES 96
3. SOLUTION FOR 'G' 101
4. COMPARISON WITH THE SIMPLE EXPRESSION 105
5. EVALUATION OF THE TRANSPORT COEFFICIENTS 106
6. COMPARISON WITH THE MAXWELLIAN EXPRESSIONS FOR THE TRANSPORT COEFFICIENTS 110
7. CONCLUSIONS 111

APPENDIX 113

REFERENCES 115

THE HIGH TEMPERATURE EXCHANGE BETWEEN OXYGEN AND METAL OXIDES

1. INTRODUCTION 117
2. PREPARATION OF THE OXYGEN 120
3. APPARATUS AND EXPERIMENTAL METHOD 123
4. RESULTS AND DISCUSSION 127
5. MEASUREMENT OF SURFACE AREAS 132
REFERENCES 137

PHOTOGRAPHS OF APPARATUS

LIST OF SYMBOLS

Only symbols of common occurrence are included; those also used by Hirschfelder, Bird and Spotz in reference [H3] are indicated thus:- [HBS]. Binary mixtures only are considered, the suffixes 1, 2 (denoted generally by i) being used to denote the lighter and heavier components respectively. Except where otherwise stated, the quantities are expressed in (c.g.s.) units.

logarithms to base 10 are written - lg, those to base e - ln.

A = $H/2K$, [HBS]

B = mean circumpherence, [HBS] = $\pi (r_1 + r_2)$

D or D_{11} = coeff. of self-diffusion

D_{12} = " " mutual "

D_T = " " thermal "

$E(r)$ = interaction energy at r

$E(o)$ = minimum $E(r)$ at r_o

F = force between moleculas

G or $G(T)$ - see equations (5-12/9)

H = horizontal diffusional transport coeff. [HBS]

K_d = vertical " " "

K_c = " convectional " "

K_p = parasitic " " "

K = $K_c + K_d + K_p$

L = length

M_i = molecular wt. of i

a, a') coeffs. of equations
b, b') = giving dependence of ln q_e on pressure.

c_i = concentration of i

$c_1 + c_2 = 1$

e = 2.718 ...

g = 981 cm.sec^{-2}

k = Boltzmann constant

k_T = thermal diffusion ratio

n = T-index of viscosity

P = pressure (atmospheres)

Q = heat flow

R = gas constant, Reynold's number, abundance ratio.

$R_T = \alpha / \alpha_{es}$

S = cross-sectional area

T = absolute temperature

T_1, T_2 = cold, hot bulb/wall temp.

$T_r, T_{13:7}$ = av. of T_1, T_2 for calc^{g} α.

V = volume, [HBS]

W = power (watts)

$W^{(\ )}(\ ;\ )$ = integrals[HBS]

q = separation factor

r = intermolecular distance

r_1, r_2 = radii of column walls

t = time

t_r = relaxation time

$u = (T_2 - T_1)(T_2 + T_1)$

v_i = vector convection velocity of i.

$v = c_1 v_1 + c_2 v_2$

$2w = (r_1 - r_2)$ = gap width

x, y, z = cartesian coordinates

Greek letters.

α = thermal diffusion constant

$\alpha_{es} = \alpha$ for elastic sphere model

$\beta = -(\partial \rho / \partial T)_p$

δ = T-index of diffusion

η = viscosity

θ = T-index of thermal conductivity

λ = thermal conductivity

ν, ν' = force indices

π = 3.1418...

ρ = density

TABLES and DIAGRAMS

Table No.		Page
	CHAPTER 2	
1	E(o)/k and r_o for various gases	12
	CHAPTER 3	
2	R_T etc. as a function of kT/E(o)	24
3	Calculation of $T_{13:7}$	26
	CHAPTER 4	
4	Relaxation times and other data for the two-bulb apparatus	35
5	α for the elastic sphere model	46
6	Results of the thermal diffusion constant measurements	47
7	Experimental thermal diffusion factors for nitrogen	50
8	Experimental thermal diffusion factors for methane	51
	CHAPTER 6	
9	Recalculation of transport coefficients for Nier's column	69
10	Carbon-dioxide - propane (Drickamer's results for-)	77
11-13	Argon-neon (Drickamer's results for-)	78
14	Drickamer column calculations	79
	CHAPTER 7	
15	Separating column results	87
16	Column heater wire data	89
17	Calculation of the transport coefficients	92/3
18	Equations for the least squares lines	94
19	Comparison between theory and experiment	94
	CHAPTER 8	
20	Quantities required for the evaluation of gas properties	99
21	Empirical equations for the gas properties	99
22	Comparison of exact and empirical equations for the gas properties	100
23	Temperature indices of viscosity	101
24	Calculation of G for nitrogen	104

25	Values of G for nitrogen	106
26	Data for evaluating the integrals in H and K_c	108
27	Transport coefficients	109
28	Maxwellian and L.J. 13:7 model transport coefficients	110
-	Surface areas of oxides	136

Figure No.		After Page No:-
1	R_T - temperature relationships	24
2	Thermal diffusion constant apparatus	35
3	Carbon monoxide preparation apparatus	35
4	Nitrogen preparation apparatus	35
5	Methane preparation and fractionation apparatus	39
6	Vapour pressure curves	39
7	Methane combustion apparatus	41
8-11	Drickamer's experimental results	78
12/3	Thermal diffusion column and auxiliary apparatus	83
14	Separating column results	87
15	The function G(T)	104
16	Differences between variously calculated G(T) values	104
I	Apparatus for electrolysis of heavy water	120
II	Apparatus for study of the exchange of oxygen with metal oxides	123
III-V	Results obtained with magnesium and zinc oxides	128
VI	Surface area apparatus	133
VII	B.E.T. plot for magnesium oxide	133

CHAPTER 1.

INTRODUCTION

Thermal diffusion is the effect whereby the application of a temperature gradient to a fluid mixture leads to a partial separation of its components. Usually the lighter species will concentrate in the hot region, the heavier in the cold. In the case of liquids the phenomenon has been known for many years as the Soret effect. The thermal diffusion of gases, however, was discovered relatively recently as a result of the independent theoretical investigations of Enskog and Chapman published in the years between 1911 and 1922 [E1, E2, C1]. It was Chapman who first reported with Dootson an experimental demonstration of the effect [C2] and suggested its potential use as a means of separating isotopes.

Enskog's general theory has been set out fully in the book by Chapman and Cowling [C3] which also contains an historical survey of the development of the kinetic theory of gases. The only recent advance in the fundamental theory has been its generalisation by Hellund and Uehling to include the effect of quantum statistics [H1, H2]. No quantitative data on the effect of the changes incurred have been published.

The general expressions obtained theoretically for the gas coefficients involve complex integrals which depend on the mode of interaction of the molecules. The coefficient of

thermal diffusion is particularly sensitive to the form of the equation used to represent this and so experimental studies of the effect should yield information about the intermolecular forces.

Until 1948 the integrals just referred to had not been evaluated for any force law sufficiently realistic to allow the quantitative prediction of thermal diffusion. In that year, however, Hirschfelder Bird and Spotz published the data required for using the Lennard-Jones 13:7 model which had already proved to be satisfactory in other connections [H3], and one of the principal aims of the present work has been to test the suitability of this force law as a means of predicting the thermal diffusion effect in isotopic gas mixtures.

There are two types of thermal diffusion apparatus; in the first the gas, as a whole, is at rest. The usual form consists of two bulbs maintained at different temperatures and connected by a vertical tube along which the diffusion processes take place. By making the upper bulb the hotter of the two no convection currents likely to cause remixing of the gas are set up. The equilibrium separation obtained in such a system is small, particularly for isotopic gas mixtures, and the apparatus is used solely for determining thermal diffusion constants.

The second design of apparatus was invented by Clusius and Dickel [C4] and combines the action of thermal diffusion with convection currents to obtain relatively enormous separations. The gas mixture is confined between two vertical

surfaces at different temperatures. The lighter component migrates by thermal diffusion towards the hotter wall and is carried to the top of the apparatus in the upward convective flow; similarly, the heavier component is concentrated at the bottom. The separation attainable is limited by the remixing effects of the convection currents and ordinary diffusion along the column. The original apparatus of Clusius consisted of an externally cooled glass tube down the centre of which was an electrically heated platinum wire; thermal diffusion took place radially. A common variant of this arrangement is the use of concentric metal tubes.

The present work is an extension of that carried out by Whalley [W1, W2, W3] who operated a concentric tube separating column thirty feet long to prepare oxygen enriched in the heavy isotope of mass 18 for use in tracer studies. Since no reliable method of obtaining the value of the thermal diffusion constant for oxygen was then available, Whalley determined this experimentally at temperatures suitable for the comparison of his column's performance with theory by the method originated by Nier [N1] when studying methane. In view of the disagreement between Nier's results and the predictions of the Lennard-Jones 13:7 force model, new measurements have been carried out and are reported here. Thermal diffusion factors have also been determined for carbon monoxide and nitrogen. A single value for the latter was published by Mann [M1] during the course of the present investigation.

A new column has been constructed having the same wall

dimensions as that of Whalley but of only one third its length. It was operated to provide data for a further comparison between experiment and theory, and was in fact unsuitable for use as a means of preparing quantities of isotopically enriched gas.

The theory of functioning of the thermal diffusion column has been worked out most completely by Furry Jones and Onsager. It is summarised in the review by Jones and Furry written in 1940 and published later [J1]. Semi-empirical modifications of their theory have been proposed by Simon [S1] and, more recently, by Drickamer [D1] who used accurately constructed columns as a means of measuring thermal diffusion factors for gas mixtures. Both of these extensions are considered later.

Up till the present, a function introduced by Furry, Jones and Onsager to describe the convection processes in a separating column has only been evaluated for the case of a gas whose molecules repel one another with a force proportional to the inverse fifth power of their separation. A method of calculation based on the more realistic Lennard-Jones 13:7 model is described later and used to treat the results presented in this thesis. It is shown that the difference between the new and customary methods is numerically small in the present case and, consequently, that use of the simpler Furry-Jones expressions is quite justifiable.

CHAPTER 2.

DIFFUSION IN GASES - THEORY

1. INTRODUCTION.

The kinetic theory of gases was originally based on the assumption that the molecules are indefinitely small perfectly elastic spheres moving independently of each other when not actually in collision. A gas of this kind is termed 'ideal' and obeys Boyle's and Charles' laws exactly. Thus :-

$$PV = RT \qquad (2 - 1)$$

where P is the pressure, V the volume, T the absolute temperature and R a universal constant. The behaviour of real gases cannot be represented by (2 - 1) with complete accuracy because molecules have a finite size and there are attractive and repulsive forces acting between them. However, for small molecules the departure from ideality at low pressures and fairly high temperatures is slight. During the nineteenth century several more elaborate equations of state for real gases were proposed, the most noteworthy being that of van der Waals [K1]. It is now more usual, however, to express experimental P-V-T data in series form:-

$$PV = RT\,[1 + B(T)/V + C(T)/V^2 + ...] \qquad (2 - 2)$$

where the functions of temperature B(T), C(T), etc., are called the second, third, etc., virial coefficients. By making an assumption as to the form of the intermolecular

forces, explicit expressions for these coefficients have been obtained which provide a means of testing the equation chosen for representing the force law against experimental data [H4, K2].

After the discovery by Maxwell and Boltzmann of the law governing the distribution of molecular velocities, expressions for gaseous diffusion, viscosity and thermal conductivity were derived by 'free path' arguments. The agreement with experiment was little better than qualitative; a strong dependence of the diffusion coefficient on the proportions of the inter-diffusing gases was predicted which is not in fact the case. The failure of these simple expressions was due to the application of an equation describing the equilibrium velocity distribution to phenomena which are essentially non-steady in nature.

In the exact theory, started by Maxwell, Boltzmann and others and which culminated in the work of Chapman and Enskog, the distribution of velocities is derived by the generalised summation of equations resulting from a detailed consideration of a binary collision. The gas molecules are considered as being spheres of finite size surrounded by spherically symmetrical force fields whose nature is unspecified. In actual fact, the theory holds quite well for non-spherical molecules, since their average shape in collision processes, assuming all orientations are equally probable, is spherical.

It was only as a result of the rigorous theory that thermal diffusion in gases was discovered. Elementary theories have subsequently been proposed which are in quite good

agreement with the exact treatment. Those of Gillespie [G1] and Fürth [F1] may be mentioned. The latter has been extended considerably by Whalley and Winter [W1, W4].

2. INTERMOLECULAR FORCE LAWS.

In all the simpler molecular models, the forces are assumed proportional to some power of the intermolecular distance r. This may be expressed by the general equation of Lennard-Jones [L1]:-

$$F = k/r^{\nu} - k'/r^{\nu'} \qquad (2 - 3)$$

The first term represents the repulsive force, ν being the force index; similarly k' and ν' denote the force of attraction between molecules. All the simple models are obtainable by insertion of appropriate values of the constants (k, ν) into (2 - 3).

a) The elastic sphere model.

No attractive forces act between the molecules (k' = o) and their behaviour on collision is perfectly elastic. Thus ν changes from infinity to zero when r becomes equal to the collision diameter. For elastic spheres, Furry Jones and Onsager showed that the thermal diffusion constant for a mixture of isotopic molecules is given by [J2]:-

$$\alpha_{es} = \frac{105}{118} \cdot \frac{M_2 - M_1}{M_2 + M_1} \qquad (2 - 4)$$

where M_1 is the molecular mass of the lighter and M_2 that of the heavier species. α_{es} is in fact the maximum possible value of the thermal diffusion constant and so experimental and theoretically obtained results are often expressed in

terms of a quantity R_T, defined by :-

$$R_T = \frac{\alpha(\text{exper. or theor.})}{\alpha_{es}} \qquad (2 - 5)$$

which enables comparison between data for different gas mixtures to be carried out more readily.

b) The inverse power model.

In equation (2 - 3), k' is zero. The molecules thus repel one another with a force proportional to the inverse ν th power of their separation. For this model, the following relationships hold for the gas properties:-

$$\begin{array}{ll} \text{(viscosity)} & \eta \propto T^n \\ \text{(thermal conductivity)} & \lambda \propto T^n \\ \text{(density x diffusion coeff.)} & \rho D \propto T^n \end{array} \qquad (2 - 6)$$

The temperature index n may be shown [K1, R1] to be related to the force index by the relation:-

$$\nu = \frac{(2n + 3)}{(2n - 1)} \qquad (2 - 7)$$

A suitable value for ν may therefore be obtained from experimental viscosity data over the appropriate temperature range.

For the inverse power case, the coefficient of self-diffusion is given by:

$$D = 6f(\nu)\eta/5\rho \qquad (2 - 8)$$

where $f(\nu)$ is a function tabulated for a range of values of the force index in reference J1, p.157. For isotopic gas mixtures of small proportionate mass difference, the mutual diffusion coefficient will differ little from the self-

diffusion coefficient of either component. Furry and Jones showed [J2] that the equation for the thermal diffusion constant obtained from the inverse power model is:-

$$\alpha = \frac{\nu - 5}{\nu - 1} \cdot C(\nu) \cdot \alpha_{es} \qquad (2 - 9)$$

$C(\nu)$ is given in the same table as $f(\nu)$ in [J1]. In the latter reference, an extended version of a table first drawn up by Brown [B1] is given which shows values of R_T (equation 2 - 5) estimated from viscosity data using the relations (2-6/7/9).

For mathematical convenience, Maxwell chose the value of five for the force index in his work on the inverse power model. It will be evident from (2 - 9) that α vanishes in this instance. Frankel [F2] showed how this interesting result may be obtained by an elementary argument [J1].

c) The Sutherland model.

The molecules are elastic spheres surrounded by inverse power attractive fields [S2]. For viscosity, Sutherland obtained:-

$$\eta = \frac{aT^{1/2}}{1 + C/T} \qquad (2 - 10)$$

where a and C are constants. This equation fails to fit experimental data over a wide temperature range, and a modification is often employed which will in fact represent the viscosities of hydrogen, neon and helium with an accuracy of one percent:-

$$\eta = \frac{aT^{n}}{1 + C/T} \qquad (2 - 10a)$$

Jones obtained an expression for the thermal diffusion constant assuming an attractive force index of seven [J2]. This model

is the first of those mentioned to predict a temperature dependence for α.

d) The Lennard-Jones models.

These are given by (2 - 3) when both indices have integral values. When the attractive force index (ν') is three, the so called special L.J. models are obtained, this value having been chosen for mathematical convenience only. The wave-mechanical theory of intermolecular forces suggests that ν' should be seven and the the repulsion should be of the form $R(r)e^{-r/a}$ where R(r) is a polynomial in r, the intermolecular distance, and (a) is a constant. In practice the repulsion is also represented by a power term, a suitable value for ν being thirteen. Shortly before these results were available, Hassé and Cookcarried out almost all the calculation necessary for use of the L.J. 9:5 model ($\nu = 9, \nu' = 5$) as a means of predicting the thermal diffusion constant. Since their method was equally applicable to the L.J. 13:7 case this was unfortunate, but pending evaluation of the integrals for the latter, Jones calculated α for the less realistic 9:5 case [J3].

3. THE LENNARD-JONES 13:7 FORCE LAW.

The first application of the L.J. 13:7 model to the prediction of gas properties was by Kihara and Kotani [K3] who compared Nier's experimental results for methane [N1] with theory and found poor agreement. Five years afterwards, Hirschfelder, Bird and Spotz [H3] presented the results of a very extensive evaluation of quantities required for use of the

model and later published a paper in which they compared a variety of experimental data with the values predicted by theory [H5].

Hirschfelder et al wrote the molecular potential function in the form :-

$$E(r) = 4E(o)[-(r_o/r)^6 + (r_o/r)^{12}] \qquad (2 - 11)$$

where E(r) is the interaction energy of two molecules r apart, and E(o) is the minimum energy corresponding to a separation r_o, the collision diameter for low velocity collisions.

Before the expressions for the gas properties resulting from (2 - 11) may be used, it is necessary to obtain suitable values for the parameters E(o) and r_o. This is done by fitting, over a wide temperature range, the experimental values for a gas property to the appropriate theoretical equation; Hirschfelder used the viscosity and, when accurate data for the latter were not available, the second virial coefficient. The temperature variation of the diffusion coefficient provides a superior method but suitable experimental results have not yet been obtained.

Tables giving values of E(o) and r_o for pure gases and mixtures are to be found in [H5]; those required for calculations described in this thesis are presented in Table 1 below. The quantity tabulated is E(o)/k (Boltzmann constant) because the integrals required in evaluating gas properties are tabulated as functions of kT/E(o).

TABLE 1

Gas	E(o)/k	r_o (angstroms)
Ne	35.7	2.80
A	124	3.418
N_2	91.46	3.681
CO	110.3	3.590
CH_4	136.5	3.822
CO_2	190	3.996
C_3H_8	254	5.061

The equations giving the gas coefficients in terms of the L.J 13:7 model are as follows:-

a) Diffusion.

The first approximation to the coefficient of diffusion of a binary mixture is :-

$$[D_{12}]_1 = \frac{0.00092916\ T^{3/2}\ [(M_1 + M_2)/M_1M_2]^{\frac{1}{2}}}{P\ (r_{12})^2\ W^{(1)}\ (1;\ kT/E(o)_{12})} \qquad (2 - 12)$$

The second approximation is given by :-

$$[D_{12}]_2 = [D_{12}]_1/1 - \Delta \qquad (2 - 13)$$

where Δ is a small quantity (< 0.03) calculated from equations given in [H5].

Where values of $E(o)_{12}/k$ and r_{12} are not available experimentally for a gas mixture, it is best to derive them from the following relations [H5, W5]:-

$$r_{12} = \frac{r_{01} + r_{02}}{2},\ E(o)_{12} = (E(o)_1 + E(o)_2)^{\frac{1}{2}} \qquad (2 - 14)$$

For isotopic mixtures, the components may be considered as

being identical in all but mass. (2 - 12) therefore simplifies to :-

$$[D_{11}]_1 = \frac{0.001314\ T^{3/2}}{P\ r_o^{\ 2}\ W^{(1)}(1;\ kT/E(o))M^{\frac{1}{2}}} \qquad (2 - 15)$$

The correction for the second approximation is of the same form as (2 - 13), but Δ is now given by:-

$$\Delta = 5(C - 1)^2/(11 - 4B + 8A) \qquad (2 - 16)$$

A, B and C are simple functions of the integrals in [H5] and are tabulated there also.

Winter [W5] summarised the experimental data on diffusion constants for isotopic and ordinary gas mixtures in cases where values of E(o) and r_o were known, and found reasonable agreement with the predictions of the L.J. 13:7 model in most instances. In a later paper [W6] he presented results from his own measurements of the self-diffusion coefficients of carbon dioxide, nitrogen and oxygen. The agreement with theory was good, particularly in the case of the two latter gases.

b) Viscosity.

The coefficient of viscosity is given by:-

$$\eta = 2.6693 \times 10^{-5}(MT)^{\frac{1}{2}}r_o^{-2}V/W^{(2)}(2) \qquad (2 - 17)$$

The slowly varying function V and $W^{(2)}(2)$ are tabulated in [H5]. (2 - 17) applies to a pure gas only.

c) Thermal conductivity.

This is given by:-

$$\lambda = 2.6693 \times 10^{-5}(T/M)^{\frac{1}{2}}r_o^{-2}.H(C_V + 9/4R)/W^{(2)}(2) \qquad (2 - 18)$$

H is given in [H5].

C_v is the specific heat at constant volume and R the gas constant, both being expressed per mole. This term results from the Eucken assumption concerning the energy distribution between translatory and internal degrees of freedom. This is not strictly true and the agreement between experiment and theory is less good for the thermal conductivity than for the other gas properties.

d) Thermal diffusion.

So far only the first approximation to the coefficient of thermal diffusion has been worked out. For an ordinary gas mixture Hirschfelder et al quote it in the form :-

$$k_T = \frac{5x_1x_2(C - 1)(s_1x_1 - s_2x_2)}{Q_1x_1^2 + Q_2x_2^2 + Q_3x_1x_2} \qquad (2 - 19)$$

where x_i is the mole fraction of species i and

$$s_1 = \frac{M_1}{5}\left(\frac{r_1}{r_{12}}\right)^2\left[\frac{2(M_1 + M_2)^3}{M_2}\right]^{\frac{1}{2}}\left[\frac{W^{(2)}(2;kT/E(o)_1)}{W^{(1)}(1;kT/E(o)_{12})}\right] - 3M_2(M_2-M_1)-4AM_1M_2$$

$$Q_1 = \frac{1}{5}\left(\frac{r_1}{r_{12}}\right)^2\left[\frac{2(M_1+M_2)}{M_2}\right]^{\frac{1}{2}}\left[\frac{W^{(2)}(2;kT/E(o)_1)}{W^{(1)}(1;kT/E(o)_{12})}\right].[6M_2^2+(5-4B)M_1^2+8AM_1M_2]$$

$$Q_3 = 3(M_1-M_2)^2(5-4B) + 4AM_1M_2(11-4B) + \frac{4}{25}\left(\frac{r_1r_2}{r_{12}^2}\right)^2 \quad X$$

$$\frac{(M_1+M_2)^3}{(M_1M_2)^{\frac{1}{2}}}\left[\frac{W^{(2)}(2;kT/E(o)_1).\ W^{(2)}(2;kT/E(o)_2)}{[W^{(1)}(1;kT/E(o)_{12})]^2}\right]$$

s_2 and Q_2 are obtained merely by changing subscripts. The expression for Q_3 given in [H5] contains two errors. In the above relations, k_T is defined by:-

$$k_T = \alpha x_1 x_2 \qquad (2 - 20)$$

and A, B and C are the functions occurring in (2 - 16).

For isotopic mixtures, considerable simplification is afforded, and the resulting expression has been reduced by Winter to the convenient form:-

$$R_T = \frac{16.9(C - 1)(1 + A)}{A(11 - 4B + 8A)} \qquad (2 - 21)$$

Values of R_T calculated from this expression are given in Table 2 and shown graphically in Figure 1.

Comparisons of experimental thermal diffusion constants with the predictions of the L.J. 13:7 model have been carried out by Grew [G2], Hirschfelder [H5] and Winter [W5], and the relevant data are discussed in the next chapter.

CHAPTER 3

DIFFUSION IN GASES - EXPERIMENTAL METHODS AND RESULTS

1. SUMMARY OF AVAILABLE METHODS FOR DETERMINING THERMAL DIFFUSION CONSTANTS

The three main methods of measuring α are:-

a) The two bulb apparatus.

This is the simplest and most commonly used technique. The experiments described in this thesis were carried out with its use, and the theory and experimental details are fully treated later.

b) The separating column.

Given a suitably realistic theoretical treatment of the thermal diffusion column, it is possible to calculate α from the performance of such apparatus. Since it is necessary to make semi-empirical modifications to an approximate and complex theory, in order to obtain a formula giving consistent α values, the method is fundamentally less sound than use of the two bulb apparatus. In its favour are the facts that the concentration changes to be measured are larger and that it is more readily applicable to studies at high pressures.

c) The diffusion thermo-effect.

This, the reverse of thermal-diffusion, has been studied by Waldmann [W7]. By measuring the temperature changes when gases diffuse into one another as a function of time, it is possible to obtain a value for the thermal diffusion factor.

The method is inapplicable to most isotopic mixtures and is not considered further.

2. THEORY OF THE TWO-BULB APPARATUS

The derivation of the expressions for the separation factor and equilibrium time for a two-bulb system is due to Jones and Furry and is taken from their review [J1].

The equation for ordinary diffusion is:-

$$c_1(v_1 - v) = c_1c_2(v_1 - v_2) = - D_{12} \text{ grad } c_1 \qquad (3 - 1)$$

where c_1 is the fractional concentration of the lighter species, c_2 that of the heavier; $c_1 + c_2 = 1$. v_1, v_2 are the corresponding convection velocities (vectors), and v is the convection velocity of the gas as a whole, defined by:-

$$v = c_1v_1 + c_2v_2 \qquad (3 - 2)$$

To include the effect of thermal diffusion, a further term is added to (3 - 1) giving:-

$$c_1(v_1 - v) = - D_{12} \text{ grad } c_1 + D_T \text{ grad } T/T \qquad (3 - 3)$$

Whilst D_{12} is independent of c, D_T, the coefficient of thermal diffusion is proportional to the product c_1c_2:-

$$D_T = \alpha\, c_1c_2\, D_{12} \qquad (3 - 4)$$

The quantity α thus defined is the thermal diffusion constant or factor, the theoretical expressions for which were given in chapter 2.

The thermal diffusion ratio is defined as:-

$$k_T = D_T/D_{12} = \alpha\, c_1c_2 \qquad (3 - 5)$$

In the two-bulb apparatus, diffusion takes place along the

vertical tube connecting the lower cold bulb and the upper hot bulb. Convection is absent and so $v = 0$. When equilibrium has been reached there is no further net transport of either component of the gas mixture in the tube, and so $v_1 = v_2 = 0$.

From (3 - 3/4) results:-

$$c_1(v_1 - v) = D_{12}[\alpha c_1 c_2 \text{ grad ln } T - \text{grad } c_1] \qquad (3 - 6)$$

which gives at equilibrium:-

$$\text{grad } c_1 = \alpha c_1 c_2 \text{grad ln } T \qquad (3 - 7)$$

If α is assumed independent of T, (3 - 7) may be integrated to give:-

$$c_1/c_2 = \text{const } xT^{\alpha} \qquad (3 - 8)$$

from which the arbitrary constant may be eliminated by considering two points A, B in the gas:-

$$\frac{(c_1/c_2)A}{(c_1/c_2)_B} = \left(\frac{T_A}{T_B}\right)^{\alpha} = q \qquad (3 - 9)$$

q is the 'separation factor', a quantity widely used when describing the performance of separating apparatus of all kinds.

In order to calculate the equilibrium time of a two-bulb system, Jones and Furry assumed that conditions in the connecting tube do not vary appreciably during the separation. If the bulbs are of large volume, they will prevent any rapid concentration build-up at the ends of the tube which would cause changes in the diffusion rate along it. The "quasi-stationary" assumption is unlikely to introduce inaccuracy

when treating such an apparatus; in any case the expression to be derived with its use is employed merely as a guide when deciding upon the time to be allowed for equilibrium to be reached. It is assumed also that the temperature gradient along the tube is linear and that the concentration change is sufficiently small to allow of the replacement of c_1c_2 by the average value $(c_1c_2)_{av}$. Let z be the co-ordinate along the connecting tube, L its length and ΔT the temperature difference between the bulbs. Then $dT/dz = \Delta T/L$. The gas is at rest and so $v = 0$. Making these changes in (3 - 6) one obtains:-

$$c_1v_1 = D\Delta T/L[\alpha (c_1c_2)_{av}/T - dc_1/dT] \qquad (3 - 10)$$

The "quasi-stationary" assumption means that ρc_1v_1 is constant. Assuming also that $\rho D/T$ is independent of T (it is actually proportional to $T^{-0.28}$), multiplying both sides of (3 - 10) by ρ and integrating with respect to T then gives:-

$$\rho c_1v_1 = D\Delta T/TL[\alpha (c_1c_2)_{av} - \Delta c_1/\ln(T_2/T_1)] \qquad (3 - 11)$$

At equilibrium:-

$$\Delta c_1 = \alpha (c_1c_2)_{av} \ln T_2/T_1 \qquad (3 - 12)$$

If the cross-section of the tube is S, ρc_1v_1S is the transport of species 1 to the hot bulb. Writing m_c and m_h for the masses of gas in the two bulbs, and t for the time:-

$$m_c\left(\frac{dc_1}{dt}\right)_1 = \rho c_1v_1S = -m_h\left(\frac{dc_1}{dt}\right)_2$$

$$\left(\frac{dc_1}{dt}\right)_1 - \left(\frac{dc_1}{dt}\right)_2 = \frac{d(\Delta c_1)}{dt} = \rho c_1v_1S[1/m_c + 1/m_h] \qquad (3 - 13)$$

From (3 - 11/13) one obtains:-

$$\frac{d(\Delta c_1)}{dt} = S[1/m_c + 1/m_h]\rho \frac{D}{L} \cdot \frac{\Delta T}{T} [\alpha (c_1 c_2)_{av} - \Delta c_1 / \ln(T_2/T_1)] \qquad (3 - 14)$$

which is of the form:-

$$d(\Delta c_1)/dt = a - b\Delta c_1 \qquad (3 - 15)$$

If $c_1 = 0$ when $t = 0$, the solution of (3 - 15) is:-

$$\Delta c_1 = (a/b)[1 - e^{-bt}] = (\Delta c_1)_{eq}[1 - e^{-t/tr}] \qquad (3 - 16)$$

where t_r is known as the "relaxation time" and given by:-

$$t_r = 1/b = \frac{L}{\rho DS} \cdot \frac{m_c m_h}{m_c + m_h} \frac{T}{\Delta T} \ln T_2/T_1 \qquad (3 - 17)$$

The time required for complete equilibrium (say 99%) is found readily from (3 - 16) thus:-

$$0.99\ \Delta c_1 = \Delta c_1[1 - e^{-t/tr}]$$

$$t = -\ln 0.01\ t_r = 4.6\ t_r \qquad (3 - 18)$$

From (3 - 17) it follows that t_r is directly proportional to the gas pressure.

Stier [S3] and Watson and Woernley [W8] quoted the following as an expression for t_r:-

$$t_r = (VL/DS)\, T_1/(T_1 + T_2) \qquad (3 - 19)$$

where V is the volume of each bulb. (3 - 19) does not result on simplifying (3 - 17) and in fact gives results only one half as great as those predicted by the latter in the 20 - 300°C temperature range often studied.

3. CALCULATION OF α FROM EXPERIMENTAL DATA

The equilibrium concentration change in a two-bulb apparatus is given by (3 - 12), and, using superscripts I and II to represent the cold and hot bulbs respectively, may be written:-

$$\Delta c_1 = c_1^{II} - c_1^{I} \qquad (3 - 20)$$

By the methods shortly to be described, experimental values are obtained for the quantity:-

$$(c_1^{II})_n - c_1 \qquad (3 - 21)$$

where n is the number of enrichment processes carried out on the gas mixture and c_1 is the initial concentration of species 1. To relate (3 - 20) with (3 - 21) it is necessary to take into account the volumes of the bulbs and connecting tube used in the experiment. Several formulae for doing this have been proposed, and that derived by Whalley and Winter was used for the present work.

Let the volumes of bulbs I and II be V_1, V_2, that of the tube between V_c. Let their temperatures be T_1, T_2 and T_m. The conservation of mass of species 1 throughout a run may be represented by:-

$$c_1[V_1/T_1+V_2/T_2+V_c/T_m] = c_1^{I}V_1/T_1+c_1^{II}V_2/T_2+(c_1^{I}+c_1^{II})V_c/2T_m \qquad (3 - 22)$$

or, in terms of c_1^{II} and Δc_1:-

$$c_1 \Sigma V/T = (c_1^{II}-\Delta c_1)V_1/T_1+c_1^{II}V_2/T_2+(2c_1^{II}-\Delta c_1)V_c/2T_m$$

$$= c_1^{II} \Sigma V/T - \Delta c_1[V_1/T_1+V_c/2T_m] \qquad (3 - 23)$$

which may be written:-

$$c_1^{II} - c_1 = \Delta c_1 [(V_1/T_1 + V_c/2T_m)/\sum V/T] \qquad (3 - 24)$$

or for n successive operations, each taken to equilibrium:-

$$(c_1^{II})_n - c_1 = n \Delta c_1 V^* \qquad (3 - 25)$$

where V^* is called the "volume factor".

From (3 - 12/25) the required expression is obtained:-

$$\alpha = \frac{(c_1^{II})_n - c_1}{nV^* (c_1c_2)_{av} \ln(T_2/T_1)} \qquad (3 - 26)$$

An exactly similar relation holds when the concentration change in the heavy species 2 is measured, as in the work of Nier [N1]. Instead of (3 - 26) he used a more simple equation derived by putting $V_1 = V_2$ and ignoring V_c:-

$$\alpha = \frac{((c_2^1)_n - c_2)(1+T_2/T_1)}{n (c_1c_2)_{av} \ln T_2/T_1} \qquad (3 - 27)$$

The error introduced by using (3 - 27) was only about 1%. The expression used by Mann [M1], namely:-

$$\alpha = \frac{c_2^I - c_2}{n c_1c_2} \times \frac{1+\beta+T_2/T_1}{(1+\beta/2)\ln(T_2/T_1)} \qquad (3 - 28)$$

where $\beta = T_2V_c/T_cV$ is identical with (3 - 26) for the case where $V_1 = V_2 = V$.

4. TEMPERATURE ALLOCATION OF EXPERIMENTAL THERMAL DIFFUSION CONSTANTS

The thermal diffusion constants measured by the two-bulb technique are average values for the temperature ranges

concerned. Before comparison with theory is possible a suitable mean temperature must be allocated to each experimental result. The arithmetic mean of the bulb temperatures immediately comes to mind, but this assumes a linear temperature dependence for α which is not the case (see Fig. 1). A simple expression for obtaining a suitable mean, denoted by T_r, was derived by Harrison-Brown as follows [H6]:(3 - 7) may be written:-

$$\frac{\text{grad } c_1}{\alpha_{es}\, c_1 c_2} = R_T \text{ grad ln } T \qquad (3 - 29)$$

Let $\bar{R}_T$ denote the experimental value, an effective average for the temperature range $T_1 - T_2$ and assume that the temperature variation of R_T is of the form:-

$$R_T = R_\infty - B/T \qquad (3 - 30)$$

Then, by definition:-

$$\bar{R}_T = R_\infty - B/T_r \qquad (3 - 31)$$

The right hand side of (3 - 29) may be expressed in terms of either $\bar{R}_T$ or R_T; equating these alternatives and integrating with respect to T between the limits T_1 and T_2:-

$$\bar{R}_T \ln T_2/T_1 = R_\infty \ln T_2/T_1 - B\int_{T_1}^{T_2} (\text{grad ln } T)/T$$

from which

$$(\ln T_2/T_1)B/T_r = B[1/T_1 - 1/T_2]$$

$$T_r = T_1T_2 \ln(T_2/T_1)/(T_2-T_1) \qquad (3 - 32)$$

This expression contains no constant derived from the equation used for representing the temperature dependence of R_T, and has been very widely used.

In view of the fact that the Lennard-Jones 13:7 intermolecular force model is satisfactory for predicting thermal diffusion factors, (justification for this statement is given in the next chapter) it would obviously be desirable to use, instead of (3 - 30), an expression derived for this particular case. It was found that a relation of the form:-

$$R_T = R_\infty[1 - e^{-kT/E(o)a}] \qquad (3 - 33)$$

holds quite well over a wide range of $kT/E(o)$ with R_∞ taken as 0.627. Rewriting (3 - 33) in the form:-

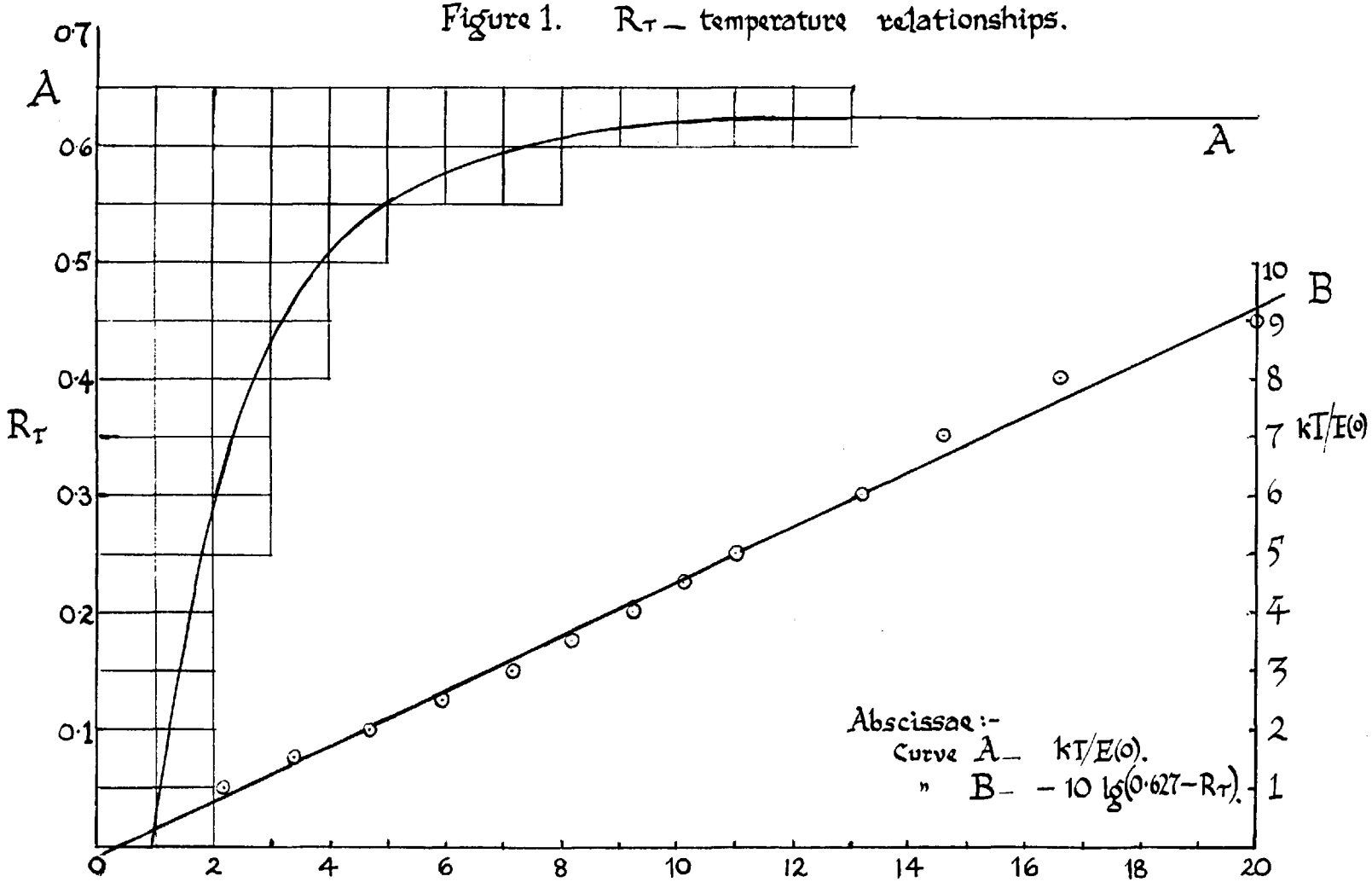
$$\lg(R_\infty - R_T) = -(1/2.303\ a)[kT/E(o)] + \text{const.} \qquad (3 - 34)$$

it is apparent that a plot of $\lg[0.627 - R_T]$ vs $kT/E(o)$ should give a straight line. From the plot (Figure 1) of the data given below in Table 2 this is seen to be the case. The slope of the line is 0.219.

TABLE 2

$kT/E(o)$	R_T	$(0.627-R_T)$	$-\lg(0.627-R_T)$
1	0.019	0.608	0.216
1.5	0.169	0.458	0.339
2	0.288	0.339	0.470
2.5	0.373	0.254	0.595
3	0.434	0.193	0.714
3.5	0.475	0.152	0.818
4	0.508	0.119	0.924
4.5	0.530	0.097	1.013
5	0.548	0.079	1.102
6	0.579	0.048	1.319
7	0.592	0.035	1.456
8	0.605	0.022	1.658
9	0.617	0.010	2.000
10	0.618	0.009	2.146
20	0.627	0	-

Figure 1. R_T — temperature relationships.



An expression for $(T_r)_{13:7}$, or $T_{13:7}$, is now derived by a method exactly analagous to that of Brown.

Writing (3 - 33) in the simple form:-

$$R_T = R_\infty[1 - e^{-AT}], \quad A = (1/a)(k/E(o)) \qquad (3 - 35)$$

one obtains by using (3 - 29) in the manner described:-

$$\bar{R}_T \ln(T_2/T_1) = R_\infty \ln(T_2/T_1) - R \int_{T_1}^{T_2} e^{-AT}/T.dT$$

from which:-

$$e^{-AT_{13:7}} \ln(T_2/T_1) = \int_{T_1}^{T_2} (e^{-AT}/T)dT$$

Taking logarithms and rearranging:-

$$T_{13:7} = (1/A)\ln[\ln(T_2/T_1)/I^*] \qquad (3 - 36)$$

where the integral has been denoted by I^* for brevity.

From the above relations it follows that:-

$$1/A = (E(o)/k)/2.303 \times 0.219 \qquad (3 - 37)$$

The integral I^* values required were obtained by graphical interpolation between published data. Jahnke and Emde's tables [J4] contain the function:-

$$-Ei(-x) = \int_x^\infty (e^{-t}/t)dt \qquad (3 - 38)$$

for a wide range of values of x. I^* is readily reduced to this form by putting $x = AT$, $dx = AdT$:-

$$I^* = \int_{T_1}^{T_2} (e^{-AT}/T)dT = \int_{x_1}^{x_2} (e^{-x}/x)dx \qquad (3 - 39)$$

$$= - Ei(-x_1) + Ei(-x_2) \qquad (3 - 40)$$

The quantities required for evaluating $T_{13:7}$ in the case of

each of the new thermal diffusion factor measurements described later are given in Table 3 below. It will be seen from Table 5 of the next chapter that $T_{13:7}$ is higher than T_r at the lower temperature ranges studied; the accuracy with which I^* was obtained is insufficient to allow of very definite conclusions, but use of $T_{13:7}$ appears to bring the theoretical into closer agreement with the experimental R_T values.

TABLE 3

Calculation of $T_{13:7}$

	T_1	T_2	x_1	x_2	I^*	$T_{13:7}$
	195	423	0.8914	1.934	0.211	284
Carbon monoxide	195	427	0.8914	1.952	0.212	286
	195	429	0.8914	1.962	0.213	286
	293	683	1.340	3.123	0.116	435
$A = 8.196 \times 10^{-3}$	294	668	1.344	3.054	0.114	432
	295	528	1.349	2.414	0.097	39x10
	296	663	1.353	3.031	0.112	432
Nitrogen	195	427	1.075	2.355	0.163	285
	195	428	1.075	2.360	0.163	285
$A = 8.701 \times 10^{-3}$	294	678	1.621	3.739	0.078	43x10
	294	683	1.621	3.766	0.078	43x10
Methane	195	433	0.7204	1.600	0.274	289
	195	435	0.7204	1.607	0.275	290
$A = 7.541 \times 10^{-3}$	295	708	1.090	2.616	0.167	448

A further equation for representing the temperature dependence of the thermal diffusion factor was used by Stier [S3]:-

$$R_T = a \ln(T_r/b) \qquad (3 - 41)$$

For a relation of this form, T_r should be calculated from :-

$$T_r = (T_1 T_2)^{\frac{1}{2}} \qquad (3 - 42)$$

as shown by Whalley [W1], not from (3 - 32) as has often been

the case. It is found by graphical comparison between the values of R_T calculated from the three empirical relations above and those given by the theoretical equation (2 - 21) that the limits of applicability of the former are as follows - [D2]:-

Equation	Range of kT/E(o)
3 - 41	0.5 - 4.0
3 - 30	1.5 - 10
3 - 36	0.5 - 10

5. PREVIOUS EXPERIMENTS WITH THE TWO-BULB APPARATUS

Most of the experimental values of thermal diffusion factors published prior to 1949 were compared with the predictions of the L.J. 13:7 model by Winter [W5]. No useful purpose would be served by a detailed recapitulation of his findings; the present summary is therefore mainly concerned with the experimental technique used by Nier in his work on methane [N1].

a) Methane.

The bulbs of Nier's apparatus were each of 100 cc. capacity and were connected by a tube 7 cm. long and of 8.5 mm. internal diameter including a three-way stopcock having a 2 mm. diameter and 1.5 cm. long bore. The arrangement of the bulbs is not given; one was in a furnace and the other in a water-bath.

To carry out a run, Nier filled the apparatus with methane and then allowed three times the relaxation-time of the system for the gas to reach equilibrium. He then isolated

the bulbs, pumped the gas from the hot one away, and allowed that remaining in the cold bulb to come to a further equilibrium between the two. This process was repeated twelve times to give a correspondingly increased concentration change. The gas remaining in the cold bulb after the run was then burned in oxygen and the resulting carbon dioxide analysed for the relative abundance of masses 44 and 45 by mass spectrometer.

The agreement between Nier's results and the values given by the L.J. 13:7 model is decidedly poor and it was for this reason that fresh experiments were performed as described in the next chapter. In an attempt to explain the discrepancy several points concerning Nier's technique may be noted.

(i) Equilibrium times - Nier probably used equation (3 - 19) when calculating the relaxation-time for his apparatus because (3 - 17) had not been published at the time. This, coupled with his allowance of 3 x t_r instead of the 5 x t_r suggested by (3 - 18) may have resulted in insufficient time being given for equilibrium to be reached at some or all stages of the separating procedure.

(ii) Enrichment procedure. Nier removed the gas from the hot bulb and re-separated that remaining in the cold when multiplying the single stage concentration change. For his lower temperature run T_1 = 295°K and T_2 = 573°K. The gas pressure was therefore reduced by a factor of 0.68 at each pumping of the hot bulb. Assuming an initial pressure of 60 cm. of mercury, the final pressure in the system would be:

$$P \text{ (final)} = 60 \times 0.68^{12} = 0.6 \text{ cm.}$$

a value sufficiently great to make it seem unlikely for over-drastic gas depletion to be the cause of his error.

It might appear from the above that Nier's experimental method of evacuating the hotter bulb between equilibria is superior to the alternative procedure of pumping the cold bulb, since it allows of more enrichments being carried out for a given loss of gas. If n_h represents the number of times the hot bulb is evacuated and n_c is the corresponding value for the cold bulb, we have for a given depletion of gas:-

$$(0.68)^{n_h} = (0.32)^{n_c}$$

$$n_h = 3.4\, n_c \qquad (3 - 43)$$

However, inspection of equations (3 - 24/6) shows that the equilibrium concentration change per stage is proportional to the volume factor concerned. Thus:-

$$(c_i)^j - c_i \propto [(V_i/T_i) + (V_c/2T_m)] \qquad (3 - 44)$$

where i = 1 or 2 according to whether the sample is taken from the hot or cold bulb respectively. From the values of V and T for Nier's system it is readily shown that by pumping the cold bulb instead of the hot he would have obtained 2.1 times the separation per equilibrium. Combining this result with (3 - 43) one sees that a 50% greater concentration change was gained from $3\frac{1}{2}$ times the number of equilibria.

In cases where the gas being studied is valuable and has to be manipulated with a Toepler pump, Nier's method is inconvenient. The time required for carrying out a run is considerably increased also and for these two reasons the cold

bulb was evacuated between separations in both Whalley's [W1] and the present work.

(iii) Combustion of samples. Nier's methane samples must have been about 10 cc. at 5 cm. of mercury pressure in quantity at room temperature. Those obtained in the present study were roughly three times this size and would have been less susceptible to accidental contamination.

(iv) Evaluation of the concentration change. Nier used a different method for calculating the concentration change from his analytical results from that employed here. It is described in the next chapter.

b) Helium.

The value of the thermal diffusion factor obtained by McInteer, Aldrich and Nier for helium previously enriched in ^3He with a hot-wire separating column was not included in [W5]. They found [M2]:-

$$\alpha = 0.059 \pm 0.005 \text{ at } T_r = 398^oK$$

For helium $E(o)/k = 6.03$, and so the value predicted by (2 - 21) for the L.J. 13:7 model is 0.079. Strictly the full equation (2 - 19) should be used for the comparison because of the high proportionate mass difference.

c) Other gas mixtures.

Mann's result for nitrogen is considered in the next chapter. Some experimental results published after [W5] was written in 1949, are those of Drickamer, Downey and Pierce [D3] who studied various hydrogen-hydrocarbon mixtures in a

two-bulb system. These authors compared their values with those given by the L.J. 13:7 model and found it necessary, in order to obtain agreement, to assume values for the minimum interaction energy ($E(o)_{12}$) and the collision diameter (r_{12}) less than those predicted using (2 - 14) with the E(o) and r_o values derived from the viscosities of the pure components.

CHAPTER 4.

THERMAL DIFFUSION CONSTANT MEASUREMENTS

1. APPARATUS AND METHOD.

The apparatus and technique used for the thermal diffusion constant measurements were similar to those evolved by Whalley and Winter in their study of oxygen [W1, W2, W3] and some parts of their apparatus were employed for the present investigation. During the course of the work numerous detail modifications were made in the design of the vacuum system used, but since none affected the principle of its operation only the final form is described. It is shown diagrammatically in Figure 2 and was constructed almost entirely of pyrex glass. Vacuum taps and joints were greased with Apiezon 'N' or 'M' except where subjected to temperatures much different from that of the laboratory when Dow-Corning silicone high-vacuum grease or picien wax were used according to requirements.

The two bulbs of the apparatus proper between which the separation in the gas mixture was obtained each had a volume of approximately one litre and were connected by wide bore tuning which contained a large (15 mm. bore) pyrex vacuum tap T_1. The volumes of the bulb and connecting tube are given with other data required for calculating equilibrium times in Table 4 below. The upper bulb was heated in the

electric furnace specially made by Whalley for the purpose which had as an inner lining an iron tube of 1/8" wall thickness to ensure an even temperature distribution throughout its length. The winding was of nichrome - total resistance 30 ohms - and was heated with current taken from the 230 V A.C. mains. The energy input into the furnace was controlled with a Sunvic bimetallic switch,a resistance in series being used to limit the 'on' current and to prevent overheating in the event of the controller sticking in the 'on' position; the hot bulb used in the first experiments with carbon monoxide was damaged by such an occurrence and had to be replaced. The temperature of the furnace was measured with a Pt - Pt/Rh thermocouple made by the Foster Instrument Company having a milliameter reading directly in ^{o}C. It was found that the temperature of the hot bulb was maintained constant to within $\pm 5^{o}C$ by the Sunvic, variation being caused by changes in laboratory temperature which affected the rate of cooling of the bimetallic strip.

The lower, cold, bulb was normally immersed in water contained in a lagged vessel. Originally a 3-litre beaker set in woolly asbestos was used, but this was later replaced by a large Dewar vessel. The improvement obtained was only required in those runs in which the bottom bulb was surrounded by solid carbon dioxide/alcohol mixture. The insulation afforded by the first vessel was barely sufficient for maintaining the bulb at a uniform low temperature overnight.

Since it was necessary to conserve the gases used for

the experiments, a Toepler pump was provided for their transference between the two bulbs and the storage bulb. The mercury level in the pump was adjusted by altering the air pressure in the filter-flask used as its mercury reservoir. This could be connected either to the backing vacuum or to an air supply. The air inlet was fitted with a capillary leak to prevent rapid changes in mercury level and connected by a line to an air compressor which enabled gas to be handled at pressures greater than otherwise possible. Compressed air was normally only used when dealing with such pressures.

Although knowledge of the gas pressure is not required when determining thermal diffusion constants, mercury manometers were connected to most parts of the system to facilitate use of the Toepler pump and aid the detection of any major gas leakage. The apparatus was evacuated with a three-stage quartz mercury condensation pump backed by a 'Metrovac' rotary pump. A trap cooled with crushed carbon dioxide was provided between the pumps and the main vacuum line, the pressure of permanent gases in the latter being measured with a rotary McLeod gauge covering the range 10^{-2} - 10^{-6} mm. of mercury.

The experimental procedure was as follows: the two bulbs, Toepler pump and connecting tubes were evacuated and at the same time, the furnace temperature was adjusted to the required value by suitably setting the Sunvic controller. In the case of low temperature runs the Dewar surrounding the bottom bulb was filled with a crushed carbon dioxide -

industrial methylated spirit mixture.

After the pumping was completed, tap T_3 was closed and most of the gas transferred from the storage bulb to the two-bulbs by equalisation of pressure through T_4, followed by use of the Toepler. Tap T_2 was closed and a sample of the gas taken for the run was removed from above T_5 in a small pyrex tube (see Figure 7) by heating the thick walled constriction with a small oxygen-gas flame and pulling off.

The two-bulb system was left undisturbed for a time sufficient to allow of equilibrium being reached in the gas mixture. This time was calculated from the equations (3 - 17/8) and the results are given in the following table.

TABLE 4

Relaxation times and other data for the two-bulb apparatus

	V_1	V_2	V_c	L/S
a)	1065	940	63.5	7.04
b)	918	934	74	7.53

Bulb volumes (a) refer to runs with normal CO only

Temp.range (^oK)	Gas	$[D_{11}]_1$	t_r (Hours) at 1 atm.
	CO	0.220	4.6
195 - 430	N_2	0.220	4.6
(T = 312)	CH_4	0.241	4.2
	CO	0.479	2.1
295 -680	N_2	0.472	2.2
(T = 487)	CH_4	0.533	1.9

$[D_{11}]_1$ was calculated from equation (2 - 15). The t_r data was worked out for the bulb volumes (b) - L/S was obtained by summation along the connecting tube, a mean cross-sectional area being taken for each part. The time actually given per

Figure 2. Thermal diffusion constant apparatus.

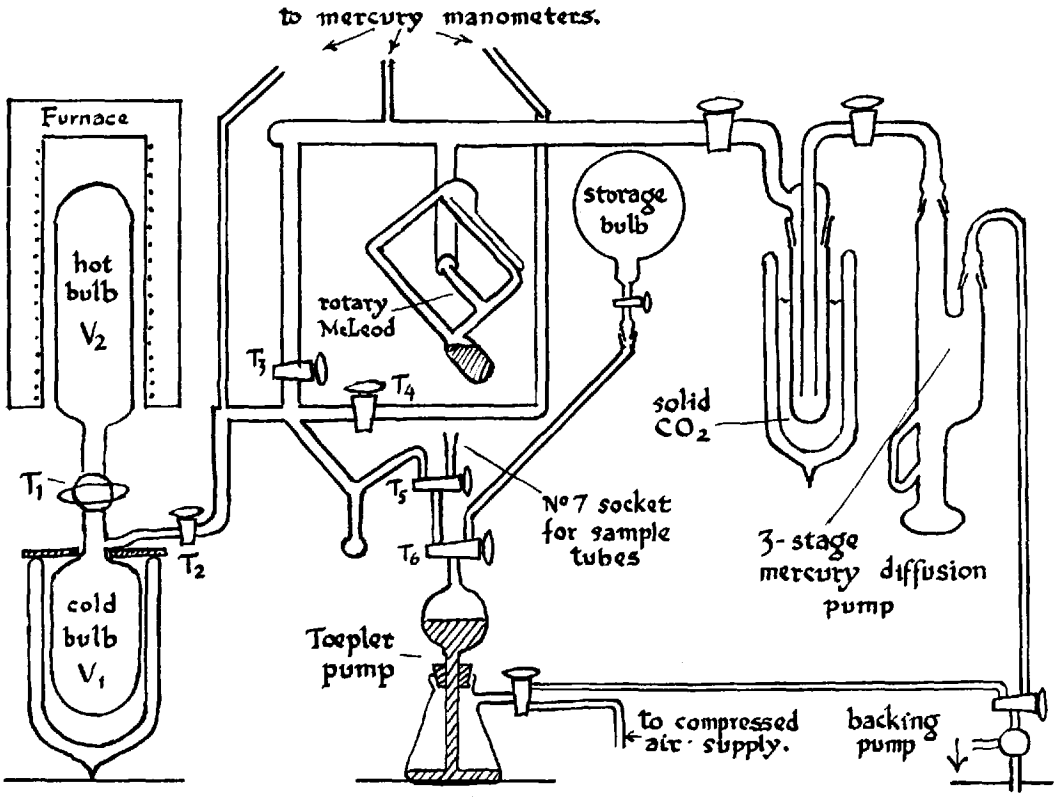


Figure 3.

Carbon monoxide preparation apparatus.

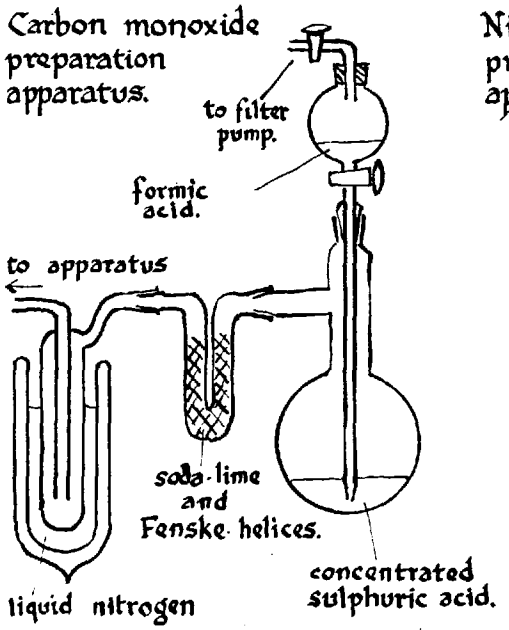
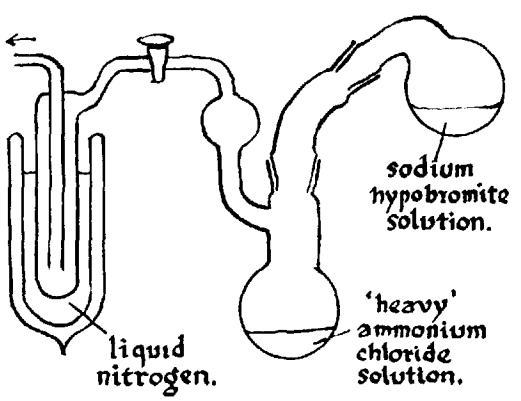


Figure 4.

Nitrogen preparation apparatus.



equilibrium varied considerably but was never less than 5 x t_r. Since the relaxation time is proportional to the gas pressure in the apparatus, the equilibrium times became progressively shorter towards the end of a run. A complete experiment lasted for a period of four to five days.

After the first equilibrium the tap T_1 was closed, and the gas from the lower bulb pumped back into the storage bulb with the Toepler; the number of operations of the latter required in doing this was thirty to forty. The bulbs were now shut off once more, by turning T_2, and T_1 re-opened to allow the slightly enriched gas from the hot bulb to come to a further equilibrium. In this way the single-stage separation was multiplied five or six times, this factor being limited by the permissible depletion of gas in the system. At the end of the run, the bottom bulb was completely evacuated and the gas from the hot bulb transferred with the Toepler pump to a standard sample tube.

Thermal diffusion constants were measured for carbon monoxide, methane and nitrogen. Since the first two were not readily obtainable in a pure state, quantities of each gas were prepared specially as described below. The nitrogen was liberated from ammonium chloride (enriched previously in the ^{15}N isotope) by oxidation.

2. PREPARATION OF THE GASES

a) Carbon monoxide.

The reaction between formic and sulphuric acids was chosen for preparing carbon monoxide. The apparatus,

illustrated by Figure 3, consisted of a specially made tap-funnel which fitted by means of a ground joint into the neck of a one-litre pyrex flask. 'Analar' formic acid was put into the tap-funnel and outgassed by boiling under water-pump vacuum using the connection shown. The concentrated sulphuric acid was in the lower flask and de-gassed by application of the backing-pump vacuum for some time. As indicated in the diagram, the stem of the dropping funnel extended below the sulphuric acid level so that any formic acid run in reacted at once, instead of evaporating into the evacuated preparation flask.

The reaction proceeded smoothly at room temperature and the gas evolved was passed through a soda-lime tube, to absorb traces of carbon dioxide, and then through a cold trap into the thermal diffusion apparatus. When a gas pressure of half an atmosphere had built up the carbon monoxide condensed in the liquid-nitrogen cooled trap. In order to fill the apparatus the liquefied gas was allowed to warm up and the excess then pumped away. So that this might safely be done, the backing pump was housed in a fume cupboard during all but the initial stages of the work.

The heavy carbon monoxide used for the later experiments was supplied by the A.E.R.E., Harwell in a six-litre flask fitted with a break-seal. The gas was transferred from this flask to one of more convenient size (3 litres) with the Toepler pump of the two-bulb thermal diffusion apparatus. The heavy isotope abundances were approximately 50% of ^{13}C and 6% of ^{18}O.

b) Nitrogen.

The experiments with nitrogen were carried out with gas obtained from some ammonium chloride in which the relative abundance of the heavy isotope, ^{15}N, had been increased to about five percent. The gas was liberated by oxidation with sodium hypobromite [P1], the reaction being:-

$$2NH_4Cl + 8NaOH + 3Br_2 \longrightarrow 6NaBr + 2NaCl + 8H_2O + N_2$$

The hypobromite was made immediately before use by the slow addition of liquid bromine to 30% caustic soda solution in a cooled flask. This liquid was at once transferred to the upper bulb of the preparation apparatus (see Figure 4). Prior to this the heavy ammonium chloride was dissolved in a small volume of distilled water and put into the lower flask. The apparatus was then fitted together and the two solutions outgassed carefully. By rotating the upper flask about the ground joint its contents could slowly be poured into the chloride solution thereby causing a steady evolution of gas.

The pressure of nitrogen in the preparation apparatus was allowed to build up appreciably before letting any gas pass through a cold trap into the pumped out storage bulb. In this way, the considerable loss of water which would have occurred due to distillation from the aqueous solutions into the liquid-nitrogen trap (used for condensing out impurities) was avoided. Towards the later stages of the preparation, the reacting solution was warmed to ensure complete evolution of the nitrogen. Afterwards, the gas remaining in the apparatus was pumped into the storage bulb with the Toepler.

c) Methane.

A survey of the literature showed that the following methods of preparing methane are practicable - (i) action of water [C5] on zinc methyl (ii) action of zinc-copper or aluminium-mercury couples on methanol and methyl iodide [B2, M3, F3], (iii) decomposition of methyl magnesium iodide with water [C6], (iv) by heating a mixture of sodium acetate and soda-lime, (v) by the action of water on aluminium carbide [B3, C5, C6, F3, S4]. Of these, the last was selected as being most suitable since it evidently gave gas of reasonable purity from simply handleable materials.

The preparation apparatus used is shown in Figure 5 which also includes a representation of those parts of a large vacuum fractionation apparatus which were used for purifying the methane. The latter system had been originally intended for a study of boron hydrides - hence the provision of the Stock type of mercury cut-offs for the storage bulbs - and was constructed entirely from soda-glass.

Two trial preparations were carried out; the first at once showed the need for having a large reaction flask to allow for the considerable frothing that takes place. The one originally fitted, of 250 cc. capacity was therefore replaced by the litre-flask used for the preparation of carbon monoxide, the same tap funnel also being employed. A connection between the latter and the reaction flask allowed the water to be outgassed conveniently by boiling under reduced pressure. The carbide was outgassed by heating the

Figure 5. Methane preparation & fractionation apparatus.
(much simplified)

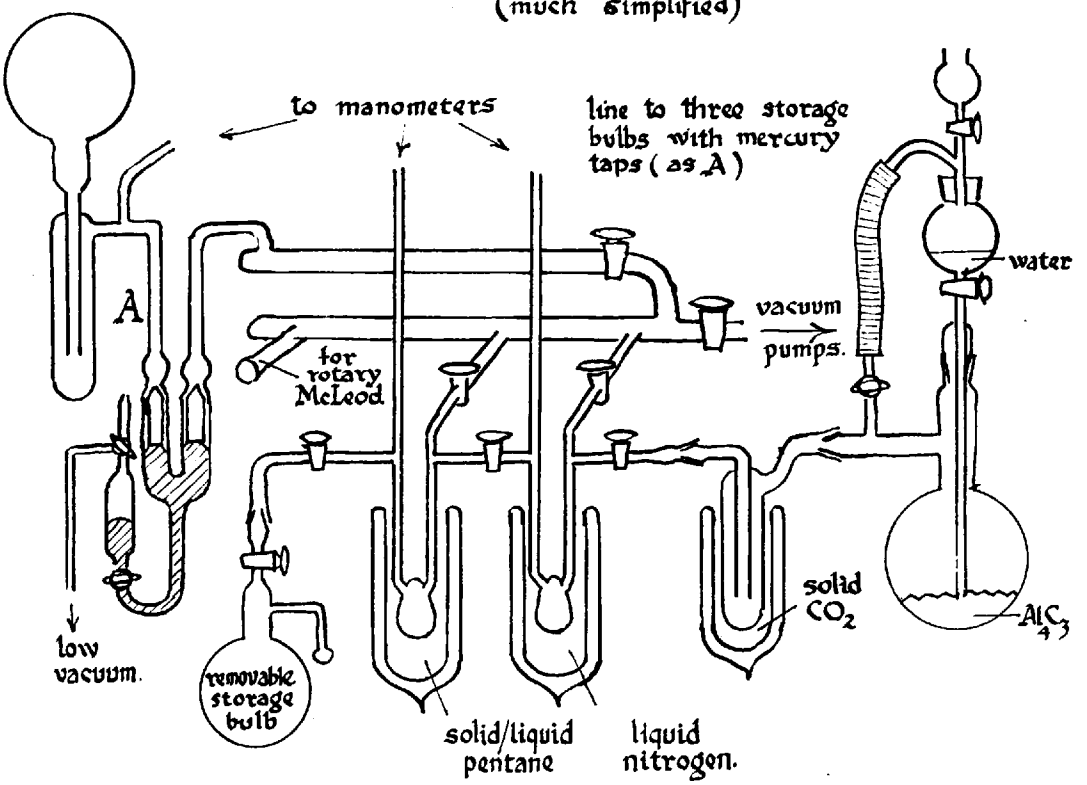
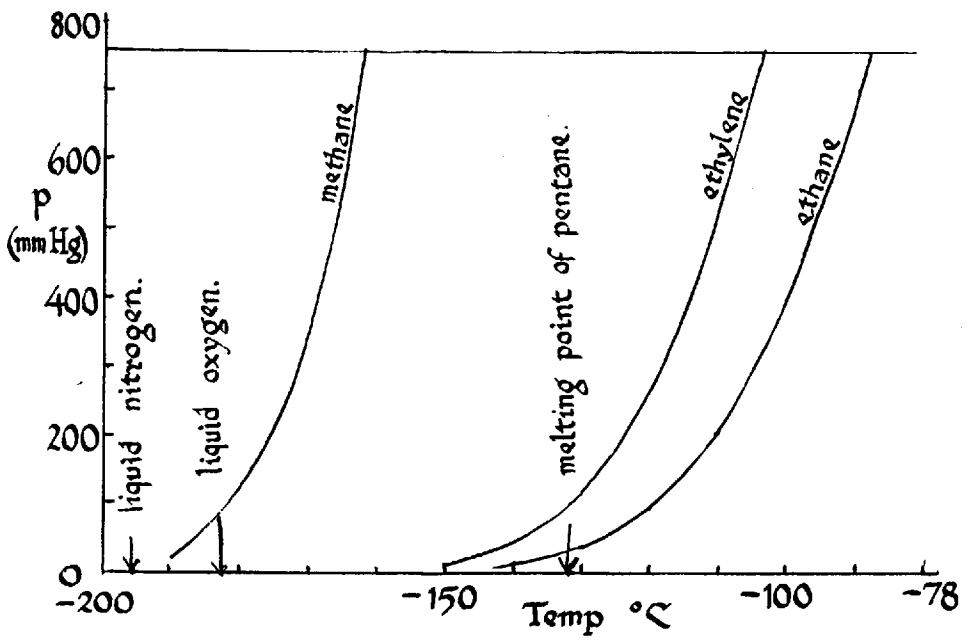


Figure 6. Vapour pressure curves.



flask carefully with a flame and pumping continuously.

After the above preliminaries an excess of water was run slowly on to the carbide. Although there was considerable gas evolution at room temperature, it was necessary to heat the reaction mixture in order to obtain complete dissolution of the carbide. The reaction is represented by the equation:-

$$Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3$$

However, as may be judged from the smell, the gas evolved contains traces of numerous impurities. Those cited in the references given include hydrogen, acetylene, ethylene, ethane, silane, ammonia, carbon dioxide, and hydrogen sulphide. Some of these gases are formed by side reactions, others from substances in the carbide.

To purify the methane the gas was first passed through a solid carbon dioxide cooled trap and condensed in one of the bulbs of the fractionating apparatus surrounded by liquid nitrogen. Pumping the liquid methane caused it to solidify and removed the 'permanent' gases - hydrogen, nitrogen etc. It was then distilled repeatedly between two bulbs at the temperatures of liquid nitrogen and melting pentane, in order to remove ethylene*, until the liquid methane had a constant vapour pressure at liquid oxygen temperature. The pentane bath was prepared by the addition of liquid nitrogen to 'Analar' petroleum ether and stirring to give a thick cream.

After purification, the methane was transferred to storage bulbs fitted with vacuum taps and standard ground joints. One of these bulbs was then attached to the thermal diffusion

* See Figure 6 for vapour-pressure curves.

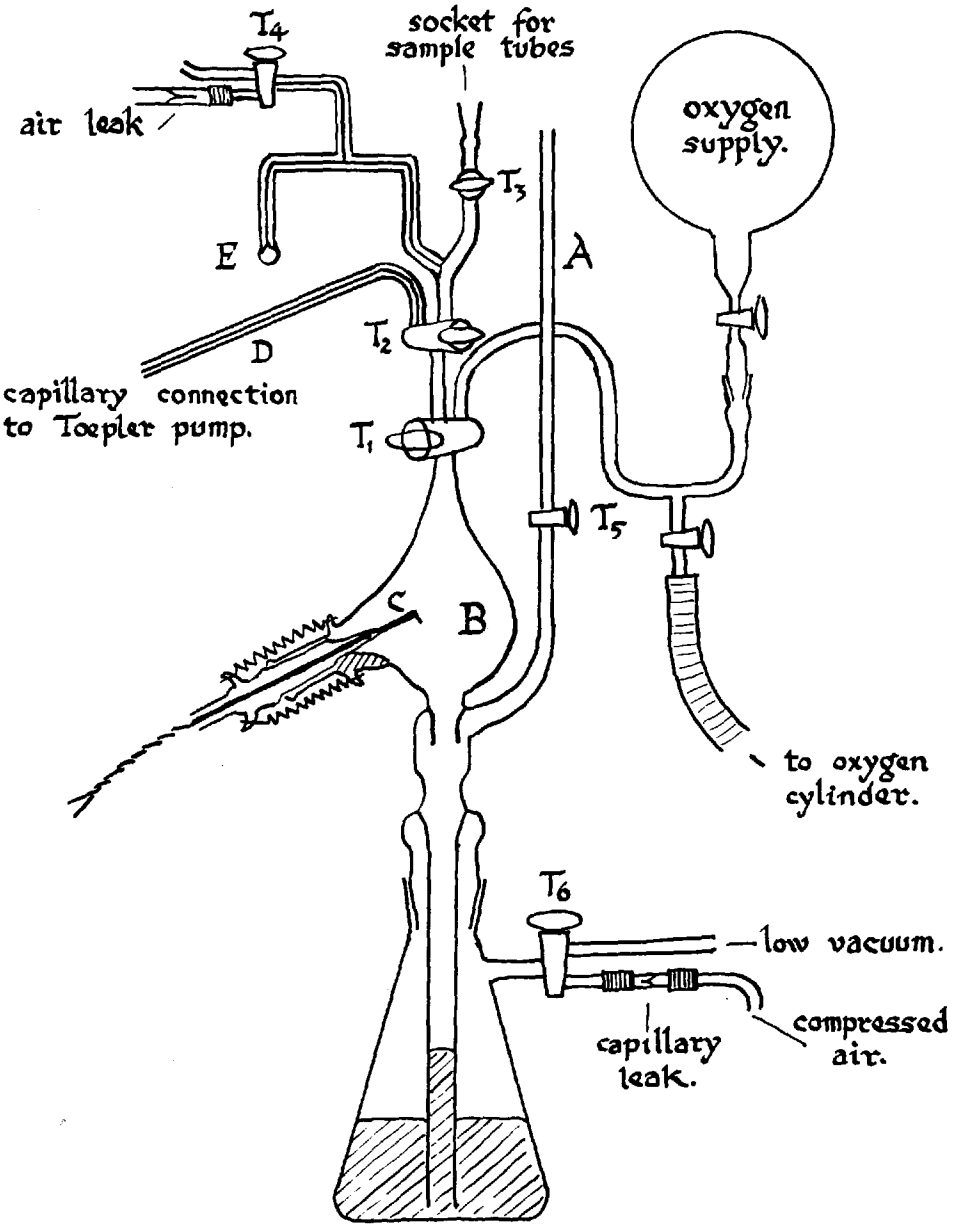
constant apparatus.

3. COMBUSTION OF METHANE SAMPLES.

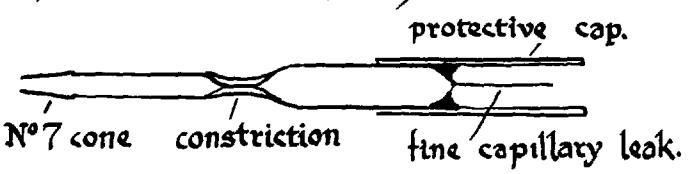
It was decided to avoid the difficulties of direct mass-spectrometric analysis of methane by converting the gas to carbon dioxide beforehand. The apparatus constructed for this is shown in Figure 7. The combustion bulb B was roughly calibrated for volume and wrapped externally with transparent adhesive tape as a precaution against possible explosions. The platinum wire filament C was spot-welded, via nickel, to two tungsten leads sealed through the tip of an extended pyrex cone and could thus be removed readily for replacement. The cone was held into the socket in the side of B by steel springs. All vacuum taps were greased with silicone to prevent contamination of the apparatus with organic matter. The pressure in B could be read directly from the tall manometer A.

The procedure for burning a sample of methane was as follows: The gas was pumped from the thermal diffusion apparatus by Toepler pump along the inclined capillary connection D into the bulb B which was evacuated previously through A and also through T_1, T_2 and T_4. Twenty times the quantity of oxygen was then admitted to B from a storage bulb filled by connecting to a gas cylinder when required. This excess was chosen from a consideration of the explosion limits of methane-oxygen mixtures - lower 6.5%, upper 51.9% by volume of methane [J5]. To cause reaction, the filament C was heated to redness with current from an accumulator. The start

Figure 7 Methane combustion apparatus.



Gas sample tube — half size



of combustion, if not the whole process, was marked by a momentary increase in the brightness of the glowing platinum wire; normally current was passed for at least one minute. Using the compressed air supply at T_6, the contents of B were now pushed into the small bulb E surrounded by liquid nitrogen where they condensed. Excess oxygen was pumped away through T_4 and the liquid nitrogen then replaced by solid carbon-dioxide alcohol mixture which retained ice and allowed the carbon dioxide resulting from the combustion of methane to expand into a standard sample tube in the socket above tap T_3. Mercury was pushed almost up to the constriction before sealing off the tube, the only loss of sample being the gas remaining in the capillary lead and bulb E. To prevent mercury rising toohigh and filling the latter, air was admitted through the capillary leak on T_4 as required.

4. MASS SPECTROMETER ANALYSIS

All gas samples were analysed with a Nier-type 60° sector mass spectrometer constructed by Dr. Winter; the instrument was essentially that described by Graham, Harkness and Thode [G5], [W9].

In an analysis, the gas is admitted at low pressure ($\sim 10^{-4}$ mm. mercury) into the ion source of the mass spectrometer where a certain proportion is ionised by electron bombardment. The positive ions produced are collimated by a system of slits and electromagnetic fields into a narrow beam which is accelerated down the spectrometer tube by a high potential. A large electromagnet spreads the beam into a mass-spectrum

and by varying either the field strength (magnet current), or the accelerating potential, ions of the desired mass may be focussed on a collector. The minute current of 10^{-14} to 10^{-10} amp. so produced is amplified and fed through suitable shunts to a galvanometer. Thus, knowing the shunt factors, the abundance ratio of any pair of ion species may be obtained from the corresponding galvanometer deflections.

The equation (3 - 26) for calculating the thermal diffusion constant from experimental results contains the concentration change and average concentrations of the isotopic species studies. These quantities have been derived from the abundance ratios of initial and final samples in the following ways [P1, p.37 ff]:-

(a) When there are only two components in the gas mixture, of fractional concentrations x and (1 - x), the abundance ratio R is given by:-

$$R = x/(1 - x) \qquad (4 - 1)$$

from which one has the simple relationships:-

$$x = R/(R + 1), \quad (1 - x) = 1/(R + 1) \qquad (4 - 2)$$

which were used when treating the results from experiments with carbon monoxide and carbon dioxide (from methane).

(b) For diatomic molecules formed from atoms of two isotopes three molecular masses are possible. Considering nitrogen, one has the molecules $^{14}N_2$, $^{14}N^{15}N$ and $^{15}N_2$. If the fractional concentration of the rare isotope of mass 15 is x, and if it is assumed that the probability of formation of the three molecular species is the same for each, then the concentration

of $^{15}N_2$ will be proportional to x^2, that of $^{14}N_2$ to $(1 - x)^2$ and that of the mixed type $^{14}N^{15}N$ to $2x(1 - x)$, Thus:-

$$R = \text{abundance of mass 28./abundance of mass 29}$$
$$= (1 - x)^2/2x(1 - x) = (1 - x)/2x \qquad (4 - 3)$$

from which:-

$$x = 1/(2R + 1)$$
$$c_1 = [2R/(2R + 1)]^2, \; c_2 = 4R/(2R + 1)^2 \qquad (4 - 4)$$

When the gas analysed contains more than two isotopes in appreciable amounts, a procedure similar to the above is complex. The heavy carbon monoxide from the A.E.R.E., Harwell used in the later experiments with this gas contained $^{12}C^{16}O$, $^{12}C^{18}O$, $^{13}C^{16}O$, $^{13}C^{18}O$, together with small amounts of $^{12}C^{17}O$ and $^{13}C^{17}O$. In face of this difficulty, method (a) was used when calculating results.

5. ALTERNATIVE METHODS OF EMPLOYING ANALYTICAL RESULTS

As noted in the last chapter (section 5(a) iv) Nier, and later Mann, calculated the concentration difference between initial and final samples from the results of mass spectrometric analysis by a method different from that used here. They took the average difference between the ratios obtained for the enriched and the normal gas and divided this by the average ratio for the latter. This procedure eliminates the need for knowing the factors for the galvanometer shunts used provided that the method of analysis is standard. It does not give the composition of the gas analysed and this information has to be obtained from other measurements.

The concentration term required is (3 - 26):-

$$2[(c_2)_F - (c_2)_I]/[(c_2)_F + (c_2)_I] \qquad (4 - 5)$$

where the subscripts denote 'final' and 'initial'. Nier used:-

$$(R_F - R_I)/R_I \qquad (4 - 6)$$

Now (4 - 5) may be written in terms of R by using (4 - 2) or (4 - 4) to give:-

$$2(R_F - R_I)/(R_I + R_F + 2R_IR_F) \qquad (4 - 7)$$

or:-

$$2(R_F - R_I)(1 - 8R_IR_F)/(4R_IR_F[R_I + R_F + 2] + [R_I + R_F]) \qquad (4 - 8)$$

respectively.

To reduce these expressions to the simple form (4 - 6) used by Nier, it must firstly be assumed that the concentration change is small enough for R_I and R_F to be virtually the same. Writing R for each, one finds that (4 - 7) becomes:-

$$(R_F - R_I)/(R + R^2) \qquad (4 - 9)$$

and (4 - 8) reduces to:-

$$(R_F - R_I)[(1 - 8R^2)/(4R^3 + 4R^2 + R)] \qquad (4 - 10)$$

If it is assumed additionally that R is sufficiently small for its square and higher powers to be negligible in comparison with itself, both (4 - 9) and (4 - 10) become equal to (4 - 6).

For normal gases the concentration of rare isotopes is small enough for the approximations of Nier to be justifiable;

but this is not the case for enriched isotopic mixtures.

6. EXPERIMENTAL RESULTS

The results obtained from experiments carried out as described in this chapter are given in Table 6. The values of α (elastic sphere model) required for calculating R_T are as under:-

TABLE 5

α for the elastic sphere model*

Molecular masses	Gas	α es x 10^2
16, 17	CH_4	2.70
28, 29	CO, N_2	1.56

* calculated from equation (2 - 4)

The data shown were derived as follows:-

Temperature range - the lower temperature was measured with a mercury in glass thermometer and did not vary by more than a few degrees. The higher temperature has a probable accuracy of $\pm$ 5°K.

Volume factor - calculated from the known bulb volumes (Table 4) and temperatures using equation (3 - 24).

Concentrations - calculated for carbon monoxide with (4 - 2) and for nitrogen and methane with (4 - 4) from the abundance ratios of initial and final samples. The error limits quoted for Δ c were derived directly from the standard deviations of the individual abundance ratios for each sample.

Thermal diffusion constant (α) - obtained by substitution of the above values into (3 - 26). The error limits are those

TABLE 6. Results of the thermal diffusion constant measurements

Temp.range	Volume factor	No.of sepns.	$(c_1)_{AV}$	$(c_2)_{AV}$	$\Delta c \times 10^4$	$\alpha \times 10^3$	T_r (°K)	$T_{13:7}$ (°K)	R_T(exp)	R_T(13:7)
Normal carbon monoxide										
294-668	0.718	6	98.96	1.04	4.1±0.2	11.3±0.6	431	432	0.72±0.03	0.50
295-528	0.674	4	98.94	1.06	1.7±0.3	10.3±1.8	389	392	0.66±0.12	0.48
195-423	0.709	4	98.95	1.05	1.2±0.3	5.3±1.3	280	284	0.34±0.08	0.37
Nitrogen										
195-427	0.677	5	91.70	8.12	14±1	7.1±0.5	281	285	0.47±0.03	0.44
195-428	0.677	5	91.70	8.12	19±3	7.8±1.2	281	285	0.50±0.08	0.44
294-678	0.688	5	91.46	8.35	20±1	9.1±0.2	434	43x10	0.58±0.01	0.54
294-683	0.689	5	91.33	8.46	20±2	8.9±0.9	435	43x10	0.57±0.06	0.54
Enriched carbon monoxide										
293-683	0.689	5	39.1	60.9	62±8	8.9±1.1	434	435	0.57±0.07	0.50
296-663	0.687	6	40.5	59.5	56±5	7.0±0.6	431	432	0.45±0.04	0.50
195-427	0.677	5	38.9	61.1	45±2	7.1±0.3	281	286	0.45±0.02	0.38
195-429	0.677	5	38.7	61.3	45±2	7.1±0.3	281	286	0.45±0.02	0.38
Methane										
295-708	0.696	5	98.91	1.08	3.5±0.1	11±0.1	443	448	0.41±0.01	0.45
295-708	0.696	5	98.89	1.11	3.6±0.2	11±0.6	443	448	0.41±0.02	0.45
195-433	0.679	5	98.91	1.09	2.1±0.2	7.2±0.7	283	289	0.27±0.03	0.30
195-435	0.680	5	98.89	1.11	2.0±0.1	6.7±0.3	283	290	0.25±0.01	0.30

due to the uncertainty in the values of the concentration changes only. Other possible sources of variation are probably negligible in comparison.

Average temperatures. T_r was calculated from (3 - 22); the $T_{13:7}$ values were obtained using (3 - 36 etc.) as shown in Table 3.

R_T values. The experimental values were obtained from the α's by division with the appropriate α_{es} (Table 5 above). The theoretical values were derived by graphical interpolation between the data of Table 2 (see also Figure 1).

It will be at once evident from the results that the determining factor in the accuracy of thermal diffusion constant measurement by this method is that of the mass spectrometer analyses. With the instrument used abundance ratios could be determined with an accuracy of 0.1% under the most favourable conditions; the minimum error asscciated with the measurement of the overall experimental concentration changes was generally about 10%. Greater precision than this may only be attained by considerable refinement of technique [L11]. The author is much indebted to Dr. E.R.S. Winter for carrying cut, as carefully as possible, all the analyses resulting from the thermal diffusion experiments. Each abundance ratio was measured from ten to twenty times, the appropriate ions being focussed by manual scanning of the accelerating potential. The mean value of the abundance ratio was then taken for calculating the composition of the sample. The initial and final samples from a thermal diffusion

constant run were always analysed consecutively on the same day.

Air leakage into the two-bulb apparatus during an experiment or into the sample-tubes would vitiate the results obtained with carbon monoxide or nitrogen. The oxygen peak of mass 32 was therefore measured for all samples to check that no such leakage had occurred. The mass 40 peak due to argon was sometimes used for the same purpose.

7. DISCUSSION OF RESULTS

a) Carbon monoxide.

The experiments with normal carbon monoxide were the first to be carried out and were therefore more subject to errors in technique than the others recorded in Table 6. Also, the concentration changes obtained were much smaller than in the later runs performed with isotopically enriched material. The high values of R_T found from the first two experiments might well be due to slight air leakage considered insignificant at the time of analysis. For these reasons the early runs are undoubtedly the least reliable of those quoted.

In the case of the heavy carbon monoxide experiments duplicate runs were performed at each of the two temperature ranges. Agreement between the individuals was fairly good. Whereas the difference between experiment and theory is negligible for the upper temperature range, a discrepancy of almost 20% exists at the lower. Since the apparatus and technique used at the time was unlikely to duplicate such an error, it may only be concluded that it was due to slight

inadequacy of the theory or the over-simplified method employed for calculating concentration changes from the abundance ratios. The second of these reasons requires that the experimental values at both temperatures are incorrect.

b) Nitrogen.

The first experiments carried out with nitrogen were spoiled - some by leakage of air into the two-bulb system and others by slight instability in the mass spectrometer circuits during sample analysis. The results quoted in Table 6 were obtained when the apparatus was in its final and most efficient form.

Shortly after the present work was started a value for the thermal diffusion factor of nitrogen obtained by Mann [M1] became available, and this is included in the table below. His method of calculating the result has already been mentioned (Chapter 3 (3), this chapter (5)).

TABLE 7

Experimental thermal diffusion factors for nitrogen.

Reference.	Temp.range (^{o}K)	$\alpha \times 10^{3}$	R_T(exptl.)*	R_T(13:7)
Table 6	195 - 428	7.1 ± 0.5	0.47 ± 0.03	0.44
[M1]	195 - 623	5.1 ± 0.5	0.33 ± 0.03	0.48
Table 6	294 - 680	9.1 ± 0.2	0.58 ± 0.01	0.54

* In this and the Table (8) below, the result with the smaller standard deviation is quoted.

It will be seen that Mann's value is low whereas those from the present work agree with the theoretically predicted values within the possible limits of experimental error. As

observed with carbon monoxide, the mean value for the lower temperature range was higher than would be expected.

c) Methane.

The experimental method used by Nier for his work on methane is considered earlier (Chapter 3 (3) and (5) a). The wide discrepancies between his results and the predictions of the L.J. 13:7 model initiated the present experiments: Nier's results and those found in this work are compared with each other and the theory in Table 8 below.

TABLE 8

Experimental thermal diffusion factors for methane.

Reference	Temp.range (^{o}K)	$\alpha \times 10^3$	R_T(exptl.)	R_F(13:7)
Table 6	195 - 434	6.7 ± 0.3	0.25 ± 0.01	0.30
[N1]	295 - 573	7.4 ± 0.7	0.27 ± 0.03	0.42
Table 6	295 - 708	11 ± 0	0.41 ± 0.01	0.45
[N1]	295 - 728	8.0 ± 0.8	0.30 ± 0.03	0.46

The agreement between the new values and theory is quite satisfactory considering the small concentration changes obtained and the chance of error associated with the combustion of the samples.

8. CONCLUSIONS

The present study affords further evidence that the detailed theory of Chapman and Enskog is suitable for predicting the thermal diffusion effect in isotopic gas mixtures, at moderate temperatures and pressures, when molecular interaction is represented by a Lennard-Jones type

equation having force indices of seven and thirteen. Where discrepancies between experiment and theory exist, the accuracy of the measurements is insufficient to allow significant criticism of the force-law.

Although thermal diffusion is the gas property most sensitive to the form of intermolecular forces acting, this advantage is outweighed by the experimental difficulty of measuring with sufficient accuracy the small concentration changes obtained with the two-bulb type of apparatus in isotopic mixtures. A mass-spectrometer giving abundance ratios with an accuracy of at least one part in ten thousand would be required to make experiments of this nature a reliable means for testing a force law in detail. Other improvements in technique would be the provision of precise temperature control for the two bulbs and the use of more detailed methods for calculating the concentration change from abundance ratios taking into account the rarer isotopic species present [P1]. Further experiments of accuracy similar to that obtained in this work would best be restricted to preliminary investigations and the clearing-up of major existing anomalies. Of the latter may be quoted the results of Stier for argon and neon which are less than half those predicted by theory at the lower temperature ranges studied [S3, W5].

With ordinary gas mixtures, much larger separations are obtainable in a two-bulb system and correspondingly greater experimental accuracy is possible. In addition, methods other than use of a mass-spectrometer may be employed for

gas analysis, thermal conductivity measurement or labelling one of the species with a radioactive isotope and determining the change in its activity being examples. It may be noted that the results obtained with mixtures of argon and neon are in better accord with theory than those mentioned above for the individual gases [G3, A1].

Evidence for the suitability or otherwise of a molecular model may be gained by the precise study of any gas property. One particularly informative in this respect is the third virial coefficient (see equation 2 - 2). Hirschfelder, Bird and Spotz recently presented a comparison between experimental virial data and the values predicted theoretically for the L.J. 13:7 case [H4]. They found good agreement for argon, methane and nitrogen; hydrogen, helium and ellipsoidal molecules, such as those of carbon dioxide, ethylene and ethane, were however, poorly represented by the model. One would expect that thermal diffusion results should show a parallel measure of agreement in these cases and the present work indicates that this is the case.

CHAPTER 5.

THE THERMAL DIFFUSION COLUMN - THEORY

1. INTRODUCTION

The thermal diffusion column was invented by Clusius and Dickel in 1938 [C4] and utilises the combined action of convection and thermal diffusion to obtain relatively large separations of the components in a gas mixture. Whereas, in all practical apparatus, the latter is confined between a heated vertical wire, or tube, and a concentric externally-cooled tube the first theoretical treatments of the separating column were derived for the case of an apparatus consisting of two parallel and vertical flat walls maintained at different temperatures. In the theories of Waldmann [W10] and van der Grinten [G4] the temperature dependences of the gas density, viscosity, thermal conductivity and diffusion coefficient were ignored; in the solution of Furry, Jones and Onsager [F4], these dependences were included in a general manner it only being necessary to specify their exact form in the final stages of the treatment. They later extended this theory to take the cylindricity of normal apparatus into account [F5]. All these results are summarised in the review article by Jones and Furry [J1] which contains, amongst other new material, an elementary treatment of the separating column. Although this simple theory gives a clearer picture of the processes taking place, an account of the detailed treatment is presented

here since a number of the equations introduced during the derivation are employed in calculations described later (see Chapter 8)

2. THEORY OF THE SEPARATING COLUMN

The apparatus consists of two vertical walls of breadth B, length L and separation 2w which are maintained at differing temperatures T_1, T_2. The temperature distribution in the gas between them is taken to be that due to conduction alone. Thus:-

$$Q = \lambda \, dT/dx \qquad (5 - 1)$$

$$2w \, Q = \int_{T_1}^{T_2} \lambda \, dT \qquad (5 - 2)$$

where Q is the heat flow between the walls, x is the coordinate perpendicular to them and λ is the thermal conductivity. The gas properties λ, ρ (density), η (viscosity) and D (diffusion constant) will vary little with changes in c_1, the concentration of the lighter component, and these dependences are ignored. For the isotopic mixtures studied in this work no inaccuracy is thereby introduced.

The hydrodynamical equation for steady viscous flow is:-

$$(\text{div } \eta \text{ grad})v = \text{grad } P - \rho g \qquad (5 - 3)$$

Using (5 - 1) to change the independent variable in the form:-

$$\partial / \partial x = (Q/\lambda) \partial / \partial T \qquad (5 - 4)$$

one finds from (5 - 3) that:-

$$(Q^2/\lambda) d/dT(\eta/\lambda) dv/dT = dP/dz - \rho g \qquad (5 - 5)$$

Since the convection velocity v must vanish at the walls,

the boundary conditions are:-

$$v(T_1) = v(T_2) = 0 \qquad (5 - 6)$$

The equation describing thermal and ordinary diffusion is (3 - 6):-

$$c_1(v_1 - v) = - D[\text{grad } c_1 - \alpha c_1 c_2 \text{ grad ln } T] \qquad (5 - 7)$$

Writing J_1 for the flux $\rho c_1 v_1$ of the lighter component:-

$$J_1 = \rho c_1 v - \rho D[\text{grad } c_1 - \alpha c_1 c_2 \text{ grad ln } T] \qquad (5 - 8)$$

For the x direction one has:-

$$J_{1x} = - (\rho DQ/\lambda)[\partial c_1/\partial T - \alpha c_1 c_2/T] \qquad (5 - 9)$$

In order to avoid undue complexity, conditions in the column at any time during the separation are assumed the same as those existing at equilibrium. Expressed mathematically:-

$$\text{div } J_1 = \text{div } J_2 = 0 \qquad (5 - 10)$$

This 'quasi stationary' assumption is similar to that involved in the derivation of the expression for the equilibrium time in a two-bulb system (Chapter 3 (2)). Thus it implies that the time rate of change of the gas composition at the ends of the column is negligible, which condition will hold when the latter are connected to large reservoirs. Bardeen showed that, even for the case of a column closed at both ends, use of the assumption introduces little error [B4]. From equations (5 - 4/8/10) one obtains:-

$$\partial/\partial T(\rho D/\lambda)[(\partial c_1/\partial T) - (\alpha c_1 c_2/T)] = (\lambda\rho/Q^2)[v(\partial c_1/\partial z) - D(\partial^2 c_1/\partial z^2)] \qquad (5 - 11)$$

The second term of the right hand side gives the longitudinal diffusion in the column. For simplicity it is omitted at this stage, a separate expression for the effect being obtained and added later.

A function G(z, T) is now introduced defined by:-

$$(\partial c_1/\partial z)G(z, T) = -(\lambda Q^3/\rho D)J_{1x}$$
$$= Q^4[\partial c_1/\partial T - \alpha c_1 c_2/T] \qquad (5 - 12)$$

Since the flow of species 1 is zero at the walls:-

$$G(z, T_1) = G(z, T_2) = 0 \qquad (5 - 13)$$

Omitting the diffusion term in (5 - 11) and substituting (5 - 12) one finds:-

$$\partial/\partial T(\rho D/\lambda)\partial c_1/\partial z.\ G(z, T) = \lambda\rho Q^2 v\,\partial c_1/\partial z \qquad (5 - 14)$$

The transport of species 1 along the tube is:-

$$\tau_1 = B\int_{-W}^{W} \rho c_1 v\, dx = (B/Q)\int_{T_1}^{T_2} \lambda\rho c_1 v\, dT = \text{constant} \qquad (5 - 15)$$

For a 'quasi-stationary' state $\partial c_1/\partial T$ is independent of z thus:-

$$\partial^2 c/\partial z.\partial T = 0 \qquad (5 - 16)$$

From (5 - 15):-

$$\partial\tau_1/\partial z = \frac{\partial c_1}{\partial z}(B/Q)\int_{T_1}^{T_2}\lambda\rho v\, dT = (\partial c_1/\partial z)\tau = 0 \qquad (5 - 17)$$

Therefore the total transport τ is zero as would be expected. From (5 - 13/14) it is possible to deduce that G(z, T) is in fact a function of the temperature only. (5 - 14) gives that:-

$$v = (1/\lambda\rho Q^2)d/dT[(\rho D/\lambda)G] \qquad (5 - 18)$$

Substitution of this result into (5 - 5) gives the following differential equation for G:-

$$(1/\lambda)d/dT(\eta/\lambda)d/dT(1/\lambda\rho)d/dT([\rho D/\lambda]G) = dP/dz - \rho g \qquad (5 - 19)$$

which is subject to the boundary conditions:-

$$G(T_1) = G(T_2) = G'(T_1) = G'(T_2) = 0 \qquad (5 - 20)$$

From equations (5 - 15/18) it follows that:-

$$\tau_1 = (B/Q^3)\int_{T_1}^{T_2} c_1\, d/dT(\rho DG/\lambda)dT \qquad (5 - 21)$$

which by use of (5 - 12). and the boundary conditions gives:-

$$\tau_1 = Hc_1c_2 - K_c\, \partial c_1/\partial z \qquad (5 - 22)$$

where H is defined by:-

$$H = (B/Q^3)\int_{T_1}^{T_2} (\rho DG/\lambda T)dT \qquad (5 - 23)$$

and represents the transport caused by thermal diffusion acting across the gas space. The constant K_c describes the remixing action of the convection currents, and is given by:-

$$K_c = (B/Q^7)\int_{T_1}^{T_2}(\rho DG^2/\lambda)dT \qquad (5 - 24)$$

The remixing due to ordinary diffusion along the tube is (assuming the process independent of the convection):-

$$\tau_1 = - K_d\, \partial c_1/\partial z$$

where

$$K_d = (B/Q)\int_{T_1}^{T_2}(\lambda\rho D)dT \qquad (5 - 25)$$

The constants H, K_c and K_d defined above are termed the

"transport coefficients" and are used in variously-derived forms for describing the performance of thermal diffusion columns.

3. EXPLICIT EQUATIONS FOR THE TRANSPORT COEFFICIENTS

Before the expressions (5 - 23/4/5) may be used, it is necessary to solve the equation (5 - 19) for the function G. In order to do this, the manner in which the gas properties therein vary with temperature must be specified and, up to the present, only relations derived from the inverse power model have been used for the purpose. Before describing the result obtained, however, the simpler case of a column with a small temperature difference between the walls is considered.

a) Solution for a small temperature difference.

When the difference between the wall temperatures is quite small it is justifiable to consider the gas properties as differing inappreciably from their values at the mean temperature. If they are assumed exactly constant, the equation for G reduces to (putting $\beta = - d\rho/dT$):-

$$d^4G/dT^4 = (\lambda^4 \beta g/\eta D) \qquad (5 - 26)$$

which, when solved using the boundary conditions (5 - 20) yields the simple result:-

$$G = (\lambda^4 g\beta/24\eta D)(T_2 - T)^2(T - T_1)^2 \qquad (5 - 27)$$

From (5 - 2):-

$$Q = \lambda \Delta T/2w \qquad (5 - 28)$$

Putting these expressions into (5 - 23/4/5) one obtains the following explicit expressions for the transport coefficients:-

$$H^{(o)} = (2w)^3 \alpha\beta\, \rho g B(\Delta T)^2/6!\,\eta T \qquad (5 - 29)$$

$$K_c^{(o)} = (2w)^7 g^2 \beta^2 \rho B(\Delta T)^2/9!\,\eta^2 D \qquad (5 - 30)$$

$$K_d^{(o)} = 2w\rho DB \qquad (5 - 31)$$

Since $\beta = \rho/T$ for a gas, these equations may be slightly simplified.

b) Solution for Maxwellian molecules.

For the inverse power model, the simplifying relationships (2 - 6) hold which reduce the equation for G to:-

$$d/dT(1/T^n)\,d^2/dT^2(1/T^{n-1})\,dG/dT = -(1/T^2)(\lambda^4 \rho g/\eta D T^{2n-2}) \qquad (5 - 32)$$

Jones and Furry give the solution of this for the cases n = 1 (Maxwellian gas) and n = 1/2 (elastic spheres). Only the former is given here, since the latter molecular model is quite unrealistic. For n = 1, (5 - 32) gives for the boundary conditions (5 - 20):-

$$G = (\lambda^4 g\rho/12\eta D)(T_2 - T)^2(T - T_1)^2/(T_1 + T_2) \qquad (5 - 33)$$

which is, in fact, identical with the result (5 - 27); Q is again given by (5 - 28). Solving for the transport coefficients yields:-

$$H = [(2w)^3 \rho^2 \alpha g B/6!\,\eta](\Delta T/T)^2 = H^{(o)} \qquad (5 - 34)$$

$$K_c = [(2w)^7 \rho^3 g^2 B/9!\,\eta^2 D](\Delta T/T)^2 = K_c^{(o)} \qquad (5 - 35)$$

$$K_d = 2w\rho DB(1 + u^2/3) = K_d^{(o)}(1 + u^2/3) \qquad (5 - 36)$$

when α, the thermal diffusion constant, is assumed proportional

to T. The quantity u is defined by:-

$$u = (T_2 - T_1)/(T_2 + T_1) = \Delta T/2\bar{T} \qquad (5 - 37)$$

c) Other solutions.

In chapter 8 a new method of solving the differential equation (5 - 19) for G is presented in which the gas properties are assumed to have a power dependence on temperature.

d) The cylindrical case.

If the cylindrical form of a normal thermal diffusion column is taken into account, the theory becomes considerably more complex. An approximate solution is available, however, for the case where the ratio of the radii (r_1/r_2) is not greater than 2.7 (e). The transport coefficients are then given by:-

$$H = H^{(o)}[1 + h_1 \ln r_1/r_2 + h_2(\ln r_1/r_2)^2 + \ldots] \qquad (5 - 38)$$

where $h_1 = 0.838\ u$

$h_2 = -0.174 + 0.363\ u^2$, and u is given by (5 - 37) above.

$$K_c = K_c^{(o)}[1 + c_1 \ln r_1/r_2 + c_2(\ln r_1/r_2)^2 + \ldots] \qquad (5 - 39)$$

$c_1 = 1.721\ u$

$c_2 = -0.213 + 1.505\ u^2$

$$K_d = K_d^{(o)}[1 + u^2/3 + d_1 \ln r_1/r_2 + d_2(\ln r_1/r_2)^2 + \ldots] \qquad (5 - 40)$$

$d_1 = -0.333\ u + 0.067\ u^3$

$d_2 = -0.022\ u^2 + 0.010\ u^4$

The constants $H^{(o)}$, $K_c^{(o)}$ and $K_d^{(o)}$ are given by (5 - 29/30/1), the gas properties being evaluated at the mean temperature.

For this 'nearly plane' case, the breadth B is taken as the mean circumference:-

$$B = \pi (r_1 + r_2) \qquad (5 - 41)$$

Also $$2w = r_1 - r_2 \qquad (5 - 42)$$

In their review [J1], Jones and Furry give expressions for the transport coefficients for the case where r_1/r_2 is large, as for a hot wire column. These are not required here, however.

4. CONSEQUENCES OF THE TRANSPORT EQUATION

The transport equation (5 - 22) may be written in the general form:-

$$\tau = Hc\bar{c} - Kdc/dz \qquad (5 - 43)$$

where $c = 1 - \bar{c}$ increases with z the coordinate along the column. At equilibrium $\tau = 0$ and so:-

$$Hc\bar{c} = Kdc/dz$$

$$dc/c\bar{c} = d \ln(c/\bar{c}) = (H/K)dz \qquad (5 - 44)$$

Integrating between the ends of the column (denoted by i, f)

$$[\ln(c/\bar{c})]_i^f = (H/K)[z]_i^f$$

from which:-

$$q_e = (c/\bar{c})_f/(c/\bar{c})_i = \exp(HL/K) = \exp 2AL \qquad (5 - 45)$$

q_e is the equilibrium separation factor (cf equation 3 - 9) and the constant A is given by:-

$$A = H/2K \qquad (5 - 46)$$

For a simple design of column, the separation obtained is less than predicted by (5 - 45). This is normally considered due

to imperfections in the gas flow causing a certain amount of remixing. An additional 'parasitic' term is included in the transport equation to describe such effects and, since the latter are convective phenomena, it is given the same pressure dependence as K_c. Thus K in equation (5 - 43 etc.) is written as:-

$$K = K_c + K_d + K_p \qquad (5 - 47)$$

K_p cannot be calculated.

The usual experimental test of the theory is to study the variation with pressure of the equilibrium separation factor. Thus (5 - 45) may be changed to:-

$$\ln q_e = HL/K \qquad (5 - 48)$$

Since the thermal diffusion constant and viscosity do not vary with pressure, the diffusion constant is inversely proportional, and the density directly proportional, it follows from (5 - 29/30/1) that:-

$$\begin{aligned} H &\propto P^2 \\ K_c &\propto P^4 \\ K_d &\neq f(P) \end{aligned} \qquad (5 - 49)$$

Using (5 - 48) one then finds that:-

$$\ln q_e = HLP^2/[(K_c + K_p)P^4 + K_d] \qquad (5 - 50)$$

where P is the pressure in atmospheres and the transport coefficients are evaluated at one atmosphere. Inverting both sides of (5 - 50) and dividing throughout by P^2:-

$$1/P^2 \ln q_e = (K_c + K_p)/HL + (K_d/HL)1/P^4 \qquad (5 - 51)$$

A plot of $1/P^2 \ln q_e$ against $1/P^4$ will be a straight line for a column whose imperfections are solely of a parasitic remixing nature.

Dividing (5 - 50) by $K_c P^4$ gives (assuming, for the moment, zero K_p):-

$$\ln q_e = (HL/K_c)(1/P^2)/[1 + (K_d/K_c)(1/P^4)] \qquad (5 - 52)$$

which is usually written:-

$$\ln q_e = (a/P^2)/(1 + b/P^4) \qquad (5 - 53)$$

For a perfect column, therefore, the coefficients a and b have values given by:-

$$a = HL/K_c, \qquad b = K_d/K_c, \qquad a/b = HL/K_d \qquad (5 - 54)$$

and the $1/P^2 \ln q_e$ vs $1/P^4$ plot has slope b/a and intercept 1/a.

When considering experimental data, the same variables are plotted and the resulting line used to determine coefficients a', b' as for a perfect column. Thus:-

$$b'/a' = (\text{slope}) \text{ and } 1/a' = (\text{intercept}) \qquad (5 - 55)$$

From (5 - 52/3) it will be evident that:-

$$a' = HL/(K_c + K_p), \quad b' = K_d/(K_c + K_p) \qquad (5 - 56)$$

if a K_p term can account for all the discrepancy between theory and experiment. An important consequence of this result is that:-

$$a'/b' = HL/K_d = a/b \qquad (5 - 57)$$

The slope of the $1/P^2 \ln q_e - 1/P^4$ plot is therefore independent of any parasitic remixing in the column. From

(5 - 54/6) it follows that:-

$$a/a' = b/b' = 1 + K_p/K_c \qquad (5 - 58)$$

Owing to experimental error and inadequacy of the theory, a/b does not equal a'/b' exactly. It seems best to use:-

$$[a/a' + b/b']/2 = 1 + K_p/K_c \qquad (5 - 59)$$

when estimating K_p, and this method is employed when treating the results described later.

The gas pressure at which the maximum separation should be obtained is found from the experimental equation for $\ln q_e$ by diffentiation and equating to zero.

$$\ln q_e = (a'/P^2)/(1 + b'/P^4) \qquad (5 - 60)$$

$$d(\ln q_e)/dP = 2a'P^{-3}[b'P^{-4} - 1] = 0$$

Hence:- $$P \text{ (optimum)} = \sqrt[4]{b'} \qquad (5 - 61)$$

5. EQUILIBRIUM TIME FOR A COLUMN

The time required for a column to reach equilibrium depends on whether there are reservoirs at the ends, and on the rate of removal of gas from the latter if it is being used for the continuous production of enriched material. The appropriate expressions for calculation of the relaxation time in these cases are given in [J1]; of these, only one need be quoted - that for a column closed at both ends, having reservoirs of inappreciable volume, and operated discontinuously:-

$$t_r = 2\mu/AH[1 + \pi^2/A^2L^2] \qquad (5 - 62)$$

Here μ is the mass of gas per unit length of the column. 'A' is best obtained from equations (5 - 45/60); the method for

calculating a suitable value of H when considering imperfect apparatus is more conveniently described later, (equation 7 - 6).

The equations giving the variation of composition with time of a gas mixture at any point in the column during the separation have been obtained by Bardeen [B5], whose treatment involved the assumption that c_1 is small enough to allow of $c_2(=1-c_1)$ being replaced by unity, and, without such approximation, by Majumdar [M4].

6. TURBULENCE

The column theory is based on the assumption that the gas flow is lamellar. The onset of turbulence is described by the Reynolds number:-

$$R = v\rho l/\eta \qquad (5 - 63)$$

where v is a velocity and l a length characteristic of the apparatus. Streamline flow ceases when R is exceeded due to an increase in operating pressure/convection rate. As shown by Onsager and Watson [O1], and Simon [S1] turbulence provides an additional mechanism for heat transfer through the gas in a column; thus if, for constant power input, the gas pressure is gradually increased, there is a sudden lowering in temperature of the hot wire, or tube, which marks the transition from lamellar to turbulent flow.

From their elementary column treatment, Jones and Furry derive the following equation for the Reynold's number:-

$$R = w^3 g \rho^2 \Delta T/48\eta^2 T \qquad (5 - 64)$$

which approximates, by use of (2 - 8), to:-

$$R = 2(K_c(o)/K_d(o))^{\frac{1}{2}} \qquad (5 - 65)$$

Onsager found that the critical value of R for a nearly plane column is about 25, and suggested that 10 should be a safe maximum to use in practice. Both he and Simon used an expression giving values for R 6.16 times those from (5 - 64). This is immaterial provided one or other formula is employed consistently.

Until recently, it has been assumed by most authors that turbulence decreases the separation attainable with a column; the experiments of Donaldson and Watson [D4] suggest that this is quite untrue and support the earlier observations of Clusius and Dickel [C7] and of Brewer and Bramley [B6] that increasing the number of spacers fitted to the wire of a hot-wire column results in an increased equilibrium separation factor. The effect is due to the introduction of complex new phenomena into the gas not, of course, to inadequacy of the Furry-Jones theory which may only be applied to columns in which turbulence is absent.

CHAPTER 6.

SOME EXPERIMENTS WITH THERMAL DIFFUSION COLUMNS AND PROPOSED MODIFICATIONS OF THE FURRY-JONES THEORY

1. THE METHANE COLUMN OF NIER

The results obtained by Nier [N2] with methane in a concentric tube separating column are first considered. When comparing experiment with theory he used transport coefficients calculated by Furry, Jones and Onsager [F4]. His operating conditions were similar to those assumed by the latter authors, and the only change he made was to substitute his own value of the thermal diffusion constant for that estimated by them from the inverse power model.

In the paper immediately following [N2], Bardeen used Nier's experimental results to illustrate his equations for the approach to equilibrium of a column [B5]; he employed imprecise values of the gas properties for evaluating the transport coefficient H, but determined A (see 5 - 46) empirically. The first accurate calculation of the transport coefficients was carried out by Jones and Furry [J1] who took, however, Nier's experimental value of the thermal diffusion constant instead of the figure they had used earlier in [E4]. The present work shows that the latter value is more nearly correct (see Table 8, Chapter 4).

In view of the uncertainties in the calculations

mentioned above, it appeared worth-while to re-evaluate the transport coefficients for Nier's column using the best obtainable values for the several gas properties. The results are presented in the following table together with those of Jones and Furry.

TABLE 9

Recalculation of transport coefficients for Nier's column

Column dimensions and operating conditions:-

$T_1 = 300^oK$ $T_2 = 573^oK$ $T = 436.5^oK$

$2w = 0.713$ cm. $B = 13.2$ cm. $L = 730$ cm.

Quantity	Jones & Furry	Source	New value	Source
ρ(gm/cms)x10^4	4.47	not stated	4.49	ideal gas laws
α	0.0077*	Nier's exptl. value [N1]	0.011	This work, Table 6
η(poise)x10^4	1.51	Exptl.value Ref. [T1]	1.55	[H3] calcd values
D (cm^2/sec)	0.474	Inverse power model T- index from [T1]	0.440	L.J 13:7 model. Equns 2-13/5/6

Transport coeffs. (equations 5 - 29/30/31, 38/39/40)

$H^{(o)}$	2.585 x 10^{-5}, [J1]	3.66 x 10^{-5}	g/sec (new value)
$K_c^{(o)}$	1.040 x 10^{-2}, "	1.10 x 10^{-2}	g.cm/sec "
$K_d^{(o)}$	1.998 x 10^{-3}, "	1.86 x 10^{-3}	g.cm/sec "

Correction for nearly-plane case:-

$H = H^{(o)} \times 1.109$ [J1]** $K_c = K_c^{(o)} \times 1.177$ $K_d = K_d^{(o)} \times 0.998$.

$= H^{(o)} \times 1.074$ (new value) (cont.)

H	2.866×10^{-5}, [J1]	3.93×10^{-5} g/sec (new value)
K_c	1.224×10^{-2}, "	1.30×10^{-2} g.cm/sec "
K_d	1.992×10^{-3}, "	1.86×10^{-3} g.cm/sec "

* Jones and Furry took the mean of Nier's two experimental results (Table 8); strictly one should take a value for α such that T_r (equation 3 - 32) equals the mean temperature of the column. The new value satisfies this condition quite closely.

** Jones and Furry used an expression, when correcting $H^{(o)}$, derived for α independent of T (equation 100, ref.[J1]).

Nier expressed his experimental results by the equation:-

$$\ln q_e = 1.34\ P^{-2}/(1 + 0.126\ P^{-4}) \qquad (6 - 1)$$

Jones and Furry's transport coefficients give:-

$$\ln q_e = 1.71\ P^{-2}/(1 + 0.163\ P^{-4}) \qquad (6 - 2)$$

and the newly calculated ones:-

$$\ln q_e = 2.21\ P^{-2}/(1 + 0.143\ P^{-4}) \qquad (6 - 3)$$

Comparison between the theoretical equations and the experimental one using the relation (5 - 59) gives values for the 'parasitic' term K_p of 0.283, in the case of (6 - 2), and 0.39 in that of (6 - 3). The rather higher value indicated by the new calculations is closer to those obtained with similar columns by other workers. The fact remains, however, that Nier's experimental results may be explained in a most satisfactory manner by the theory of Furry, Jones and Onsager.

2. THE SEMI-EMPIRICAL TREATMENT OF SIMON

The paper by Ralph Simon [S1], although concerned with the performance of a hot-wire column, is considered here because it contains a semi-empirical modification of the theory with several interesting features. At the time of publication, Furry, Jones and Onsager had not extended their theory to cover the cylindrical case.

Simon rewrote the flat-wall expressions given in [F4] for a Maxwellian gas with α independent of T as follows:-

$$H/2K_c = (63\alpha/4g\ w^4)(D\eta/\rho)_{av} \qquad (6 - 4a)$$

instead of:-

$$(63\alpha/4g\ w^4)(D\eta/\rho)f(\Delta T/T) \qquad (6 - 4b)$$

and:-

$$K_d/K_c = (1890/g^2w^6)[(D\eta/\rho)^2]_{av}\ \ln(r_o/w) \qquad (6 - 5a)$$

instead of:-

$$(1890/g^2w^6)(D\eta/\rho)^2(T_1^2 + T_1T_2 + T_2^2)/\Delta T^2 \qquad (6 - 5b)$$

The Furry-Jones equations (6 - 4/5b) differ from those obtainable from (78/9, 82/3) of their review [J1] since the latter are simplifications of their earlier results.

Simon gave no justification for the changes introduced - other than that they made his results agree well with theory! The interest in his treatment lies, however, in his ingenious use of the inverse-power model for determining the temperatures at which the gas properties in (6 - 4/5a) should be evaluated.

For the inverse-power case, $\lambda \propto T^n$ (see 2 - 6). Using this relation and considering the radial heat flow through the

gas space. Simon deduced that:-

$$r = r_o \, e^{-\gamma x} \qquad (6 - 6)$$

where r is the radius, x is T^{n+1} and r_o and γ are constants involving the radii of the hot and cold walls (a and b) and their temperatures (as x_1, x_2).

The mean q th power of the temperature in the column is given by:-

$$(T^q)_{av} = [1/\pi (b^2 - a^2)] \int_a^b T^q \, 2\pi r \, dr \qquad (6 - 7)$$

which, by using (6 - 6) becomes:-

$$(T^q)_{av} = [2\gamma r_o^2/(b^2 - a^2)] \int_{x_1}^{x_2} x^{q/n+1} \, e^{-2\gamma x} \, dx \qquad (6 - 8)$$

Before this result may be used it is necessary to find a suitable value for the index n; the latter varies slowly with T. Simon did this by determining the dependence of the gas pressure in his column on the hot wire temperature which was of the form:-

$$p = p_o[1 + (T_2 - T_1)/7.2 \, T_1] \qquad (6 - 9)$$

He then calculated from the gas laws the temperature T' that would produce the same pressure increase when applied uniformly to all the gas, as a given T_2 normally caused in the column. T' is readily shown to be the reciprocal of the mean reciprocal temperature, $1/(T^{-1})_{av}$. Equation (6 - 8) was therefore solved, with q equal to minus one, for a range of values of n using the appropriate operating temperatures etc. The desired value of n was then found by interpolation

between the calculated data for the experimental T'. From the relations (2 - 6) it follows that $(D\eta/\rho)$ is proportional to T^{2n+2}, and so these properties are to be evaluated at a temperature given by (6 - 8) with $q = 2(n + 1)$ in the case (6 - 4a) and with $q = 4(n + 1)$ in the case of (6 - 5a). It so happens that (6 - 8) is exactly integrable for both these forms of q.

The most interesting feature of Simon's treatment is his method for determining a suitable value of the viscosity index (n) by studying the pressure - wire-temperature relationship. This empirical n was then used for estimating the coefficients of diffusion and thermal diffusion with equations (2 - 7/8/9). Were it not for the fact that reliable means of calculating gas properties are now available, a procedure such as Simon's might well have become quite widely used. Further theoretical and practical work would be required to investigate the authenticity of his equations (6 - 4/5a).

3. THE WORK OF DRICKAMER AND COLLABORATORS

a) The modified theory.

Drickamer and co-workers have published a series of papers on the performance of thermal diffusion columns. They have studied gases up to their critical pressure and also some liquid mixtures. [D1, D5, D6]. In order to obtain consistent values for the thermal diffusion factor from the results of runs carried out in two columns and at widely varying pressures, Drickamer modified the Furry-Jones expressions for the transport coefficients as described

below:-

From equations (5 - 29/30/31/48) one finds that:-

$$\alpha' = [\ln q_e \, 2g\rho w^4/63LD\eta][1 + 5670(\eta DT/w^3\rho g \Delta T)^2] \quad (6 - 10)$$

This is given incorrectly in [D1] the last term being quoted as:-

$$(\eta D \Delta T/w^3 \beta g)^2 \quad (6 - 11)$$

where $\beta = (-\partial\rho/\partial T)_p = \rho/T$

Drickamer modified (6 - 10) to read:-

$$\alpha = [\ln q_e 2g\rho w^4(\phi')^3\phi/63LD\eta][1 + (5670/\phi)(D\eta T/w^3\rho g\phi'^3\Delta T)^2] \quad (6 - 12)$$

or more simply:-

$$\alpha = [\ln q_e(\phi')^3\phi/AC][1 + BC^2\phi(\phi')^6] \quad (6 - 13)$$

where constants A and B depend on the column and its operating conditions and C is a property of the gas.

ϕ is the fraction of the gap width presumed available for the horizontal diffusion processes. Drickamer postulated that at high convection rates a proportion of the gas between the walls is in a turbulent condition due to the entraining action of the oppositely moving streams of gas adjacent to them, and assumed that ϕ is in fact proportional to the maximum vertical convection velocity. Schmidt and Beckmann found that near a single heated plate this is given by:-

$$v_{max} \propto [h\beta \Delta T g/\rho]^{\frac{1}{2}} \quad (6 - 14)$$

Now ϕ depends on the ratio of the horizontal diffusional transport rate and v_{max}, and on this basis Drickamer defined a quantity ψ given by:-

$$\psi = [D^2\rho/w^2L\beta\,\Delta Tg]^{\frac{1}{2}} \qquad (6 - 15)$$

to which he related ϕ by the following empirical expressions:-

$$\begin{aligned} \phi &= 1260\ \psi^{1.2} && \psi < 1.35 \times 10^{-3} \\ &= 13.6\ \psi^{0.512} && 6.3\times10^{-3} > \psi > 1.35\times10^{-3} \\ &= 1 && \psi > 6.3\times10^{-3} \end{aligned}$$

The fraction ϕ', the proportion of the gap width in vertical convection, was considered less than unity for low flow rates. The quantity used for describing the convection was the Grashof number defined by:-

$$G_r = \rho\,\beta\,g\Delta T w^2 L/\eta^2 \qquad (6 - 16)$$

which is similar in form to the Reynolds number but involves w^2, not w^3 (cf equation 5 - 64). The empirical relations used for giving ϕ' were:-

$$\begin{aligned} \phi' &= 1 && G_r > 1.2\times10^5 \\ &= 0.576[G_r]^{0.0486} && 1.2\times10^5 > G_r > 6\times10^3 \\ &= 0.866 && G_r < 6\times10^3 \end{aligned}$$

It is difficult to see how (6 - 12) was derived from the stated definitions of the fractions ϕ, ϕ'. It is reasonable to suppose that if w were replaced by ϕw in the expression for H, by $\phi' w$ in that for K_c, the desired result would be obtained. Doing this, however, yields:-

$$\alpha = [\ln q_e(\phi')^7/\phi^3 AC][1 + BC^2/(\phi')^7] \qquad (6 - 17)$$

which is similar to, but certainly not identical with, Drickamer's equation.

In view of the fact that the latter was found to contain a gross error in both [D1] and a subsequent paper, it was

decided to check some values of α and α' quoted by Drickamer in order to establish what expression he had actually used. Details of this calculation are given in the appendix and the conclusion was that (6 - 12) was employed.

The values of α obtained from (6 - 12) are undoubtedly more consistent than the α''s from the Furry-Jones equation (6 - 10). In view of the large number of additional parameters introduced by Drickamer, this could hardly be otherwise. It is difficult to imagine that ϕ and ϕ' have any real significance in the sense defined because high convection velocities would not be expected in many of the runs. From data given in [D1] and the expression for the Reynold's number (5 - 64) one finds for the two precisely-made columns (see later) that:-

$$\begin{aligned} R \text{ (column I)} &= 2670\rho^2 \\ R \text{ (column II)} &= 316\rho^2 \end{aligned} \qquad (6 - 18)$$

Since the maximum densities of the gas mixture used in these columns were 0.076 g/cc (col.I) and 0.13 g/cc (col.II):-

$$R \approx 15 \quad \text{(col.I)}$$

$$R \approx 5.4 \quad \text{(col.II)}$$

These are both less than the limiting value of 25 found by Onsager and Watson for the onset of turbulence between cylinders. Whilst it must be admitted that (5 - 64) is approximate in nature and is unlikely to be applicable with any precision at very high pressures, it still seems probable that turbulence was by no means prevalent in Drickamer's experiments.

b) A new comparison with theory.

It is of considerable interest to examine Drickamer's results in the more conventional manner outlined in Chapter 5 and already illustrated with reference to Nier's experiments with methane (section 1 of this chapter). This has been done for the three sets of experimental results given in [D1], and the following data obtained. The original tables have been condensed and rearranged; the run numbers are therefore quoted for convenience when referring back to the actual paper.

TABLE 10

Carbon dioxide - propane [D5]

Run No.	Pressure (atm)	q_e	$1/P^4$	$1/P^2 \ln q_e$
21	0.312	1.35	105.4	34.12
7	0.390	1.70	43.21	12.27
30	0.433	1.85	28.44	8.672
13	0.510	2.22	14.78	4.835
4	0.625	2.91	6.552	2.397
15	0.744	3.90	3.263	1.329
2	0.836	4.58	2.047	0.9414
29	0.924	4.42	1.372	0.7886
1	1.116	5.01	0.6451	0.4489
23	1.805	2.35	0.0942	0.3593

The plot of $1/P^2 \ln q_e$ vs $1/P^4$ is shown in Figure 8. It will be seen that all the points do not fall exactly on a straight line, as would ideally be the case, that from the lowest pressure run being particularly out with reference to the remainder. This series of experiments was, however, the first to be performed, and the apparatus lacked the precision of the columns used in the later work with argon-neon mixtures.

A selection of the results obtained for the latter is presented in Tables 11 - 13 below, the corresponding graphs showing $1/P^2 \ln q_e$ plotted against $1/P^4$ being figures 10, 11 and 9.

Argon-Neon: TABLE 11 Column I T = 303°K

Run No.	P (atm)	q_e	$10^8/P^4$	$10^4/P^2 \ln q_e$
38	10.37	1.960	8646	138.1
37	10.40	2.057	8551	128.1
36	15.24	4.238	1856	29.82
34	30.2	10.47	120.2	4.668
33	31.4	10.22	102.9	4.363
32	40.6	6.391	36.81	3.271
30	58.2	3.046	8.72	2.651

TABLE 12 Column II T = 303°K

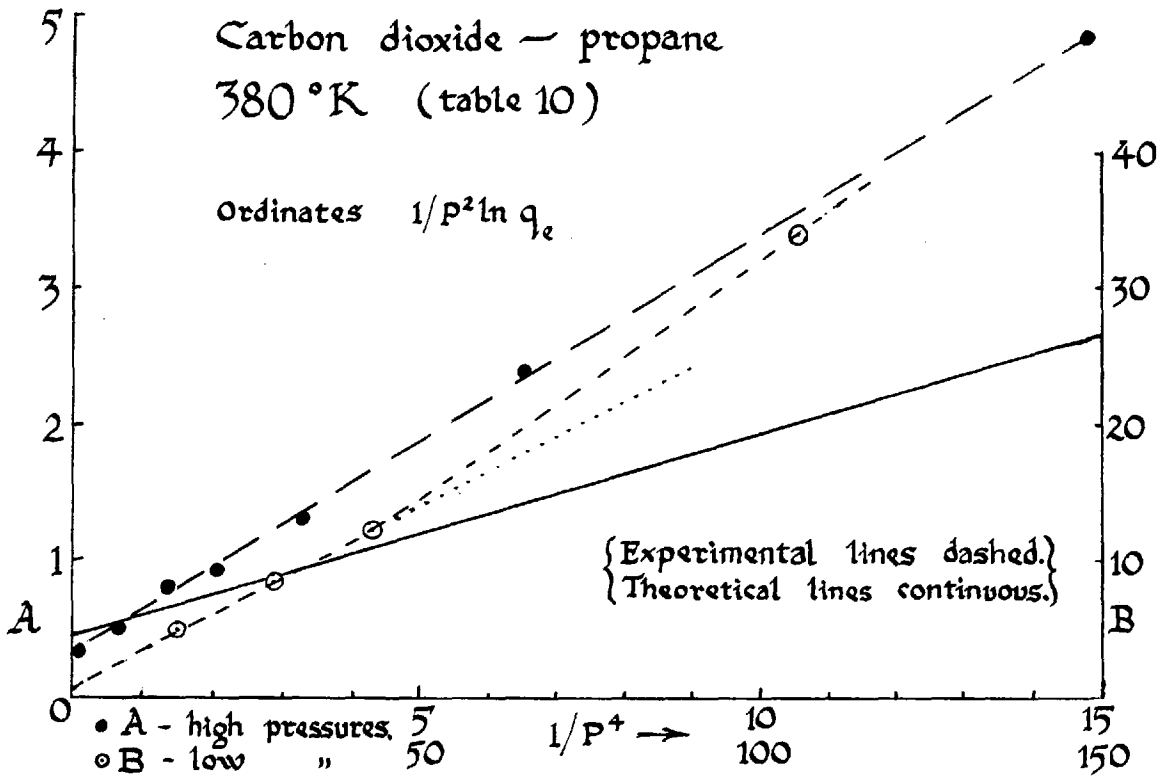
12	15.64	1.336	1672	141.1
2	15.78	1.416	1613	115.4
1	29.5	4.488	132.0	7.658
14	39.3	19.95	41.92	2.163
13	40.9	18.18	35.75	2.061
16	58.6	364.0	8.480	0.494
10	79.6	355.2	2.491	0.269
4	102.2	210.3	0.916	0.179

TABLE 13 Column II T = 325°K

23	10.53	1.155	8136	626.6
24	10.67	1.144	7720	652.1
22	16.57	1.387	1320	111.0
21	32.8	5.059	86.38	5.731
18	59.0	123.9	8.249	0.596
9	82.5	396.9	2.158	0.245
7	104.3	332.0	0.845	0.158

Rather than calculate the individual transport coefficients for Drickamer's columns and operating conditions, it was found convenient to obtain the slopes and intercepts of the theoretical $1/P^2 \ln q_e - 1/P^4$ plots directly. From equations

Figures 8 & 9. Drickamer's experimental results.



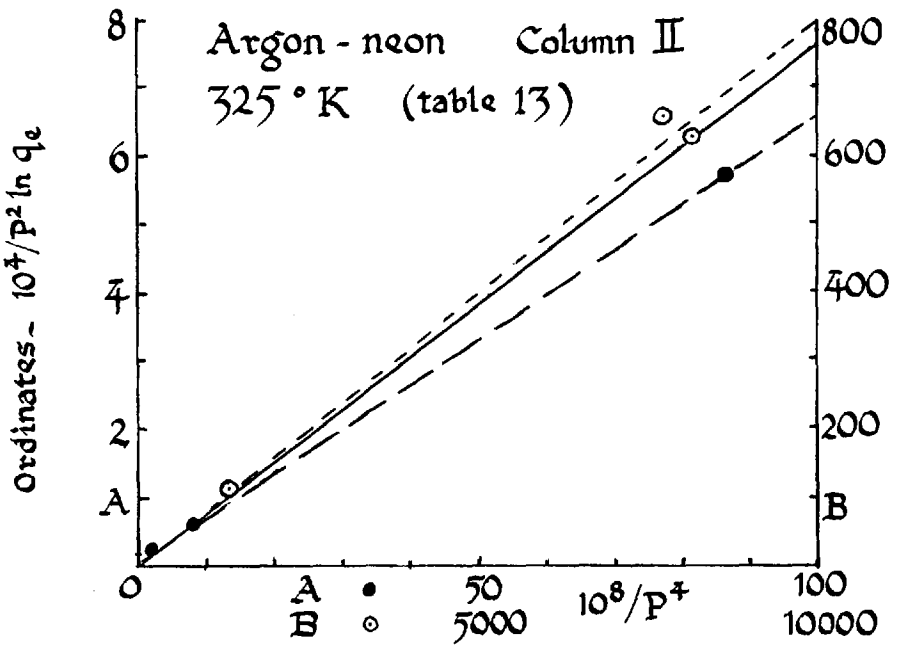
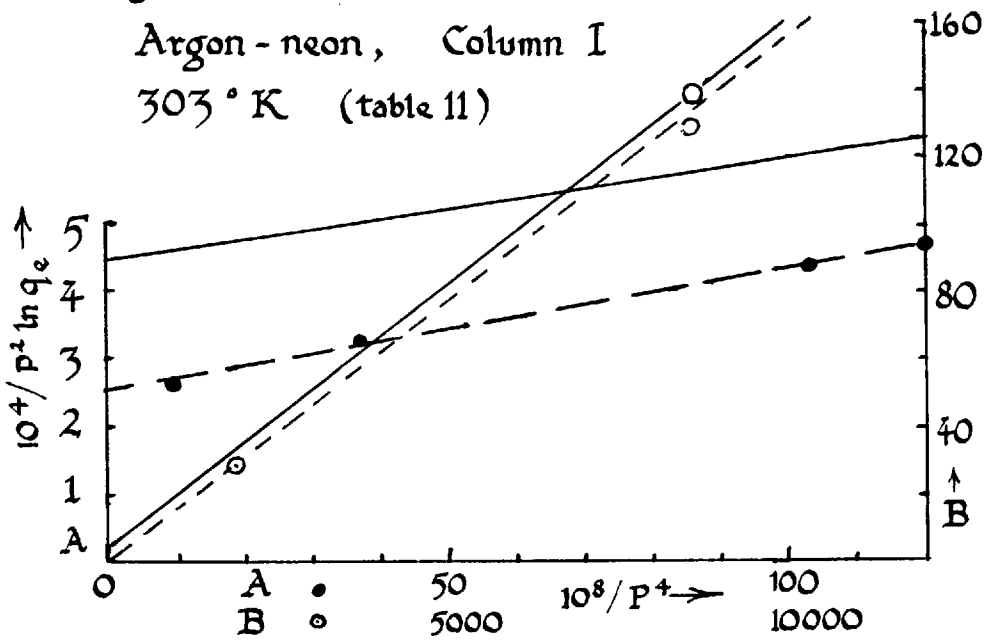
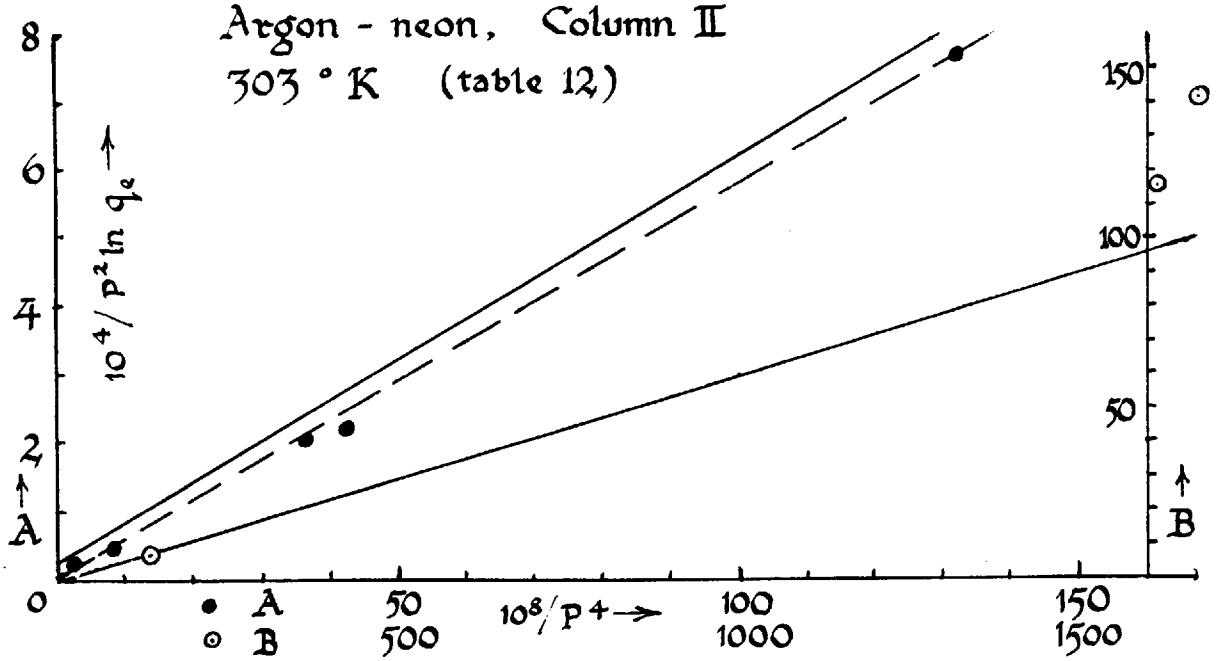


Figure 10.



Experimental lines broken — theoretical lines continuous

Figure 11



(5 - 29/30/31/54) one obtains:-

$$\text{Slope} = b/a = [6!\,\eta D/(2w)^2 \alpha \rho g L](T/\Delta T)^2 \qquad (6 - 19)$$

$$\text{Intercept} = 1/a = (2w)^4 \rho g/504\ \eta DL \qquad (6 - 20)$$

The numerical data required when using the above expressions are conveniently summarised in a table:-

TABLE 14

Drickamer column calculations

For column:-		I	II	II	Source or ref:-
Gas mixture	55%CO_2 45%C_3H_8		56.4%A-43.6%Ne		D1
Length (cm)	244	40.0	41.6		D1
2w (cm)	0.308	0.1016	0.0508		D1
T (^oK)	380	303	303	325	D1
ΔT (^oK)	180	20	20	21	D1
α (theor)	0.0120 (0.0116)	0.175 (0.171)	0.175 (0.171)	0.178 (0.175)	Appendix [D1]
α (exptl)	0.0076	0.210	0.220	0.215	D1
$10^4\eta$(poise)	1.430	2.605	2.605	2.738	T2, T3
$10^3\rho$(g.cm^{-3})	1.43	1.26	1.26	1.18	Gas laws
D(cm^{2}sec^{-1})	0.126	0.322	0.322	0.358	Equ^n(2-12)
Slope (theor)	0.148	156	598	763	" (6-19)
" (exptl)	0.266	152	580	800	Figs.8-11
Intercept (theor)	0.475	4.46×10^{-4}	2.67×10^{-5}	2.11×10^{-5}	Equ^n(6-20)
Intercept (exptl)	0.35	2.5×10^{-4}	$< 10^{-5}$	$\sim 10^{-5}$	Figs.8-11

The values quoted for the thermal diffusion constant were calculated from the full equations (2 - 19). In view of their length, details of these computations are given in the

Appendix. Also given in Table 14 are the values computed by Drickamer (in parenthesis) who presented the data with the aid of small graphs. In view of the difficulty of interpolating from the latter with any high accuracy, it will be seen that his and the newly calculated theoretical values differ insignificantly. The mean experimental results obtained for the runs in Tables 11-13 by use of (6 - 12/5/6) are then quoted.

Some of the quantities required when calculating the diffusion constants are contained in the Appendix; the viscosities were graphically interpolated from experimental data in the references cited; the densities were obtained from those of the pure components at N.T.P. the values being corrected for temperature using the ideal gas laws.

c) Discussion.

The theoretical $1/P^2$ ln q_e - $1/P^4$ lines have been included in Figures 8 - 11 (the continuous lines) as well as the experimental points. From lines drawn through the latter, the slope and intercept values in Table 14 were obtained.

For the series of runs with a mixture of carbon dioxide and propane the agreement between experimental and theoretical slopes is extremely poor. Since an error of this nature could not result from parasitic convection currents in the gas, it can only be assumed due to inadequacy of the equations (2 - 19) used for calculating the thermal diffusion constant, and of the intermolecular force law. Since the gases are of identical molecular weight, thermal diffusion in their mixture is due entirely to differences in the detailed nature

of their force fields. Both carbon dioxide and propane have non-spherical molecules and the theory is strictly not applicable to either. It is possible, however, that use of values for r_{12} and $E(o)_{12}$ determined from the viscosity of their binary mixtures, instead of values obtained using (2 - 14), might result in improved agreement with experiment.

The columns (I and II) used for the later experiments with an argon-neon mixture were constructed with great precision, care being taken to ensure temperature uniformity of the walls. In every case the temperature difference employed was sufficiently low to justify use of gas properties evaluated at the mean temperature, and the gap width was small enough compared with the tube radii to make each apparatus similar to a flat-wall column. One could thus expect the equations (6 - 19/20) to be very nearly accurate and this is in fact the case. The only serious discrepancy between theory and experiment observed in all three sets of experiments is in the case of runs 2 and 12 (Table 12) which give points on Figure 11 considerably above the theoretical line. It is unfortunate that results are not available for the pressure range 16 - 30 atmospheres; as it is, these two runs are isolated from the remainder.

Figures 10 and 11 show that the simple equation (6 - 19) holds with considerable accuracy, even at pressures as high as 50 - 100 atmospheres. It must be admitted that the methods used for obtaining values for the gas properties could not be expected to hold exactly in this range and the agreement

must, in some measure, be due to cancellation of errors. The greater deviation between theory and experiment shown by Figure 9 at high pressures, and for a slightly greater mean temperature, may thus be caused by a less favourable combination of inaccuracies.

The intercepts quoted in Table 14 were obtained from the high pressure sections of the experimental plots and hence may not be used for estimating K_p values. In order of magnitude, however, they agree well with the theoretical intercepts, and in view of the small tolerances permitted in the construction of the columns, it seems highly improbable that any parasitic convection currents existed in the columns.

From the above discussion it will be apparent that Drickamer's later experimental results may be accounted for almost exactly by means of the simple Furry-Jones expressions for the transport coefficients, using theoretical values of the thermal diffusion factor. As mentioned at the end of Chapter 4, the latter are, for argon-neon mixtures, in close accord with the results of two-bulb measurements. By modifying the simple equation (6 - 10) in an empirical and unexplained manner, Drickamer obtained more consistent values for α -all 25% greater than predicted by theory. It is natural to wonder whether the gain in consistency is offset by a loss of reliability. The processes taking place in a separating column are complex by nature and such apparatus can hardly be expected to provide a suitable means for measuring fundamental constants. Thus, whilst Drickamer's experimental work is of the highest quality, his arbitrary modification of the column theory seems unnecessary and of doubtful authenticity.

CHAPTER 7.

THE THERMAL DIFFUSION COLUMN - EXPERIMENTAL

1. DESCRIPTION OF THE COLUMN

The separating column constructed for this work was basically similar in design to that used by Whalley in his study of the thermal diffusion of oxygen [W1], the only radical difference between the two being that the length of the new apparatus was only one third that of the old. This enabled single lengths of tubing to be used for its construction - a great practical convenience. It was decided to employ tubes of the diameters used previously in order to facilitate comparison between the performances of the two columns, should this be desired.

The main features and dimensions of the new separating column are given in Figure 12. The tubes between which the gas was confined were of brass, and held concentric at the top by a turned plug of this metal; vacuum tight joints were made by hard soldering. In order to keep the inner tube central throughout its length, spacers were fitted at several points. Originally each consisted of three short lengths of screw regularly spaced around a brass collar which was a sliding fit on the tube. When the column was dismantled, however, the collars were dispensed with and the spacing screws soldered directly into the tube. The later arrangement caused considerably less obstruction to the gas flow in

Figure 12. Thermal diffusion column.

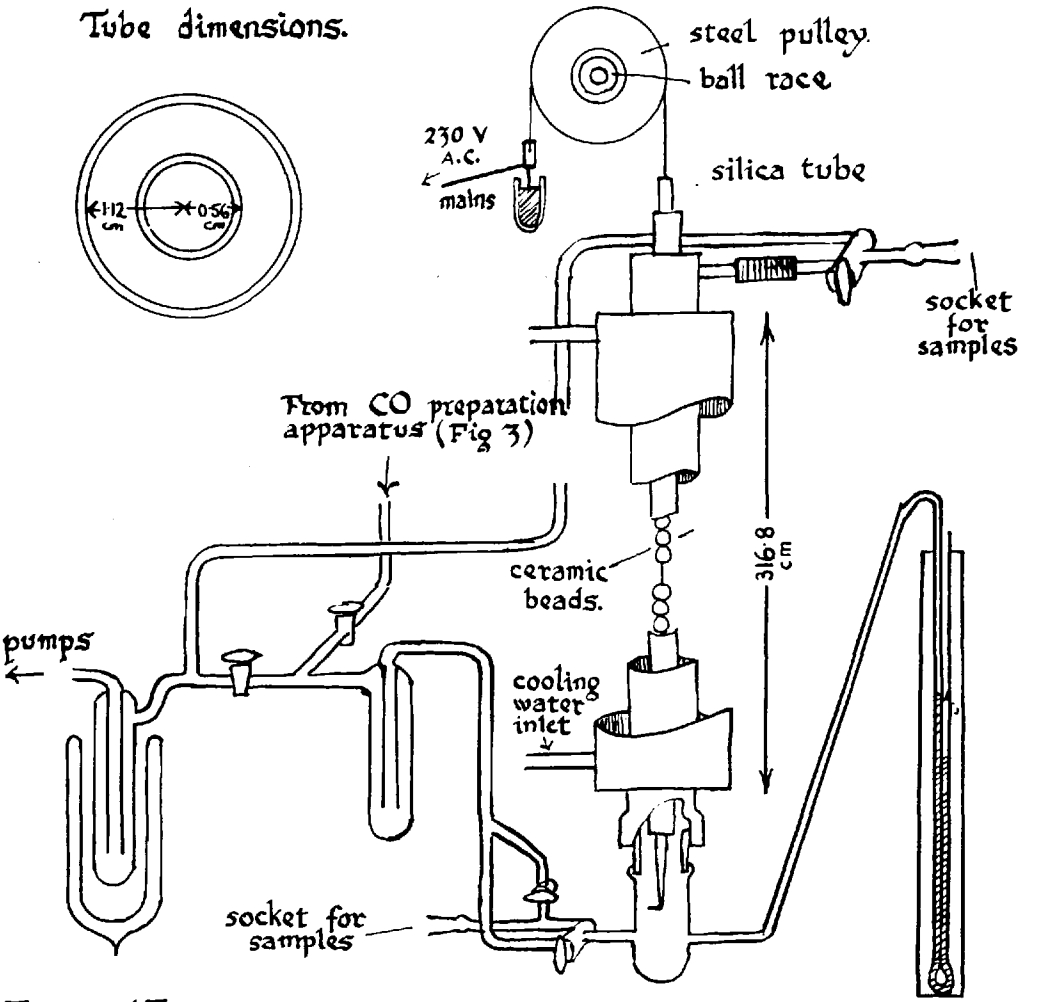
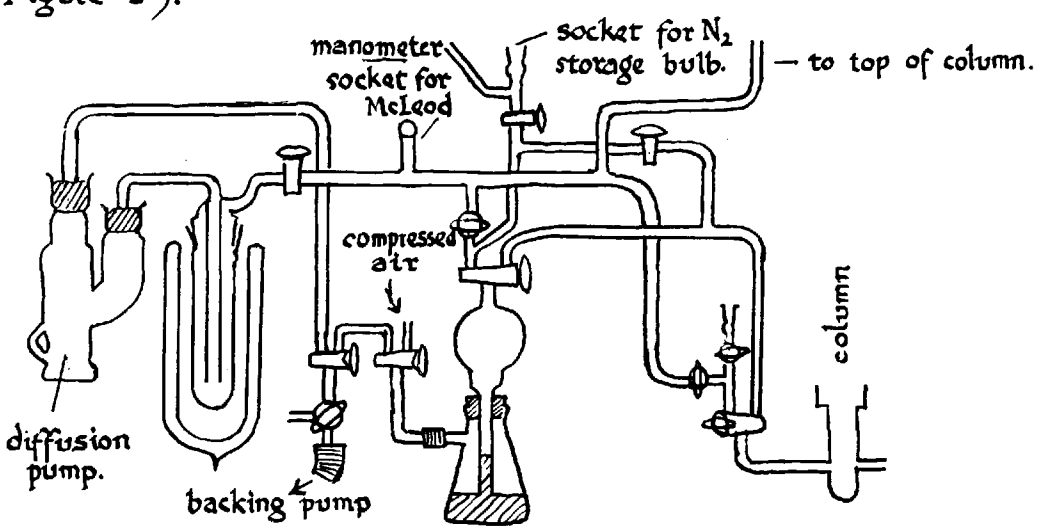


Figure 13.



the column than did the original design.

The central tube was heated by an axial nichrome wire down which current from the A.C. mains was passed to earth. Ceramic beads were threaded on to the wire actually inside the column, the bottom being silver-soldered into a plug at the lower end of the tube. This plug carried a pointer used when measuring the expansion of the central tube. The upper end of the heating wire was passed over a pulley above the top of the column and weighted. Originally two brass pulleys were fitted, but on prolonged heating in contact with this metal the nichrome wire became brittle and broke readily. After the first few experiments, the column had to be dismantled and a new wire provided; the brass pulleys were replaced by a single steel one, of larger diameter, which proved to have no effect on hot nichrome.

The outer brass tube was cooled by a continuous flow of tap water through a surrounding jacket of iron tubing. A copper-pyrex seal was soft soldered to the bottom so that the tip of the pointer used for measuring the temperature of the inner tube could be seen, and the glass auxiliary apparatus sealed on. The connection between the brass side-arm at the top of the gas space and the two-way tap used for removing samples was of rubber pressure tubing painted with a glyptol resin.

2. AUXILIARY APPARATUS

a) Carbon monoxide.

The vacuum system used during the runs with carbon

monoxide is shown in Figure 12. The apparatus was evacuated with a single-stage mercury diffusion pump backed by a Hyvac rotary pump. The latter was sited in a nearby fume cupboard so that any unwanted gas could safely be pumped away. The method used for preparing carbon monoxide has been described already (Chapter 4 (2)a), and so only the connection to the apparatus and the liquid nitrogen trap used removing impurities are included in the diagram. Since gas could be prepared quite conveniently whenever required it was not conserved. Thus in a series of runs the column was filled at the start to the maximum required pressure, and gas then carefully pumped away between successive experiments to give the desired operating pressures.

b) Nitrogen.

The nitrogen used for the column experiments was enriched in the heavy mass 15 isotope, and the apparatus had therefore, to be designed so as to cause no loss of material other than that removed as samples for analysis, see Figure 13.

3. EXPERIMENTAL PROCEDURE

When the column had been made satisfactorily vacuum-tight it was outgassed by heating the central tube to above its normal running temperature and pumping continuously for a number of hours. It was not possible to heat the outer wall of the gas space and this will account in part for the fact that a vacuum of less than 10^{-4} mm. of mercury pressure was seldom obtained in the apparatus. However, the column maintained a vacuum over long periods and so any leaks that

were not detected must have been exceedingly slight. Examination of the gas samples from the column experiments showed inappreciable quantities of oxygen and argon.

After outgassing, the heating current was adjusted and the gas required for the experiment let into the column. The apparatus was then left undisturbed for at least twenty-four hours in order to allow of equilibrium being reached. The gas pressure was measured with a U-tube mercury manometer having a mirror-scale, readings being taken frequently throughout each run. The wall temperatures were recorded likewise and maintained as nearly constant as possible; the chief cause of variation was fluctuation of the mains voltage. At the end of a run, samples of gas were taken from top and bottom of the column in standard pattern tubes (Figure 7). By means of the connections shown in Figures 12 and 13 these were pumped out and tested for leaks before use. The pairs of samples were then analysed consecutively by mass spectrometer.

4. RESULTS

The results from all the column experiments performed are summarised in Table 15 below.

The separation factor q_e was obtained simply by division of the abundance ratios for the top and the bottom samples from a run. The c_2 values were calculated using (4 - 2) for carbon monoxide and (4 - 4) for nitrogen.

TABLE 15

Separating column results

Carbon monoxide (first series) - T_1=290±3°K T_2=610±8°K

P (atm)	c_2(top)	c_2(bottom)	q_e	$1/P^2 \ln q_e$	$1/P^4$
0.524	0.94	1.30	1.38	11.08	13.3
0.708	0.96	1.35	1.41	5.09	3.98
0.792	0.95	1.42	1.49	4.00	2.54
1.05	1.00	1.36	1.37	2.89	0.83
Carbon monoxide (second series) - T_1=294±3°K T_2=594±10°K					
0.256	0.86	1.11	1.30	57.9	231
0.424	0.81	1.18	1.46	14.7	31.0
0.494	0.84	1.27	1.52	9.54	15.9
0.563	0.83	1.30	1.58	6.90	9.94
0.635	0.84	1.27	1.50	6.11	6.28
0.788	0.87	1.26	1.45	4.33	2.59
Nitrogen - T_1=296±3°K T_2=596±8°K					
0.255	6.61	8.23	1.24	71.4	235
0.305	6.61	8.83	1.36	34.9	115
0.358	6.41	9.28	1.49	19.6	60.9
0.500	6.32	9.80	1.59	8.62	16.0
0.664	6.84	10.02	1.52	5.41	5.13
0.836	7.03	9.97	1.46	3.78	2.05

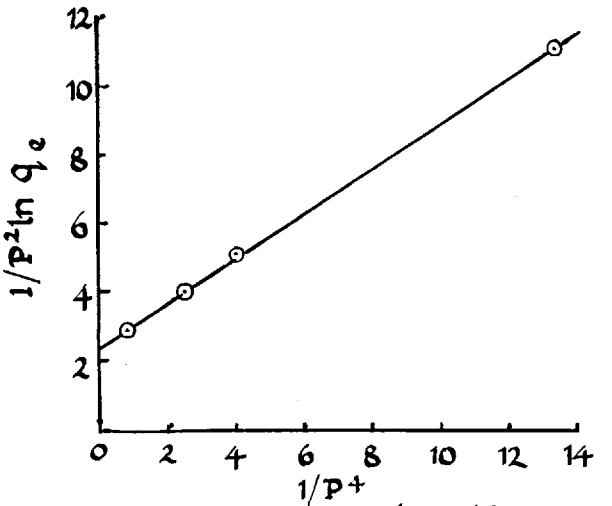
The $1/P^2 \ln q_e$ - $1/P^4$ plots drawn from the above data are shown in Figure 14 from which it will be seen that quite good straight-line relationships were obtained. Before considering the results further, however, several numerical aspects of the design and operation of the column will be treated.

5. A QUANTITATIVE TREATMENT OF THE COLUMN OPERATING CONDITIONS

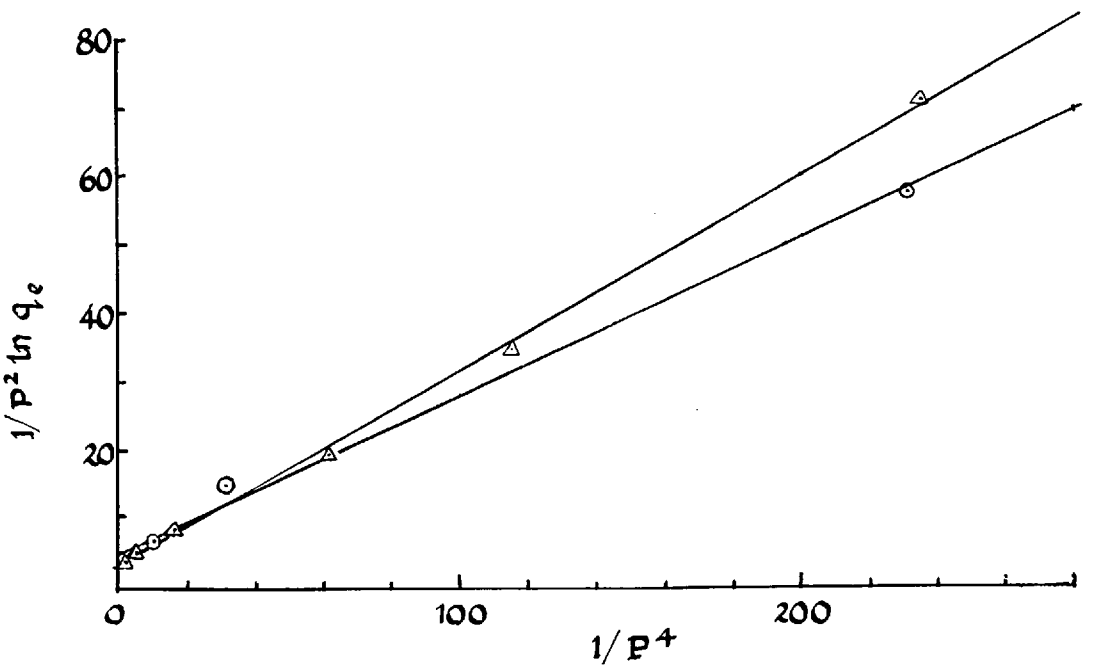
a) Electrical heating and power consumption.

The original heater wire was of Nichrome IV and its tensile strength at bright red heat was found in a preliminary

Figure 14 Separating column results.



carbon monoxide (first series)



carbon monoxide (o) and nitrogen (△)

experiment to be 560 g. A tension on the wire of 100g.wt. was initially chosen, this providing, it was felt, an ample safety margin. As mentioned earlier, however, the nichrome wire soon became brittle when heated in contact with the brass pulley used for allowing its free expansion and contraction, and then broke under negligible tension.

It was intended that the second heater should operate from the 110 V D.C. supply without external resistances in series. Wire was selected, therefore, such that the power dissipated with this voltage would be the same as for the original heater of finer gauge. This equality was in fact achieved, but it was found that the desired hot wall temperature was not obtained. This may have been due to the fact that a given power output will produce a greater temperature in a wire of smaller surface area. In the absence of a suitable transformer, resistances were used in series with the A.C. mains as previously.

The rise in temperature of the inner tube was calculated from its expansion. For the first few runs a cm. mirror-scale was used for measuring this, but later a scale calibrated directly in degrees was provided. The coefficient of linear expansion of brass was taken to be 19×10^{-6}, and the free length of the inner tube was 325 cm. The following table gives full details of the two heating wires.

TABLE 16

Column heater wire data

Both wires of nichrome and heated with current from the 230 V A.C. mains.

	Original wire	New wire
Diameter (inches)	0.012	0.022
Ohms Resistance/yard(nominal)	13	4.2
Length	340 cm. = 3.72 yards	
Observed resistance (cold)	52	-
" " (hot)	58	17
Volts across wire	205	112
Current (amps)	3.5	6.7
Power (watts)	707	750
Resultant temp. rise	320°	300°

It is of interest to compare the experimental and theoretical values for the power transmitted by conduction through the gas. The former value was determined by measuring the power required to maintain the inner tube at its normal operating temperature when the gas space was evacuated, and subtracting this from that necessary with gas present; a result of 340 watts was obtained. The only published formula for calculating the heat conduction is:-

$$W = 4.18 \lambda LB \Delta T/2w \qquad (7 - 1)$$

where W represents the power in watts and the other symbols have their usual significance. The equation was first used by Nier [N2] when carrying out a comparison with theory for

his methane separating column, and is derived by considering conduction through a rectangular slab of gas L x B in area, 2w thick and of thermal conductivity λ, when a temperature difference ΔT is applied. It ignores the temperature variation of λ and the cylindrical shape of the apparatus, but, for want of a better expression, was used in the original calculations for the present column outlined in [D2]. Values of 280 and 270 watts were then found for carbon monoxide and nitrogen respectively. In the course of the theoretical investigations described in the next chapter, accurate empirical equations, of a simple power type, were obtained for representing the temperature dependence of λ. With these it is possible to derive a new equation for W lacking the assumptions inherent in (7 - 1).

Let the heat flow in unit length of the column be Q cals/sec, and consider a cylindrical volume element of radium r and thickness δr. If the temperature difference across this be δT, one has from the definition of λ that:-

$$Q = -2\pi r \lambda \delta T / \delta r$$

rearranging and proceeding to the limit ($\delta r \rightarrow 0$):-

$$Q dr/r = -2\pi \lambda \, dT \qquad (7 - 2)$$

Now λ may be represented by(Table 21):-

$$\lambda = k_\lambda T^\theta \qquad (7 - 3)$$

and so:- $$Q dr/r = -2\pi k_\lambda T^\theta dT \qquad (7 - 4)$$

The boundary conditions are that $T = T_1$ at $r = r_1$, and $T = T_2$ when $r = r_2$ ($T_2 > T_1$, $r_2 < r_1$)

Integrating (7 - 4) between these limits:-

$$Q(\ln r)_{r_2}^{r_1} = 2\pi k_\lambda [T^{e+1}/(e+1)]_{T_1}^{T_2}$$

$$Q = \frac{2\pi k_\lambda (T_2^{e+1} - T_1^{e+1})}{(e+1)(\ln r_1 - \ln r_2)} \qquad (7 - 5)$$

For the present column, $(r_1/r_2) = 2$, $T_1 = 295^oK$, $T_2 = 595^oK$. Also $e = 0.7193$ and $k_\lambda = 9.896 \times 10^{-7}$ for carbon monoxide and 9.984×10^{-7} for nitrogen. Inserting these values into (7 - 5) and multiplying by 4.18 L one finds that W = 300 watts for both gases. The agreement with the experimental 340 watts is quite as good as may be expected, considering that the convection processes in the column have been assumed to have no effect on conduction, a condition unlikely to hold exactly.

b) Equilibrium time.

The relaxation time for a column is given by (5 - 62) and can readily be shown to increase as the pressure decreases. Values were therefore calculated at the lowest pressure studied (1/4 atmosphere) for carbon monoxide and nitrogen. μ, the mass of gas per unit length in the column, was obtained from the tube dimensions and gas densities at the mean temperature (Table 17), (A) from the experimental equations for ln q_e (Table 19, (5 - 60)) and H as the mean of the corresponding theoretical (maximum) and experimental (minimum) values according tc the equation:-

$$H = (1/2)[H(\text{theoretical}) + (Kd/L)_{\text{theor}} \times (a'/b')] \qquad (7 - 6)$$

A result of $1\frac{1}{2}$ hours was found for both gases. From (3 - 18) it follows that 8 hours would have sufficed for equilibrium to be reached in the ideal case. The column had in fact, a small reservoir at the lower end ($\sim$ 75 cc.) which would have increased this period a little; the twenty-four hours normally allowed was shown, however, to be more than sufficient in practice.

c) Turbulence.

The Reynold's number obtained from equation (5 - 64) was about 3 for both carbon monoxide and nitrogen, substantially less than that found by Onsager and Watson as the critical value for the onset of turbulence (R = 25).

6. CALCULATION OF THE TRANSPORT COEFFICIENTS AND COMPARISON BETWEEN THEORY AND EXPERIMENT

The column dimensions, and values used for the gas properties are summarised in Table 17.

The error limits quoted for H were derived directly from those of α, the experimental value for the thermal diffusion constant.

TABLE 17

Calculation of the transport coefficients

Column dimensions.

r_1 = 1.12 cm. r_2 = 0.56 cm. L = 316 cm.

B = $(r_1 + r_2)$ = 5.28 cm. 2w = $(r_1 - r_2)$ = 0.56 cm.

continued on next page

Table 17 cont.

Quantity	CO (series I)	CO (series II)	N_2	Source
T^oK	450	444	446	Table 15
T^oK	320	300	300	"
$\alpha \times 10^3$	8.2±1.8	8.2±1.8	9.0±1.0	Table 6
η(poise)$\times 10^4$	2.44	2.42	2.45	Ref.H5(exptl)
D $cm^2 sec^{-1}$	0.418	0.409	0.408	Equn(2-15)
ρ(g/cc)$\times 10^4$	7.58	7.68	7.65	Gas laws
$H^{(o)} \times 10^5$	1.23	1.15	1.23	Equn(5-29)
$K_c^{(o)} \times 10^3$	2.14	2.09	2.00	" (5-30)
$K_d^{(o)} \times 10^4$	9.37	9.29	9.23	" (5-31)
Correction factors for Maxwellian molecules and 'nearly-plane' case.				
For $H^{(o)}$	1.14	1.13	1.13	Equn(5-38)
" $K_c^{(o)}$	1.41	1.38	1.38	" (5-39)
" $K_d^{(o)}$	0.961	0.961	0.961	" (5-40)
H x 10^5	1.40±0.31	1.30±0.28	1.39±0.15	H is in g/sec,
K_c x 10^3	3.02	2.88	2.76	K_c and K_d in g.cm/
K_d x 10^4	9.00	8.93	8.87	sec.

Using the relations (5 - 54) the coefficients a and b of the theoretical equation (5 - 53) giving the pressure dependance of the equilibrium separation factor were calculated from the transport coefficients. Experimental coefficients, a' and b', were obtained from the equations for the regression lines of $1/P^2$ ln q_e (Y) on $1/P^4$ (X) by using (5 - 55).

The slope of the regression or 'least squares' line is given by:-

$$m = (\sum XY - \sum X \sum Y/N)/(\sum X^2 - [\sum X]^2/N) \qquad (7 - 7)$$

and the intefcept is readily found by using the fact that the line passes through the point $(\overline{X},\overline{Y})$.

The least squares lines fitting the results of Table 15 have been drawn on Figure 14 their slopes and intercepts being:-

TABLE 18

Equations for the least squares lines

	Slope	Intercept
Carbon monoxide (series I)	0.655	2.38
" " (series II)	0.230	5.22
Nitrogen	0.287	3.21

From this data, K_p values were then determined using (5 - 59). The results of these calculations may be summarised as follows:-

TABLE 19

Comparison between theory and experiment

	CO (series I)	CO (series II)	N_2
a	1.46±0.32	1.43±0.31	1.59±0.17
b	0.298	0.310	0.321
a'	0.420	0.192	0.312
b'	0.275	0.0442	0.0895
a/b	4.9±1.1	4.6±1.0	5.0±0.5
a'/b'	1.53	4.35	3.48
a/a'	3.5±0.8	7.5±1.1	5.1±0.5
b/b'	1.1	7.0	3.6
K_p/K_c	1.3±0.4	6.2±0.6	3.3±0.2

The measure of agreement between experiment and theory is seen by comparing the a/b and a'/b' values. It is very poor for the few early runs with carbon monoxide, excellent for the second series, and fairly good for those with nitrogen.

The experiments with the latter were, however, from the practical viewpoint, the most satisfactory; a better $1/P^2$ ln q_e - $1/P^4$ plot was obtained than with carbon monoxide. The low pressure run with the latter (P = 0.256 atm) was carried out some time after the remainder and should, perhaps, not be combined with them. This was done, however, because the results from low pressure runs give a considerably more reliable esitmate for the slope of the line than do those at pressures of about 0.35 atmosphere or greater.

The K_p values for the present column are very high compared with those obtained with similar columns in the past. Thus Whalley [W1] obtained $K_p = 1.1\ K_c$ with his oxygen column, which had identical tube diameters, and Nier's methane apparatus had $K_p = 0.39\ K_c$ (see Chapter 6 (1)). It can only be assumed that the slight bending of the inner tube which almost inevitably took place during the dismantling of the column and soldering-in of the new spacers was responsible.

CHAPTER 8.

A NEW METHOD OF EVALUATING THE TRANSPORT COEFFICIENTS

1. INTRODUCTION.

Up till the present, only the equations derived by Furry and Jones for Maxwellian molecules have been used for calculating the transport coefficients of columns operated with an appreciable temperature difference between the walls. In view of the satisfactory manner in which the Lennard-Jones 13:7 intermolecular force model predicts the thermal diffusion effect in gas mixtures, it would be of considerable interest to evaluate the transport coefficients with its use. From the theory of the column (Chapter 5 (2)) it will be apparent that the problem resolves itself into the solution of the differential equation (5 - 19) for G subject to the appropriate boundary conditions. In order to do this it is necessary to obtain equations describing the temperature variation of the gas properties D, η, λ and ρ for the chosen force-law.

2. TEMPERATURE VARIATION OF THE GAS PROPERTIES

The temperature dependent quantities in the equation for G are $1/\lambda$, η/λ, $1/\lambda\rho$ and $\rho D/\lambda$. In the first attempted solution, these were evaluated for nitrogen over the range of kT/E(o) 2 - 10 using equation (2 - 15) for D, (2 - 17) for η, (2 - 18) for λ and the ideal gas laws for ρ. It was found that the following relations hold with reasonable

accuracy:-

$$\begin{aligned} \rho D/\lambda &= 3.900\ (\pm 0.004) \\ \eta/\lambda &= 2.970\ (\pm 0.003) \\ 1/\lambda\rho &= 1.13 \times 10^{-7}\ [1 + T/1000] \\ 1/\lambda &= 9.55 \times 10^{5}\ T^{-0.711} \end{aligned} \qquad (8 - 1)$$

Substitution of these into (5 - 19 or 8 - 10) gave:-

$$d^2/dT^2(1/\lambda\rho)dG/dT = - g\rho\lambda/B + A_1\lambda \qquad (8 - 2)$$

where:- $$B = \rho D\eta/\lambda^2$$

and A_1 is an arbitrary integration constant. (8 - 2) is readily soluble, with use of (8 - 1), by direct integration. The result turns out to be quite unsuitable for numerical purposes, however, since the small function G (of the order 10^{-8}) is given as the product of a large quantity ($\sim 10^{26}$) and a sum of small terms known with an accuracy of three significant figures. The simple expressions (8 - 1) cannot therefore be used.

Equations of the form:-

$$\text{(gas property)} = \text{(constant)} \times T^n \qquad (8 - 3)$$

were next considered, and their use led ultimately to the satisfactory solution described in this chapter.

Constants and temperature indices were originally obtained for the equations (8 - 3) representing D, η and λ from the slopes of the log (gas property) vs log (temperature) plots. These values did not, however, lead to a meaningful solution for G, and it soon became apparent that the value of this function is extremely sensitive to the temperature indices and the relationship between them. The gas property-

temperature equations finally used were derived directly from the expressions of the L.J 13:7 model as follows.

Equation (2 - 15) for the self-diffusion constant may be written as:-

$$D = \text{constant} \times T^{1.5}/W^{(1)}(1;\ kT/E(o)) \qquad (8 - 4)$$

(2 - 17) for the viscosity as:-

$$\eta = \text{constant} \times T^{\frac{1}{2}}\ V/W^{(2)}(2) \qquad (8 - 5)$$

and (2 - 18) for the thermal conductivity as:-

$$\lambda = \text{constant} \times T^{\frac{1}{2}}\ H/W^{(2)}(2) \qquad (8 - 6)$$

Temperature indices for the integrals in (8 - 4/5/6) are given by:-

$$(\text{index}) = \Delta \lg (\text{integral}) / \Delta \lg (kT/E(o)) \qquad (8 - 7)$$

which are then combined with the indices already present in these equations to give the values required in the empirical expressions (8 - 3).

In order that the same temperature indices might be used for both nitrogen and carbon monoxide, they were evaluated for the range of kT/E(o) from 3 to 6 whose limits are intermediate between the values corresponding to the column wall temperatures in the two cases. This will be seen from the Table 20 below, which contains all the gas-property integrals used for deriving the empirical equations and determining their accuracy. The data was taken from [H3] interpolation between published values being carried out where necessary.

The constants in (8 - 4/5/6) were obtained from the intercepts of the lg(integral) - lg(temperature) plots, the molecular weight (28 in each case) and r_o (Table 1).

(Cv + 9/4 R) was taken as 9.409 for nitrogen and 9.411 for carbon monoxide in the equations giving λ .

TABLE 20

Quantities required for the evaluation of gas properties

kT/E(o)	Temperature (°K)		$W^{(1)}(1)$	$W^{(2)}(2)$	H	V
	CO	N_2				
2.675	295	-	0.4898	1.072	1.0043	1.0028
3	331	274	0.4745	1.039	1.0052	1.0034
3.225	-	295	0.4655	1.020	1,0058	1.0038
4.034	445	-	0.4410	0.9683	1.0076	1.0049
4.866	-	445	0.4234	0.9318	1.0088	1.0057
5.394	595	-	0.4152	0.9148	1.0094	1.0060
6	662	549	0.4062	0.8963	1.0095	1.0061
6.506	-	595	0.4004	0.8854	1.0102	1.0066

TABLE 21

Empirical equations for the gas properties (8 - 3)

Property	Temp.index	Symbol	Constant		Symbol
			Nitrogen	Carbon monoxide	
D	1.7242	ε	1.096×10^{-5}	1.100×10^{-5}	k_D
η	0.7171	n	2.977×10^{-6}	3.004×10^{-6}	k_η
λ	0.7193	e	9.896×10^{-7}	9.984×10^{-7}	k_λ
ρ	-1	none	3.412×10^{-1}		k_ρ

In order to discover how accurate the equations summarised in Table 21 are, the properties D, η and λ were evaluated with their use at the wall and mean temperatures of the column for both gases, and the results compared with those obtained from the complete expressions (2 - 15/7/8). Details are as under:

TABLE 22

Comparison of exact and empirical equations for the gas properties.

Temp.(°K) Equⁿ	Nitrogen D	Nitrogen $10^4\eta$	Nitrogen $10^5\lambda$	Carbon monoxide D	Carbon monoxide $10^4\eta$	Carbon monoxide $10^5\lambda$
295 accurate	0.1995	1.763	5.931	0.1993	1.761	5.926
approx.	0.1987	1.757	5.916	0.1995	1.773	5.968
error %	-0.4	-0.3	-0.3	0.1	0.7	0.7
445 accurate	0.4062	2.374	7.998	0.4100	2.399	8.084
approx.	0.4037	2.360	7.952	0.4052	2.381	8.022
error %	-0.6	-0.6	-0.6	-1.2	-0.8	-0.8
595 accurate	0.6643	2.892	9.747	0.6734	2.939	9.913
approx.	0.6663	2.907	9.799	0.6687	2.933	9.886
error %	0.3	0.5	0.5	-0.7	-0.2	-0.3

It will be seen that the agreement was to within one percent in all but a single instance, and it is doubtful whether the ideal procedure of deriving temperature indices exactly for the individual gases would give appreciably better concordance, since a power type relationship is not, in any case, strictly applicable - the log (gas property) - log (T) plots are not quite linear. Use of a polynomial such as:-

$$(\text{gas property}) = a + bT + cT^2 \text{ etc.} \qquad (8 - 8)$$

might fit the L.J 13:7 model expressions more accurately, but the solution of the differential equation for G would become even more complex.

Apart from convenience of multiplication, power equations, have some theoretical interest. From (2 - 6) for the inverse-power model, one has that:-

$$\eta \propto T^n, \ \lambda \propto T^n, \ D \propto T^{n+1} \qquad (8 - 9)$$

Inspection of Table 21 shows that these relationships are

practically obeyed. Taking 0.720 as a suitable mean value for n, one finds from (2 - 7) that the corresponding force index is 10.1. This n value may be compared with those found experimentally:-

TABLE 23

Temperature indices of viscosity (from [J1], Table 3)

Nitrogen		Carbon monoxide	
n	T^oK	n	T^oK
0.737	333	0.72	347
0.713	398	0.69	450

It will be seen to correspond to the observed values at 350°K for both gases; it was derived for mean temperatures of 410°K (N_2) and 496°K (CO) - see Table 20.

3. SOLUTION FOR 'G'

The equation (5 - 19) giving G may be written:-

$$(1/\lambda)\,d/dT(\eta/\lambda)\,d/dT(1/\lambda\rho)\,d/dT[(\rho D/\lambda)G] = -[g\rho + A] \qquad (8 - 10)$$

and is subject to the boundary conditions:-

$$G(T_1) = G(T_2) = G'(T_1) = G'(T_2) = 0 \qquad (8 - 11)$$

Substitution of the empirical relations given in Table 21:-

$$\begin{aligned} D &= k_D\, T \\ \eta &= k_\eta T^n \\ \lambda &= k_\lambda T^\theta \\ \rho &= k_\rho T^{-1} \end{aligned} \qquad (8 - 12)$$

into (8 - 10) then gives:-

$$d/dT(T^{n-\theta})\,d/dT(T^{1-\theta})\,d/dT(T^{\delta-\theta-1}G) = -k_\lambda^4\,[gk_\rho T^{n+\theta} + AT^\theta]/k_\eta k_D \qquad (8 - 13)$$

Successive quadrature of (8 - 13) now leads to the desired

solution:-

$$G = \frac{-gk_\lambda^4 k_\rho T^{(4e-\delta-n+2)}}{k_D k_\eta e(2e-n+1)(3e-n+1)} X \left[1+A_1T+A_2T^{-e}+A_3T^{(n-2e-1)}+A_4T^{(n-3e-1)}\right] \quad (8-14)$$

$$G' = \frac{-gk_\lambda^4 k_\rho T^{(4e-\delta-n+1)}}{k_D k_\eta e(2e-n+1)(3e-n+1)} X \left[x+(x_1+1)A_1T+(x-e)A_2T^{-e}+ (x+n-2e-1)A_3T^{(n-2e-1)}+(x+n-3e-1)A_4T^{(n-3e-1)}\right]$$

where x has been written in place of $(4e-\delta-n+2)$ for brevity and the A_i are arbitrary integration constants.

For the inverse power model, the relations (8 - 9) simplify the solution for G (8 - 14) as follows:-

$$G = \frac{-gk_\lambda^4 k_\rho T^{(2n+1)}}{k_D k_\eta n(n+1)(2n+1)} \left[1+A_1T+A_2T^{-n}+A_3T^{-(n+1)}+A_4T^{-(2n+1)}\right] \quad (8-16)$$

Substituting the values for the constants and indices given in Table 21 into (8 - 14) yields:-

$$G = -\phi T^{2.4359}\left[1+A_1T+A_2T^{-0.7193}+A_3T^{-1.7215}+A_4T^{-2.4408}\right] \quad (8-17)$$

where the quantity ϕ has the value 3.255×10^{-12} for nitrogen and 3.330×10^{-12} for carbon monoxide. Using the fact that $G = G' = 0$ at 295^o and 595^oK, the column wall temperatures, one obtains the following equations:-

$$1+295\ A_1+(1.67285\times10^{-2})A_2+(5.60017\times10^{-5})A_3+(9.36825\times10^{-7})A_4 = 0$$

$$1+595\ A_1+(1.00993\times10^{-2})A_2+(1.67367\times10^{-5})A_3+(1.69028\times10^{-7})A_4 = 0$$

$$2.4359+1013.59\ A_1+(2.87161\times10^{-2})A_2+(4.00076\times10^{-5})A_3-$$

$$-(0.0459044\times10^{-7})A_4 = 0$$

$$2.4359+2044.36\ A_1+(1.73365\times10^{-2})A_2+(1.19567\times10^{-5})A_3$$

$$-(0.0082824\times10^{-7})A_4 = 0$$

Equations (8 - 18)

Solving for the integration constants A_i and substituting the values obtained into (8 - 17) gives:-

$$G = \phi T^{2.4359}[1-(4.25637\times10^{-4})T-(110.3814)T^{-0.7193}$$

$$+(29045.3)T^{-1.7215}-(698646)T^{-2.4408}]$$

$$= \phi\ T^{2.4359}\ x\ f(T) \qquad (8 - 19)$$

which is the desired solution. Whilst of simple form, its use involves fairly heavy computation since it is necessary to work to an accuracy of six significant figures. This will be evident from Table 24, which gives full details of the calculation of f(T), and of G for nitrogen - G for carbon monoxide is simply obtained therefrom by multiplying with (ϕ_{CO}/ϕ_{N_2}). Both f(T) and G are shown graphically in Figure 15.

TABLE 24. Calculation of G for nitrogen

$G = \emptyset.T^{2.4359} [1-f_1(T)-f_2(T)+f_3(T)-f_4(T)] = \emptyset.T^{2.4359} \times f(T)$

T(°K)	$f_1(T)$	$f_2(T)$	$f_3(T)$	$f_4(T)$	-f(T)	$\emptyset.T^{2.4359} \times 10^6$	$-10^8.G$
295	0.125563	1.846515	1.626586	0.654508	0.000000	-	0.000
325	0.138332	1.722250	1.376793	0.516716	0.000505	4.278	0.216
350	0.148973	1.632855	1.211889	0.431217	0.001156	5.124	0.592
370	0.157486	1.568875	1.101328	0.376522	0.001555	5.867	0.912
390	0.165998	1.510577	1.005910	0.331121	0.001786	6.671	1.191
400	0.170255	1.483317	0.963007	0.311279	0.001844	7.094	1.308
415	0.176639	1.444555	0.903870	0.284528	0.001852	7.760	1.437
430	0.183024	1.408128	0.850276	0.260908	0.001784	8.461	1.509
440	0.187280	1.385035	0.817282	0.246671	0.001703	8.949	1.524
450	0.191537	1.362825	0.786268	0.233505	0.001599	9.452	1.511
460	0.195793	1.341449	0.757074	0.221308	0.001476	9.972	1.472
470	0.200049	1.320857	0.729557	0.209991	0.001340	10.508	1.408
475	0.202178	1.310841	0.716396	0.204637	0.001260	10.782	1.359
485	0.206434	1.291344	0.691149	0.194491	0.001120	11.344	1.271
500	0.212819	1.263359	0.655842	0.180556	0.000892	12.217	1.090
515	0.219203	1.236782	0.623304	0.167988	0.000669	13.129	0.878
530	0.225588	1.211502	0.593246	0.156619	0.000463	14.080	0.652
545	0.231972	1.187425	0.565418	0.146305	0.000284	15.071	0.428
565	0.240485	1.157038	0.531404	0.133985	0.000104	16.454	0.171
580	0.246869	1.135435	0.507966	0.125685	0.000023	17.538	0.040
595	0.253254	1.114775	0.486122	0.118091	0.000002	-	0.000

Figure 15. The function G(T).

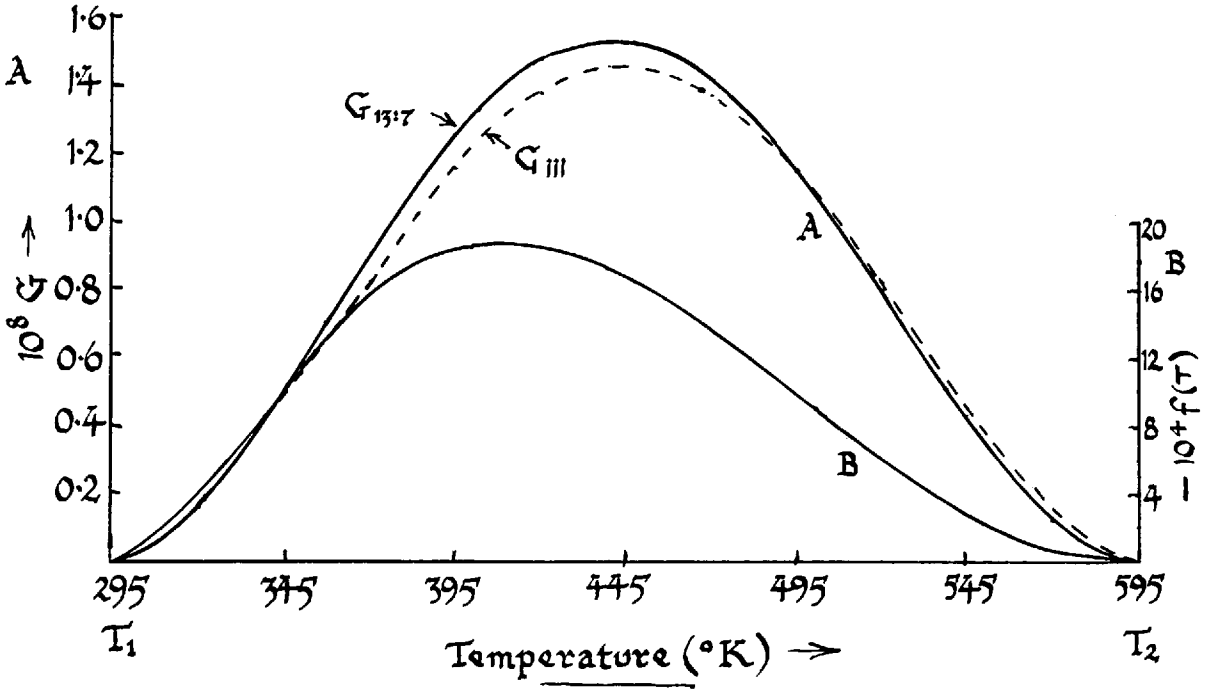
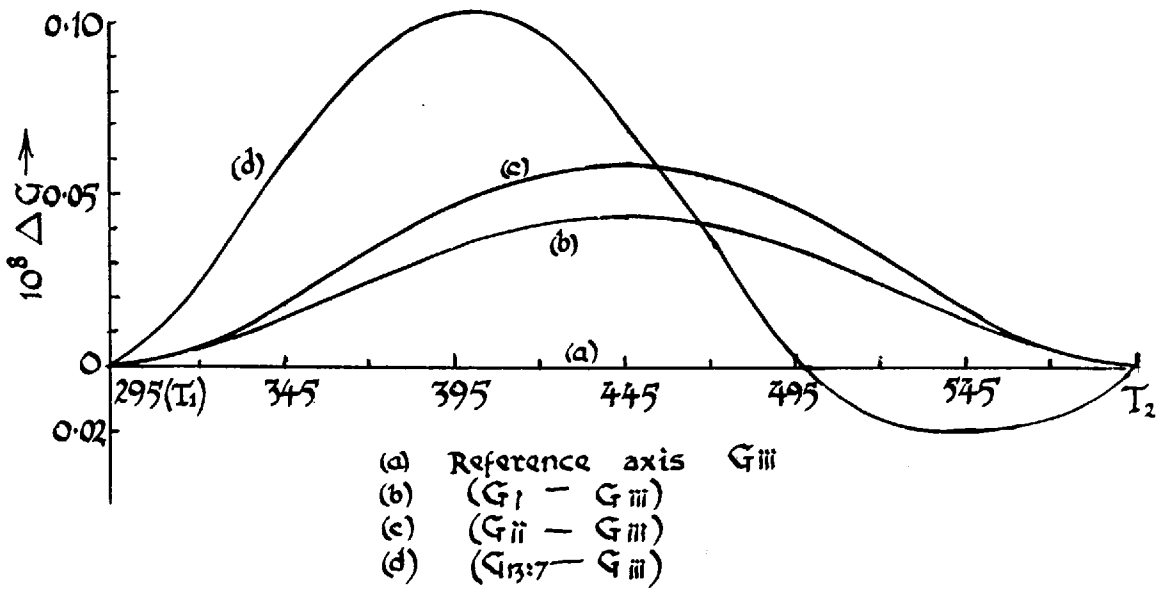


Figure 16. Differences between variously calculated G(T) values.



4. COMPARISON WITH THE SIMPLE EXPRESSION

The Maxwellian solution for G is (5 - 33) namely:-

$$G = \frac{\lambda^4 g \rho}{24 \eta D T} (T_2 - T)^2 (T - T_1)^2 \qquad (8 - 20)$$

where the gas properties are evaluated at the mean temperature T. There are three ways in which G may be calculated from (8 - 20) for the present experiments:-

i. By use of the empirical equations summarised in Table 21 and represented by (8 - 12).

ii. By use of gas properties calculated accurately.

iii. By use of the values employed in the original comparison with theory.

Method i.

Substitution of (8 - 12) into (8 - 20) yields:-

$$G_i = g k_\lambda^4 k_\rho \bar{T}^{(4\theta - \delta - n - 2)} (T_2 - T)^2 (T - T_1)^2 / 24 k_\eta k_D \qquad (8 - 21)$$

which in the case of nitrogen leads to:-

$$G_i = 2.954 \times 10^{-17} (595 - T)^2 (T - 295)^2 \qquad (8 - 22)$$

Method ii.

By substituting the accurately calculated values of the gas properties given in Table 22 for nitrogen at 445°K one obtains from (8 - 20) that:-

$$G_{ii} = 2.984 \times 10^{-17} (595 - T)^2 (T - 295)^2 \qquad (8 - 23)$$

Method iii.

Putting into (8 - 20) the values used in the original evaluation of the transport coefficients (see Table 17) gives:-

$$G_{iii} = 2.868 \times 10^{-17}(595 - T)^2(T - 295)^2 \qquad (8 - 24)$$

Values calculated by the three methods (8 - 22/3/4) are given below:-

TABLE 25

Values of G for nitrogen

T (°K)	$10^{-8}(595-T)^2(T-295)^2$	G_i	G_{ii}	G_{iii}
320 and 570	0.473	0.140	0.140	0.136
345 " 545	1.563	0.462	0.466	0.448
370 " 520	2.848	0.841	0.850	0.817
395 " 495	4	1.182	1.194	1.147
420 " 470	4.785	1.428	1.428	1.372
445	5.063	1.495	1.511	1.452

It will be seen that G_{iii} is smallest and the transport coefficients of Table 17 must therefore be low. G_{iii} is compared with $G_{13:7}$ in Figure 15 where the slight skewness of the latter function will be evident. In order to show more clearly the divergence between the variously obtained values of G, the differences between them and G_{iii} are shown plotted in Figure 16. Remembering that it is the area under the curve of G which affects the transport coefficients, it is clear that G_{ii} and $G_{13:7}$ are, to all intents and purposes, identical. This result is of considerable interest since it provides the first justification for the use of the Maxwellian expression for G in the case of real gases.

5. EVALUATION OF THE TRANSPORT COEFFICIENTS

The transport coefficients are given, for the plane case, by equations (5 - 23/4/5) and have been evaluated numerically. Occurring in all three equations is the mean circumference B

(= 5.28 cm. - see Table 17), and the heat flow Q, given by (5 - 2):-

$$Q = (1/2w)\int_{T_1}^{T_2} \lambda \, dT \qquad (8 - 25)$$

which on using (8 - 12) becomes:-

$$Q = (1/2w)[k_\lambda T^{e+1}/(e + 1)]_{T_1}^{T_2} \qquad (8 - 26)$$

$$= (k_\lambda/0.56)[T^{1.7193}/1.7193]_{295}^{595} = 4.288k_\lambda \qquad (8 - 27)$$

from which:-

$$Q_{N2} = 4.243 \times 10^{-2}, \quad Q_{CO} = 4.281 \times 10^{-2} \text{ cals/cm}^2\text{sec.} \qquad (8 - 28)$$

The expression (5 - 25) for K_d may be written as:-

$$K_d = (B/Q)\int_{T_1}^{T_2} (k_D k_\lambda k_\rho) T^{(\delta+e-1)} dT \qquad (8 - 29)$$

which on integration gives:-

$$K_d = (B/Q) k_D k_\lambda k_\rho [T^{2.4435}/2.4435]_{295}^{595} \qquad (8 - 30)$$

Substituting in this result appropriate values for the constants (Table 21 etc.) one has:-

$$(K_d)_{N2} = 9.34 \times 10^{-4} \text{ gm.cm/sec} \qquad (8 - 31)$$

$$(K_d)_{CO} = 9.38 \times 10^{-4} \quad "$$

The transport coefficients H and K_c contain integrals involving G which have to be integrated numerically. For this operation the following formula has been used (Weddle's rule):-

$$\int_a^b f(x)dx = [(b-a)/20][y_o+y_2+y_4+y_6+5(y_1+y_5)+6y_3] \qquad (8 - 32)$$

The integration interval is divided into six sections of

equal widths, the ordinates separating these being denoted by y_o, y_1 .... y_6.

Using the empirical relations (8 - 12), the equation for H, becomes:-

$$H = (B/Q^3)[k_D k_\rho \alpha_{es}/k_\lambda] \int_{T_1}^{T_2} R_T G T^{(\delta - e - 2)} dT \qquad (8 - 33)$$

and that for K_c:-

$$K_c = (B/Q^7)[k_D k_\rho / k_\lambda] \int_{T_1}^{T_2} G^2 T^{(\delta - e - 1)} dT \qquad (8 - 34)$$

The integrals in these equations were evaluated with (8 - 32) in two parts in order to give improved accuracy. The required values of R_T and G were obtained graphically, using the data of Tables 2 and 24, and are presented in Table 26 below together with those of the integrands. As mentioned at the end of section 3 of this chapter, the values of G for nitrogen may be used also when calculating for carbon monoxide, being corrected subsequently by the factor ϕ_{CO}/ϕ_{N_2}. This was done in the present case and explains the appearance of only a single set of values for G in the table.

TABLE 26

Data for evaluating the integrals in H and K_c

T(°K)	R_T		$10^8 G$	$10^{12} R_T G T^{-0.995}$		$10^{16} G^2 T^{0.0049}$
	N_2	CO		N_2	CO	
320	0.475	0.424	0.16	2.4	2.2	0.03
345	0.493	0.445	0.51	7.5	6.8	0.27
370	0.510	0.463	0.91	12.9	11.7	0.85
395	0.522	0.481	1.25	17.0	15.7	1.61
420	0.534	0.496	1.47	19.3	17.9	2.23
445	0.545	0.508	1.52	19.2	17.9	2.38
470	0.555	0.520	1.41	17.2	16.1	2.05
495	0.563	0.530	1.15	13.5	12.7	1.36
520	0.571	0.539	0.80	9.1	8.6	0.66
545	0.577	0.548	0.43	4.7	4.5	0.19
570	0.583	0.555	0.12	1.3	1.2	0.01

The integrals in the expressions for H and K_c, and the values of these transport coefficients are as follows:-

TABLE 27

Transport coefficients

	Carbon monoxide	Nitrogen
$\int_{T_1}^{T_2} R_T G T^{-0.9951} dT$	2.94×10^{-9}	3.10×10^{-9}
$\int_{T_1}^{T_2} G^2 T^{0.0049} dT$	3.06×10^{-14}	2.92×10^{-14}
$H(g/sec) \times 10^5$	1.16	1.26
$K_c(g.cm/sec) \times 10^3$	2.30	2.35

These data are for a flat wall column and so the nearly-plane case correction factors must be used before a comparison with experiment, or the originally calculated transport coefficients, may be carried out. It must be remembered that the expressions for these factors correct also for the neglect of the temperature dependence of the gas properties in the derivation of the equations giving $H^{(o)}$, $K_c^{(o)}$ and $K_d^{(o)}$ (5 - 29/30/1). In the present calculations the $u^2/3$ introduced into the expression for correcting K_d (5 - 40) must therefore be eliminated. Combining (5 - 36/40) one obtains:-

$$K_d \text{ (nearly plane)} = \frac{K_d(\text{flat wall})}{(1 + u^2/3)}[1+u^2/3+d_1 \ln(r_1/r_2)+ \ldots] \qquad (8 - 35)$$

which is the required result.

6. COMPARISON WITH THE MAXWELLIAN EXPRESSIONS FOR THE TRANSPORT COEFFICIENTS

The transport coefficients obtained for the Lennard-Jones 13:7 model [(8 - 28), Table 27], after multiplication by the nearly plane case correcting factors [5 - 38/9, 8 - 35], have the following values (Table 28). The other quantities required for a comparison between theory and experiment are also given.

TABLE 28

Maxwellian and L.J. 13:7 model transport coefficients

(The Maxwellian values are in parenthesis)

	Carbon monoxide		Nitrogen	
$H \times 10^5$	1.31	(1.30)	1.43	(1.39)
$K_c \times 10^3$	3.18	(2.88)	3.25	(2.76)
$K_d \times 10^4$	8.68	(8.93)	8.65	(8.87)
a	1.30	(1.43)	1.39	(1.59)
b	0.273	(0.310)	0.266	(0.321)
a/b	4.77	(4.6)	5.22	(5.0)
a'/b'	4.35		3.48	
K_p/K_c	5.5	(6.2)	2.8	(3.3)

It will at once be evident that no striking changes have been caused by the use of the newly calculated transport coefficients. If anything, agreement between the experimental data and theory, as judged by the concordance of a'/b' and a/b, has been worsened. In view of the length and complexity of the calculations for the transport coefficients, the

changes in a/b can have very little significance, if any at all.

7. CONCLUSIONS

The theoretical investigation described in this chapter shows that, despite the various assumptions and approximations brought into their derivation, the Maxwellian case expressions for the transport coefficients are reliable enough for practical purposes when treating the experimental results summarised in Table 15. It is reasonable to suppose that this conclusion will be applicable in the case of other experimental studies for which the conditions do not differ too markedly from those in the present work, and this is borne out by the results of Nier and Whalley.

The function G obtained by the new method (equation 8 - 19, Table 24) differs so little from that calculated using the Maxwellian expression (8 - 20) with theoretical values for the gas properties that the error incurred in using the simple equation will certainly be no greater than that inherent in the more rigorous treatment. Thus the latter was found to be extremely sensitive to the values chosen for the indices in the empirical equations representing the temperature variation of the gas properties.

The method described in section 5 of this chapter for evaluating the transport coefficients, once G has been obtained, would appear to be of much greater potential use. None of the approximations used by Furry, Jones and Onsager for describing the temperature dependence of the thermal

diffusion constant (α) is at all realistic over a wide temperature range; by using the theoretical values for α and reliable data for the other gas properties, more trustworthy values for the horizontal diffusional transport coefficient could be calculated.

At the time the column described in this thesis was built and operated, Drickamer and co-workers had not published details of their experiments with precisely constructed columns. The discussion of their results in chapter 6 shows that it is possible, given suitable constructional facilities, to make concentric tube columns whose performance may be predicted exactly by the Furry-Jones theory. Whilst the present author's column corresponds to what may be built cheaply by simple methods, it is clear that Drickamer's apparatus sets a new standard against which all future equipment designed for a study of the separating-column theory will be judged.

APPENDIX

1. Calculations performed for determining whether Drickamer et al used equation (6 - 12) or equation (6 - 17) when calculating their results. See Chapter 6, 3(a).

Quantity	Column I.Run 38	Column II.Run 2	Source
w (cm)	0.0508	0.0254	Table 14
L (cm)	40.0	41.6	"
T ^{o}K	304	303	D1
ΔT deg.	20.5	19.4	"
P (atm.)	10.37	15.78	Tables 11/2
q_e	1.96	1.42	"
D (@ P,T)	0.0331	0.0204	Table 14,D 1/P
η(poise)x10^4	2.61	2.61	"
ρ(@ P,T)	0.0131	0.0199	" , gas laws
G_r x 10^3	17.3	9.84	Equations(6-16)
ϕ'	0.926	0.900	"
ψ x 10^2	1.19	1.57	" (6-15)
ϕ	1	1	"
α' (F.J)	0.169	0.156	(6 - 10)
	0.164	0.149	D1
α (Drickamer)	0.211	0.215	(6 - 12)
	0.143	-	(6 - 17)
	0.212	0.213	D1

It is clear from the above that (6 - 12) was used for calculation of the data in D1.

2. Calculation of α for argon-neon and carbon dioxide - propane mixtures studied by Drickamer.

The parameters $E(o)/k$ and r_o for the mixtures were determined using (2 - 14). The symbols (o) have been dropped for brevity in the table below. For the meaning of the quantities tabulated see equations (2 - 19/20).

	CO_2 (1) - C_3H_8(2)		Ne (1) - A (2)	
x_i	0.55	0.45	0.436	0.564
M_i	44	44	20	40
r_i	3.996	5.061	2.80	3.418
r_{12}	4.528		3.109	
T (^oK)	380		303	325
kT/E_1	2.00		8.487	9.104
kT/E_2	1.496		2.444	2.621
kT/E_{12}	1.730		4.550	4.881
s_1	-887		-3143	-3143
s_2	1105		3436	3412
Q_1	14760		7395	7428
Q_2	26500		13690	13610
Q_3	39720		20690	20700
k_T	0.00298		0.04314	0.04377
α	0.012		0.175	0.178

REFERENCES

A1	Atkins, Bastick and Ibbs	Proc.Roy.Soc.	A172	142	(1939)
B1	Brown	Phys.Rev.	57	242	(1940)
2	Bone and Wheeler	J.Chem.Soc.	81	541	(1902)
3	Barrer	Trans.Farad.Soc.	32	486	(1936)
4	Bardeen	Phys.Rev.	58	94	(1940)
5	"	" "	57	35	(1940)
6	Brewer and Bramley	Science	90	165	(1939)
C1	Chapman	Phil.Trans.	216A	279	(1916)
2	Chapman and Dootson	Phil.Mag.	33	248	(1917)
3	Chapman and Cowling - "The Mathematical Theory of Non-uniform Gases"			C.U.P.	(1939)
4	Clusius and Dickel	Naturwiss	26	546	(1938)
5	Campbell and Parker	J.Chem.Soc.	103	1292	(1913)
6	Childs and Jahn	Proc.Roy.Soc.	A169	428	(1939)
7	Clusius and Dickel	Z.f.physik.Chem.	44	397	(1939)
D1	Drickamer, Mellow & Tung	J.Chem.Phys.	18	945	(1950)
2	Davenport and Winter	Trans.Farad.Soc.	47	1160	(1951)
3	Drickamer, Downey & Pierce	J.Chem.Phys.	17	408	(1948)
4	Donaldson and Watson	Phys.Rev.	82	909	(1951)
5	Drickamer, O'Brien, Bresee & Ockert	J.Chem.Phys.	16	122	(1948)
6	Drickamer et al.	J.Chem.Phys.	18	950,1027,1031,1380	(1950)
E1	Enskog	Physik.Zeits.	12	56,533	(1911)
2	" Doctoral dissertation, Uppsala				(1917)
F1	Fürth	Proc.Roy.Soc.	A179	461	(1942)
2	Frankel	Phys.Rev.	57	661	(1940)
3	Farkas and Melville "Experimental Methods in Gas Reactions" MacMillan				(1939)
4	Furry, Jones and Onsager	Phys.Rev.	55	1083	(1939)
5	Furry and Jones	" "	69	459	(1946)
G1	Gillespie	J.Chem.Phys.	7	530	(1939)
2	Grew	Proc.Phys.Soc.	A62	358	(1949)
3	"	" " "	A189	402	(1947)
4	van der Grinten	Naturwiss.	27	317	(1939)
5	Graham, Harkness and Thode	J.Sci.Instr.	24	119	(1947)
H1	Hellund and Uehling	Phys.Rev.	56	818	(1939)
2	Hellund	" "	57	319	(1940)
3	Hirschfelder, Bird & Spotz	J.Chem.Phys.	16	968	(1948)
4	" " "	" " "	18	1395	(1950)
5	" " "	Chem.Rev.	44	205	(1949)
6	Harrison Brown	Phys.Rev.	58	661	(1940)

J1	Jones and Furry	Rev.Mod.Phys.	18	151	(1946)
2	Jones	Phys.Rev.	58	511	(1940)
3	"	" "	59	1019	(1941)
4	Jahnke and Emde, "Tables of Functions"				
5	Jost, "Explosion and Combustion Processes in Gases" McGraw Hill (1946)				
K1	Kennard, "Kinetic Theory of Gases" McGraw Hill (1938)				
2	Kihara	J.Phys.Soc.Japan	3	265	(1948)
3	Kihara and Kotani	Proc.Phys.Math.Soc.Jap.	25	602	(1943)
L1	Lennard-Jones	Proc.Phys.Soc.	43	461	(1931)
M1	Mann	Phys.Rev.	73	412	(1948)
2	McInteer, Aldrich and Nier	" "	72	510	(1947)
3	MacWood and Urey	J.Chem.Phys.	4	402	(1938)
4	Majumdar	Phys.Rev.	81	849	(1951)
N1	Nier	Phys.Rev.	56	1009	(1939)
2	"	" "	57	30	(1940)
O1	Onsager and Watson	Phys.Rev.	56	474	(1939)
P1	"Preparation and Measurement of Isotopic Tracers" Ann Arbor, Mich. (1946)				
R1	Lord Rayleigh	Proc.Roy.Soc.	66	68	(1900)
S1	Simon	Phys.Rev.	69	596	(1946)
2	Sutherland	Phil.Mag.	36	507	(1893)
3	Stier	Phys.Rev.	62	548	(1942)
4	Stock and Henning	Ber.Dtsch.Chem.Ges.	54	1125	(1921)
T1	Trautz and Sorg	Ann.der Physik	10	81	(1931)
2	Trautz and Kurz	" " "	9	981	(1931)
3	Trautz and Binkele	" " "	5	569	(1930)
U1	Urey	Rev.Sci.Instr.	21	724	(1950)
W1	Whalley Ph.D.Thesis, London (1949)				
2	Whalley, Winter and Briscoe	Trans.Farad.Soc.	45	1085	(1949)
3	Whalley and Winter	" " "	45	1091	(1949)
4	Whalley	" " "	46	517	(1950)
5	Winter	" " "	46	81	(1950)
6	"	" " "	47	342	(1951)
7	Waldmann Naturwiss 31,32, Z.Naturforsch 1,2a,Z.Physik 123.				
8	Watson and Woernley	Phys.Rev.	63	181	(1943)
9	Winter	Analyst	73	653	(1948)
10	Waldmann	Z.für Physik	114	53	(1939)

THE HIGH TEMPERATURE EXCHANGE BETWEEN OXYGEN AND METAL OXIDES

1. INTRODUCTION

In view of the great importance of metal oxides as catalysts, much research has been done in an endeavour to elucidate their mode of action. As is so often the case with practical processes, their empirical development has far outstripped fundamental knowledge of the mechanisms involved. Indeed many of the techniques required for the study of catalytic action have only recently become available [1].

Whilst the crystal structures of oxides are well known from x-ray diffraction measurements, this information is of limited usefulness when considering phenomena such as ionic diffusion and conductivity which depend for their existence on structural imperfection. The electronic applications of semi-conductors have led to much work being carried out on the electrical behaviour of oxides, and the mobility and nature of their lattice defects are now becoming known [2]. By using very thin layers prepared by controlled oxidation of evaporated metal films, the surface properties have been studied [3].

It is now believed that the first step in many catalytic processes consists of the dissociative adsorption of the reactants on to the catalyst surface. The reactionsfor which

oxide catalysts are mainly employed involve the transfer of hydrogen, oxygen or water between the reactants, the solid surface providing a region in which such processes may more readily take place. Thus when oxygen gas is adsorbed at sufficiently high temperature on to an oxide, the molecules are dissociated into atoms which then migrate readily along the solid surface until trapped at some fault. Alternatively they may diffuse into the interior of the lattice or exchange with ions at its surface.

In order to study these fundamental surface exchange phenomena, Winter and co-workers [4-8] have used simple isotopic tracer techniques. Whalley [4] showed that oxygen exchanges readily between water vapour and oxides at temperatures as low as 20°C, in the case of γ-alumina, and 120°C in those of thoria and titania; he distilled water labelled with the heavy ^{18}O isotope repeatedly through a tube filled with the oxide and followed the exchange reaction by water density measurements. For γ-alumina, the surface area derived from the exchange results was shown [5] to agree well with that found from the low-temperature adsorption of nitrogen on the oxide.

Subsequent exchange studies have been carried out with isotopically enriched oxygen [6]. The oxide sample is outgassed under controlled conditions and, after the temperature has been adjusted to the value required for the experiment, a known quantity of oxygen containing $\sim$1.2% ^{18}O is let into the system. The course of the exchange reaction is then

determined by following the change in ^{18}O content of the gas with time. When this process is rapid, a practically continuous record may be obtained by allowing a minute quantity ($\sim 10^{-5}$ g/hr.) of the gas from the exchange vessel to leak continuously into the ion-source of the mass spectrometer used for analysis - the ^{18}O concentration may then be determined as often as required by measuring the abundance ratio (mass 34)/(mass 32) and using equation (4 - 4). All the results so far obtained that have warranted detailed quantitative consideration were measured in this way.

When only a slow exchange reaction is being studied, the apparatus need not be connected directly to the mass spectrometer, gas samples being withdrawn at suitable intervals and analysed subsequently. This technique was used by Houghton [6] in some preliminary experiments with alumina, thoria, titania and zinc oxide, and also for the present work.

Winter and collaborators have shown [6 - 8] there to be two fairly distinct stages in the oxygen exchange process; a relatively rapid reaction at the surface of the oxide and a slow exchange presumed due to the replenishment of the normal oxygen ions in the surface by diffusion of ^{18}O into the bulk of the solid. The present experiments were carried out in an attempt to study the latter diffusion process, high temperatures being exployed in order to render it the more readily followable.

The surface exchange obeys first-order kinetics and, from the rate constants, values for the activation energy (E) of the exchange reaction have been obtained [8]. In the case of

chromic oxide, a change of mechanism is observed at 410°C; below this temperature, desorption of oxygen appears to be the rate-determining step (E = 29 ± 0.5 k cal/mole), at higher temperatures the exchange proper (E = 1 ± 4 k cal/mole.). Detailed investigations of such surface exchange phenomena are at present being carried out by Barnard and Winter*

* Private communication.

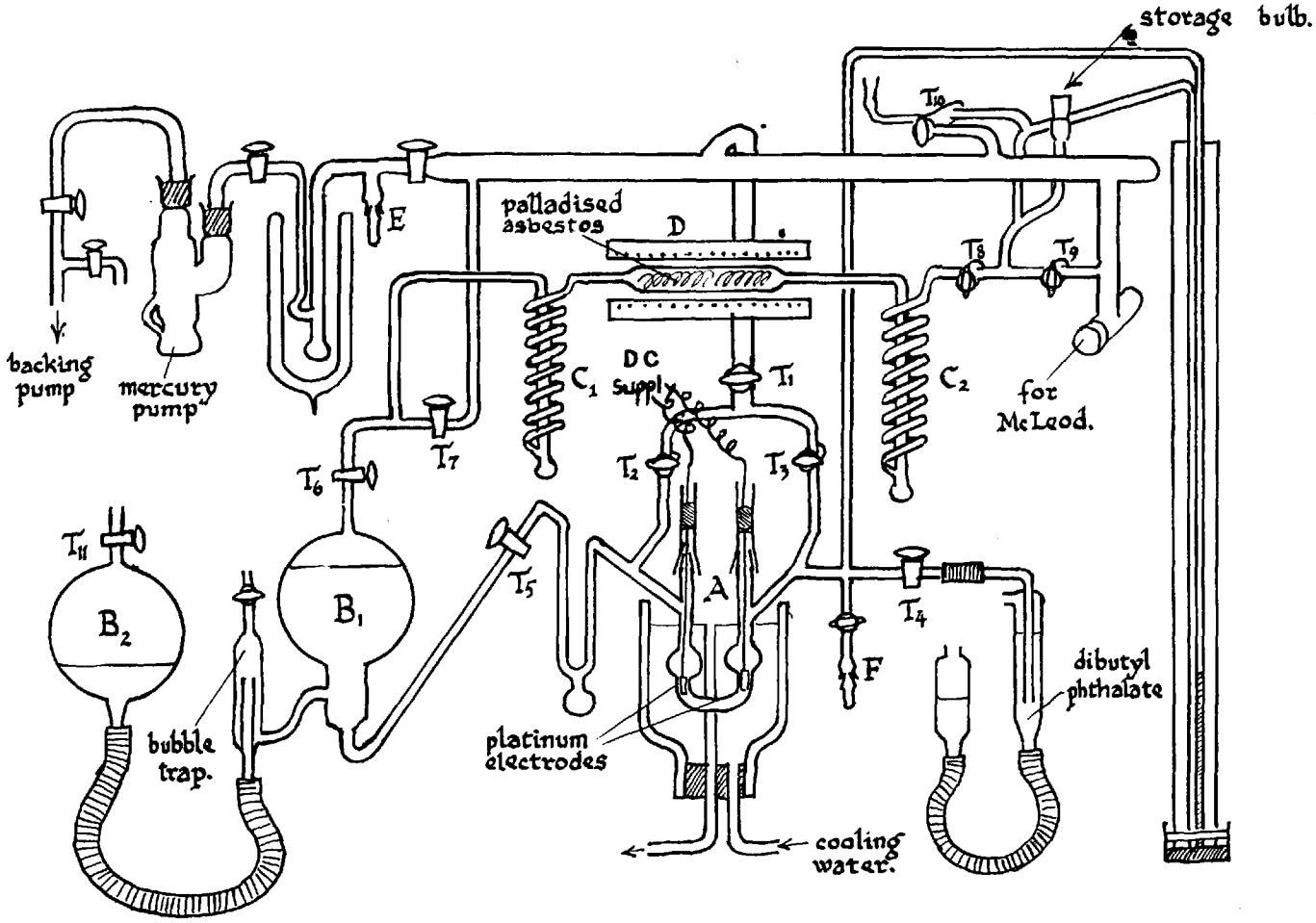
2. PREPARATION OF THE OXYGEN

The oxygen used for the work on oxide exchange was obtained by electrolysis of water enriched in ^{18}O. The apparatus constructed for this purpose was, in main features, similar to that designed by Singleton [9] for the liberation of deuterium from heavy water.

The cell (A - Figure 1) was provided with efficient water cooling and its platinum foil electrodes were sited as near to the bottom as possible in order to keep to a minimum the volume of water that could not be electrolysed. The platinum wire electrode-leads were sealed through soda-glass sockets which fitted over pyrex cones on each limb of the cell. The short lengths of tubing above the seals were used as mercury cups for making connection with the direct-current supply; the current passed through the cell was measured with a moving-coil meter and controlled by a rheostat.

During electrolysis, the hydrogen produced was bubbled to waste through dibutyl phthalate; the oxygen was collected over paraffin in the litre bulb B_1 connected by rubber pressure-

Figure I. Apparatus for electrolysis of heavy water.



tubing to the adjustable reservoir B_2. Before an electrolysis the liquid paraffin was outgassed by continued pumping and careful warming of the two bulbs, a temperary rubber connection being provided between T_{11} (on B_2) and the air inlet for the backing pump.

At the start of a preparation, the water was put into the cell (A) using a drawn-out glass tube as a dropper. Cylinder nitrogen (dried by bubbling through concentrated sulphuric acid) was now passed through the inlet F and each side of the cell in turn, to expel air. The gas flow was maintained and crushed ice put into the cell cooling jacket whilst 10% by weight of clean sodium wire was dissolved in the water to make it suitably conducting. The electrodes were then put in position and the gas pressure in the cell and adjoining tubes reduced to about 5 cm. mercury by cautious pumping through taps T_1, T_2 and T_3. T_1 was now closed and a small current passed through the electrolyte until the cell pressure had increased to about 20 cm. mercury. This electrolytic gas was then pumped away, taking with it dissolved air removed from the electrolyte by the preliminary electrolysis. The cell was next brought up to atmospheric pressure by careful further electrolysis - considerable frothing occurs at low pressure - the liquid levels being kept equal by allowing hydrogen to expand via T_3 into the tubing between the taps T_1, T_2 and T_3 as often as necessary. After each withdrawal of gas, T_3 was closed and the section of tubing used re-evacuated.

When a pressure of slightly greater than one atmosphere was reached in both sides of the cell, the vacuum in the paraffin reservoir B_2 was destroyed and this bulb then adjusted so that the liquid level therein was slightly below that in B_1 and caused a slight negative pressure in the latter. T_4 and T_5 were then opened allowing the oxygen to pass into the collecting bulb B_1; the electrolyte levels were maintained equal by altering the head of dibutyl phthalate through which the hydrogen was bubbled.

The current used for electrolysis was 0.9 A, any increase causing unduly high frothing and passage of hydrogen round the bottom bend of the cell. When a convenient quantity of oxygen had accumulated in B_1, electrolysis was stopped, taps T_5 and T_7 closed, and tap T_6 opened very slightly to allow the gas to expand into the previously evacuated storage bulb. The oxygen passed successively through a solid-carbon dioxide cooled spiral trap (C_1), to remove low boiling paraffins, a tube (D) containing palladised asbestos and heated to about 300°C, to cause combustion of any hydrogen present, and a second trap (C_2) to remove water so formed.

The quantity of oxygen prepared for the experiments to be described was approximately three litres at one atmosphere pressure and laboratory temperature. Samples of the gas were taken occasionally during the electrolysis, being removed in standard tubes (see Figure 7) from the ground socket on tap T_{10}: these samples were checked for purity on the mass spectrometer.

3. APPARATUS AND EXPERIMENTAL METHOD

The apparatus is shown in Figure II and is conveniently described jointly with the normal experimental procedure.

The oxide specimen was weighed accurately into a platinum boat which was then carefully pushed to the end of the silica reaction tube. The latter was now fitted on to the standard cone at E; the joint, being close to the end of the furnace tube, was greased with silicone, held together by two steel springs (stretched between glass hooks on the apparatus and a special detachable collar on the exchange tube) and surrounded by a water-cooled coil of 'compo' tubing.

The furnace, at the desired outgassing temperature, was now slid into place over the silica tube, free expansion of the air inside being allowed by removing the small bulb G. G was now replaced and the air from the exchange system pumped out very slowly over a period of some five minutes or so. Too rapid pumping, or evacuation of the silica tube before heating, caused the exceedingly fine oxide powders to be blown out of the boat by desorbing air and moisture. The connection with the main vacuum line was then fully opened and the sample outgassed over-night under the best obtainable vacuum. With the silica three-stage mercury pump and backing pump used, this was 10^{-5} - 10^{-6} mm. mercury pressure as indicated by a rotary McLeod gauge.

The enriched oxygen for the exchange was expanded from the storage bulb (A) - transferred from the electrolysis apparatus - into a doser bulb (B), which was then isolated

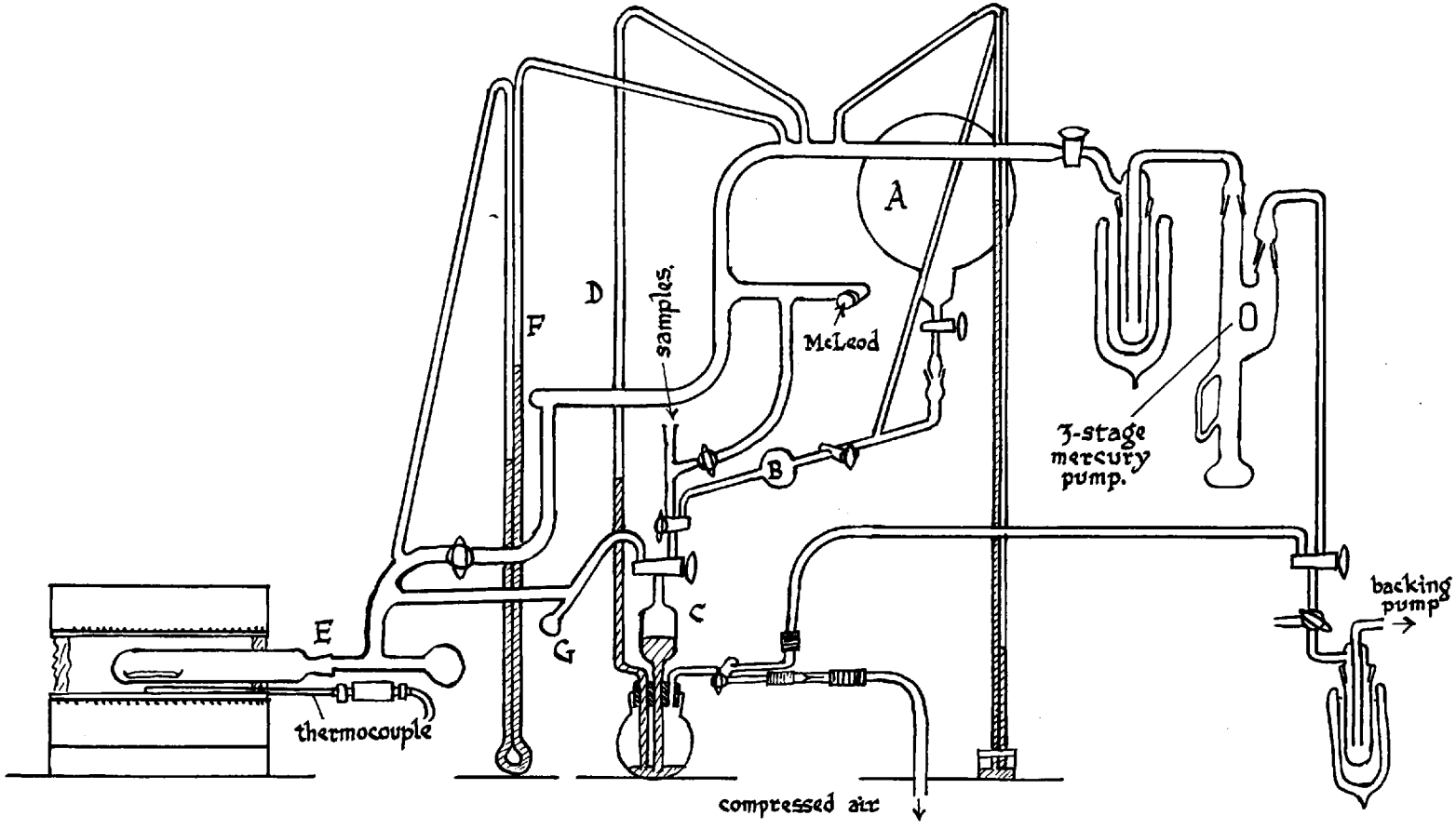


Figure II Apparatus for study of the exchange of oxygen with metal oxides.

from (A) before being connected with the Toepler pump (C). This avoided the necessity of joining A and C directly with the consequent risk of losing gas. By adjusting the mercury level in the Toepler bulb to either of two volume calibrations, the quantity of gas therein could be found directly by reading the attached manometer (D).

After outgassing the sample, the furnace temperature was lowered to that required for the ensuing run and the measured quantity of oxygen admitted to the exchange tube. The bulb connected with the latter was merely to increase the oxygen capacity of the exchange system so that sample removal would have a smaller effect on the gas pressure; the demountable bulb (G) was primarily fitted to prevent mercury from the Toepler pump from getting into the hot regions of the apparatus near the furnace.

Samples of gas were withdrawn from the exchange vessel, measured with the calibrated Toepler and then taken off in standard tubes (Figure 7) from the ground socket shown on the diagram. A direct connection to the main vacuum line was provided for evacuating and testing sample tubes before use. The pressure in the exchange tube before and after the removal of each sample was measured to ensure that no air leakage escaped notice.

Samples were analysed by mass spectrometer for the percentage of ^{18}O; the author is much indebted to J.A. Barnard who performed carefully the many analyses resulting from this work.

The important parts of the apparatus are now considered in more detail:-

The furnace

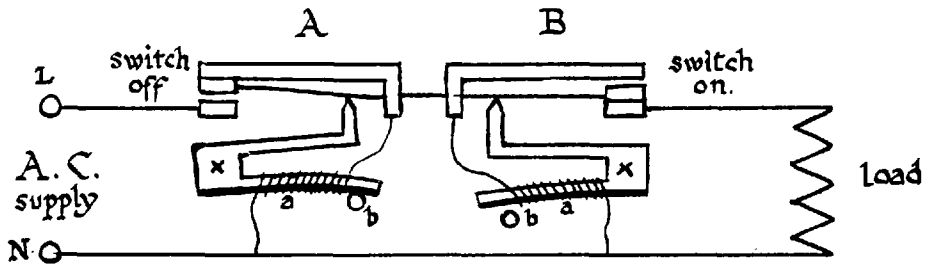
The electric furnace employed was one built and used for previous work. Unfortunately some material had been spilled on the silica furnace tube and caused the latter to become spongy and crack. The outer surface of any silica object heated in the furnace was also soon spoiled by this volatile impurity - presumably vapour from a metal salt or soda-glass. After the first few experiments with a sintered silica tube, therefore, the furnace was reconstructed on a new 'sand' silica core. The winding was of nichrome embedded in alundum cement and had a resistance of 30 ohms.

Temperature control and measurement

Temperature control was by means of a Sunvic bi-metallic energy regulator in the primary circuit of a Variac auto-transformer. This arrangement was satisfactory until heavy sparking corroded the contacts and caused the controller to stick in the on-position with the unfortunate result later described. After a period when the voltage applied to the furnace was adjusted manually, a safety device was made, using two Sunvic controllers, which cut off the furnace current in the event of the main controller jamming. (See diagram on next page).

The furnace temperature was measured with the Pt - Pt/Rh thermocouple used for the thermal diffusion experiments

Use of a Sunvic controller (B) as a safety cut-out



Sunvic A gives energy control; B is wired in reverse and set so that the time required for its bimetal strip(a) to bend sufficiently to contact the stop(b) and switch current off is greater than for A.

described earlier. It was checked against the boiling points of sulphur, benzophenone and naphthalene.

Owing to imperfect winding of the furnace, there was a temperature gradient of some 20 degrees per inch in the air space outside the exchange tube adjacent to the sample boat. Conduction in the silica and platinum will have resulted in there being a much smaller temperature unevenness in the actual sample. The recorded run temperatures were obtained with the hot junction of the thermocouple as near as possible to the centre of the platinum boat.

Reaction vessel

For the first experiments, a sintered silica tube was used as reaction vessel. When it was shown that exchange was taking place between it and the oxygen gas used for

studying the reaction, a fused silica tube was obtained. This was, however, spoiled when new by the furnace temperature control failing; from the partial collapse and devitrification observed at its end, a central furnace temperature of 1350 - 1400°C must have been attained. After removal of the worst-affected portion of the tube, it was used for a number of further experiments until shown to have become reactive.

The third exchange tube was similar to the second but of smaller wall thickness.

4. RESULTS AND DISCUSSION

Although practically a year was spent on the oxygen exchange experiments, no reliable quantitative data were obtained. The reason for this was two-fold: firstly, exchange was found to occur between oxygen and the surface of the silica reaction vessels to a very considerable extent; secondly, the temperature control provided for the furnace proved neither sufficiently accurate nor reliable. The realisation of these facts was delayed by the mass spectrometer used for sample analysis either being out of order, or working somewhat unreliably during a period of several months following the completion of the first and promising preliminary experiments. The results obtained are therefore presented in graphical fashion only. Since, however, the experience gained should be of some value to future workers in this field, a summary of the experiments performed is given.

The first run with magnesium oxide in the sintered silica tube, at 945°C (see Figure III) gave a reasonable 18-oxygen concentration ($[^{18}O]$) - time (t) plot which suggested that the relative amounts of oxide and oxygen chosen were suitable*. After making some improvements to the apparatus, two further runs were carried out with less promising results, this being attributed to inaccurate isotope analyses. Standard outgassing conditions (about 1000°C) were then chosen and a series of four runs carefully performed. A check of tube exchange was next carried out and it was found that $[^{18}O]$ was reduced in an appreciable amount of gas (10 cc. at N.T.P.) from 1% to 0.45%. The gas samples from the runs done previously were therefore destroyed. A blank run was not performed at the outset since no exchange trouble had been experienced in previous work and the surface area of the tube would not in any case be expected to be more than a few percent of that for half a gram of a fine powder (in the case of MgO - 7 m^2).

After considerable delay, a transparent silica tube was obtained and the furnace rebuilt also. After the misfortune with the former, mentioned at the end of section 3, it was found still to be usable; in a blank run $[^{18}O]$ in 4 cc. at N.T.P. was reduced from 1.10-1.06%. Five further runs with magnesium oxide were therefore carried out with results shown in Figure IV. Two were spoiled by air leakage due to

* 0.5 g. MgO - 100 cc. oxygen @ 30 cm. Hg. pressure, 20°C.

Magnesium oxide

Figure III

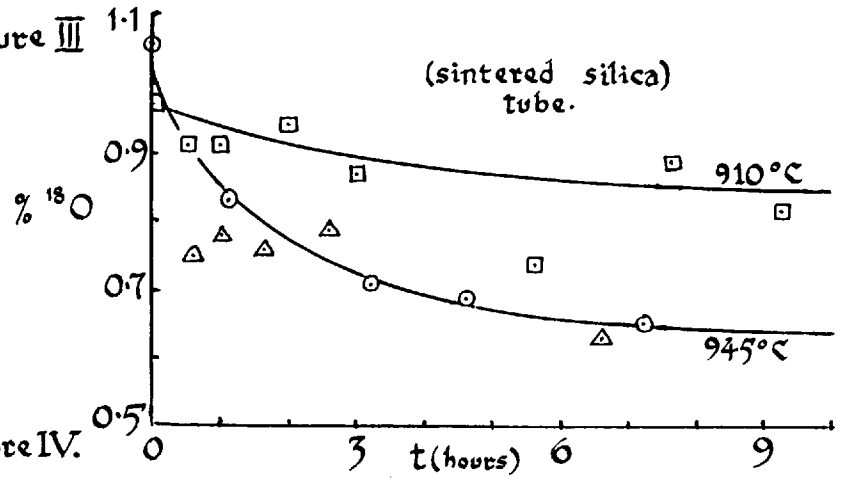


Figure IV.

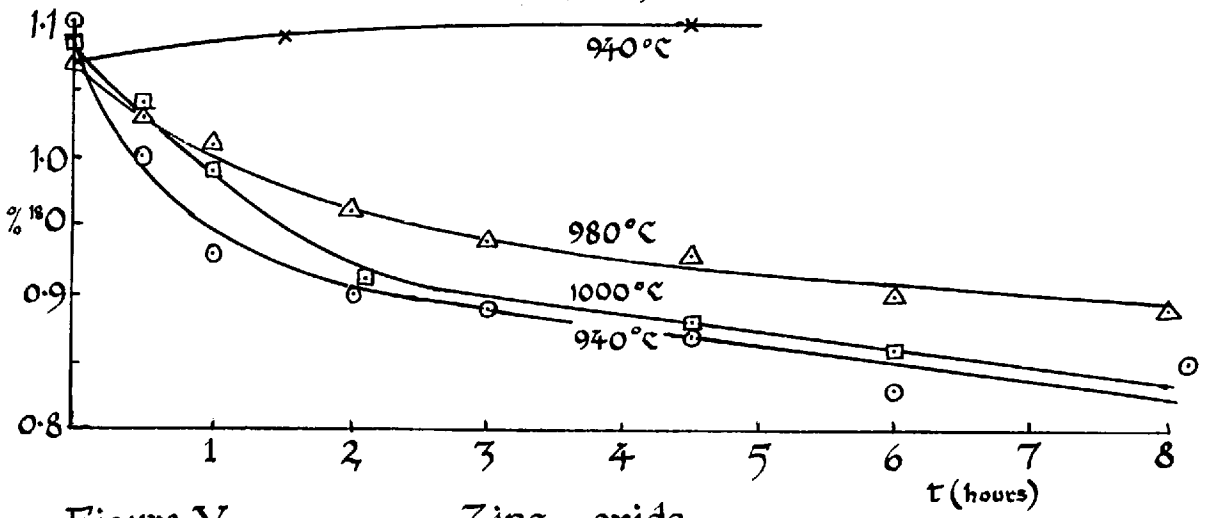
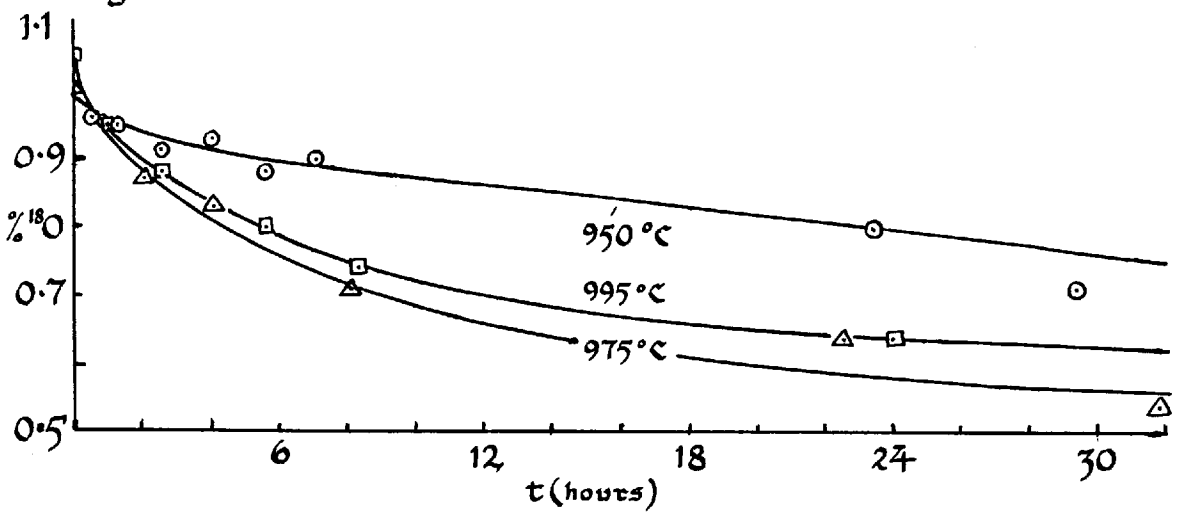


Figure V. Zinc oxide



striation of the silicone-greased joint between the reaction tube and the rest of the apparatus; strong springing of this joint was found essential for runs of long duration. A further blank run showed that this clear tube now exchanged with oxygen.

A second fused-silica tube was then obtained, and after giving a satisfactory blank, used for a run with magnesium oxide at 940°C. No exchange occurred - in fact $[^{18}O]$ increased by about 0.03% (Figure IV). A rough calculation shows* that this order of enrichment might be caused by thermal diffusion in what was, effectively, a horizontal two-bulb system.

In view of the unexpected nature of this result, a repeat run was performed after cleaning carefully the apparatus in case some form of contamination had been responsible. An identical result was obtained.

Since the time available for the work was by now limited, it was decided to work with another oxide - that of zinc. Some trouble was here experienced due to loss of metallic zinc from the oxide during outgassing. The three runs performed gave quite good $[^{18}O]$ - t plots (see Figure V), but

---

* From the apparatus dimensions and operating conditions:-

V_1 = 120 cc., V_c = 45 cc., V_2 = 45 cc., V^* = 0.97

T_1 = 300°K, T = 750°K, T_2 = 1200°K, T_r = 554°K

For oxygen:- α_{es} = 0.027, $(R_T)_{13:7}$=0.59, α = 0.016

Also, c_1 = 0.02. Hence Δc = 0.04%.

For the formulae used in the above calculation see Chapters 2 and 3.

owing to the furnace temperature becoming too high during outgassing, there was some doubt as to the weight of oxide participating in the exchange experiment at 995°C.

A blank run then showed the second fused-silica exchange tube to have become active.

The lack of exchange with magnesium oxide might perhaps be explained as being due to extensive sintering; one would, however, at least have expected instantaneous surface exchange to have reduced the ^{18}O concentration to some extent. Although the experimental observation appeared a true one, more careful work is necessary for its satisfactory confirmation. Further speculation seems unprofitable at the moment.

An attempt was made to treat the results obtained with zinc oxide quantitatively and evaluate the diffusion coefficient (D) for oxygen ions in the solid phase at the temperatures studied and hence determine the diffusional activation energy.

As an approximation, the oxide powders used may be considered as consisting of small spheres, their effective mean radius being readily found from the surface area (A) and density (ρ). Thus for 1 gram:-

$$4\pi r^3 \rho n/3 = 1$$

$$4\pi r^2 n = A$$

$$\therefore r = 3/A\rho \qquad (6)$$

For zinc oxide ρ = 5.47 g/cc and A = 0.52 m^2/g (see next section) hence r = 1.1 x 10^{-4} cm.

The equation for diffusion from a limited amount of fluid into a sphere (10) has been shown by Barrer (11) to approximate for small (Q_t/Q_∞) to :-

$$Q_t/Q_\infty = \frac{6}{r}\frac{Q_0}{Q_0 - Q_\infty}\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} \qquad (7)$$

where Q_t is the amount of flow (material or heat) that has taken place in time t and Q_∞ is the limiting value of Q_t. (7) holds only for:-

$$D_t/r^2 \not> 0.1 \qquad (8)$$

By plotting $[^{18}O]t/[^{18}O]_\infty$ against $(t)^{\frac{1}{2}}$, values of D were obtained from the slopes of the lines of order 10^{-10} - 10^{-11}. $[^{18}O]_\infty$ was simply calculated by assuming a uniform distribution of all the ^{18}O atoms throughout all the O atoms, being 0.0041 and 0.0043 for the zinc oxide runs at 950° and 975°C respectively. Substituting the above D values into (8) leads to the result that equation (7) is applicable for about twenty seconds! In view of the uncertain nature of the experimental data, an appropriate solution for the diffusion equation was not sought.

The experimentalevidence suggests that silica reaction tubes soon, if not immediately, become active in high temperature experiments with oxides. A run with powdered silica was carried out and considerable exchange shown to take place at 990°C. It follows that as soon as a sample had reduced the $[^{18}O]$ in the gas to below that in the wall of

the reaction tube, the latter will have put [^{18}O] back into the gas and given an apparently lower exchange rate. This may also explain the greater speed of the lowest temperature run in Figure IV. The activation of the fused silica was almost certainly due to fine oxide particles reaching it during outgassing and breaking up the surface structure. At the temperatures used the surface mobility of metal ions would be very high, and minute quantities of oxide could readily affect the whole inner surface of the reaction tube.

For future experiments on high temperature oxygen exchange, two improvements in apparatus will be essential.

i) Provision of temperature control and measurement accurate to at least 1 degree.

ii) Use of a non-reactive exchange vessel.

For the latter, a platinum-lined thick walled metal tube would appear suitable and should give an even temperature distribution. In view of the elegance of the simple isotopic tracer technique for studying oxides, well illustrated by the results obtained for surface exchange at lower temperatures by Winter and co-workers, further work at high temperatures would doubtless prove of considerable interest.

5. MEASUREMENT OF SURFACE AREAS

Experimental.

The surface areas of the magnesium and zinc oxides used for the exchange experiments were determined using the low

temperature nitrogen adsorption technique of Brunauer, Emmett and Teller which has been simply described by Bugge and Kerlogue [12]. Owing to an experimental slip, only an inaccurate result was obtained for zinc oxide and the author is indebted to Dr. E.R.S. Winter for its redetermination.

The apparatus used was constructed by J.A. Barnard from an earlier one of similar but less convenient design, and is shown in Figure VI. The sample was weighed into the adsorption bulb which was then sealed on to the system and slowly evacuated. Care was required because desorption of air and moisture caused the finely powdered oxide to seetheviolently with the consequent risk of blocking the capillary-lead to the bulb. The sample was now surrounded by a small electric furnace, heated cautiously to 120°C and outgassed overnight with a mercury diffusion pump backed by a rotary oil pump.

Nitrogen for the adsorption was taken from a cylinder, being passed through a heated tube packed with metallic copper, to remove oxygen, and a solid carbon dioxide trap to freeze out water.

The oxide was isolated from the rest of the apparatus after outgassing, and nitrogen let into the gas burette. This was calibrated in 0.1 cc. divisions from 0 - 200 cc. and immersed in a water jacket (as was the thermometer used for measuring the gas temperature). The tubing between the burette, manometer and adsorption bulb was of capillary, and to keep this 'dead volume' constant the manometer was adjusted before each pressure reading so that the mercury level on the

Figure VI. Surface area apparatus.

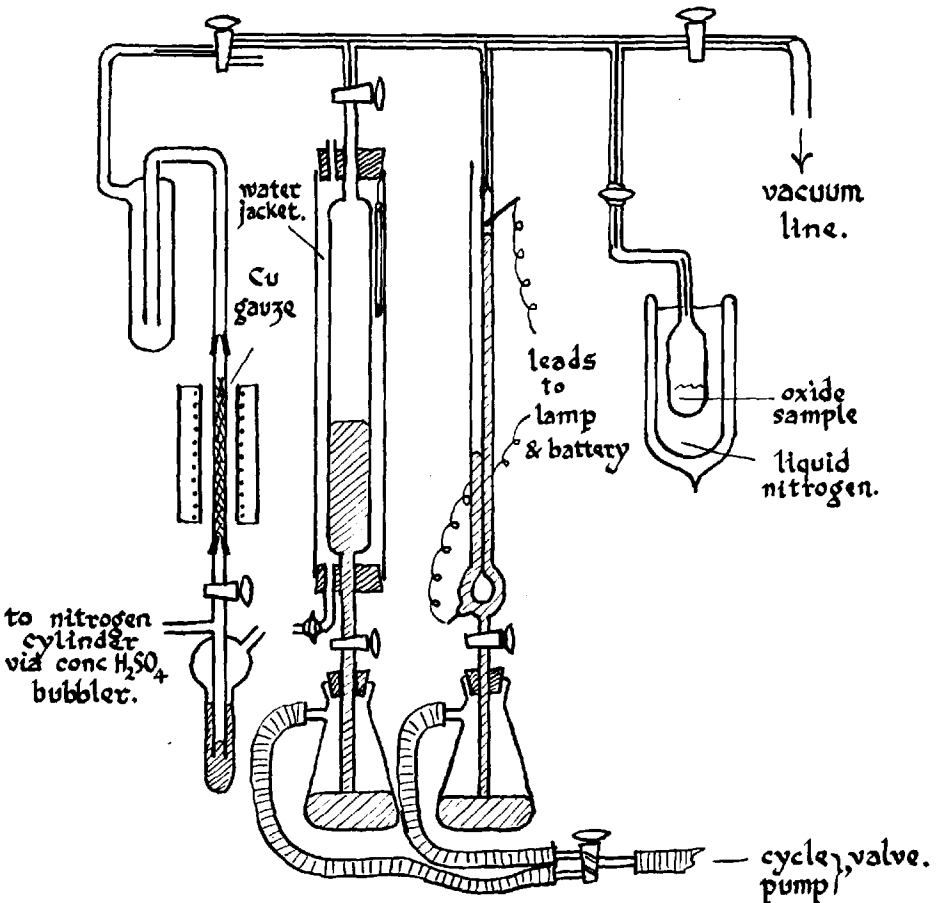
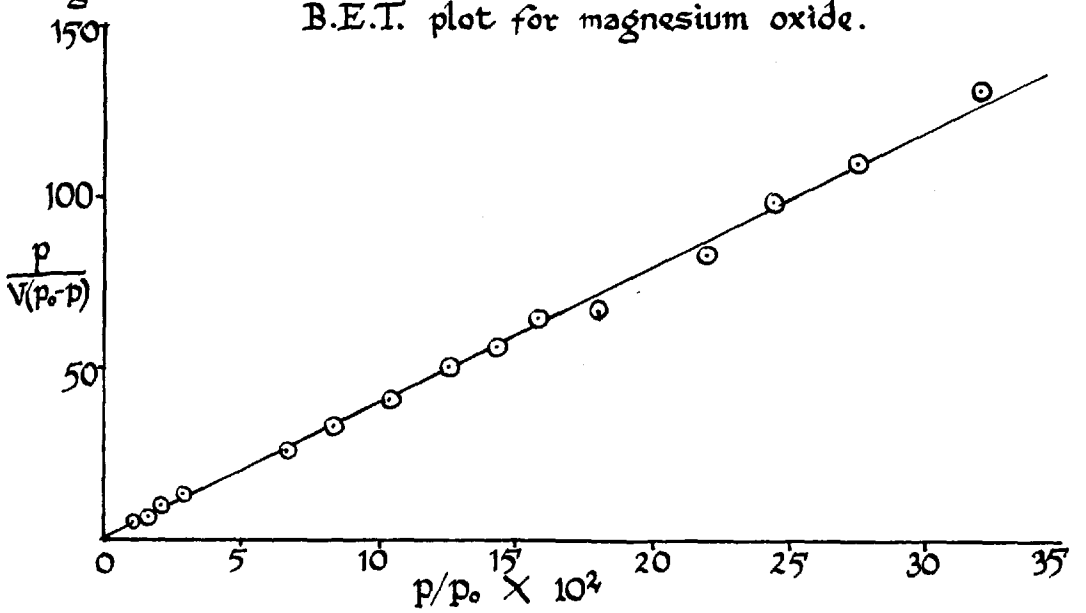


Figure VII. B.E.T. plot for magnesium oxide.



adsorbent side of the U tube was the same. This was facilitated by a contact sealed through the manometer such that the mercury caused a lamp to light when above the reference level.

The adsorption bulb was now immersed in liquid nitrogen contained in a narrow-necked Dewar. The temperature of the former was measured before and after each run with an oxygen vapour pressure thermometer, the mean of these two readings being used when calculating the results. The gas burette was then connected with the oxide and, after a few minutes, the pressure recorded. The mercury level in the burette was raised in stages and successive values for the pressure and gas volume therein recorded. In order to cover the desired range, one (sometimes two) additional quantities of nitrogen were added; when doing this the oxide was isolated, the mercury level in the burette lowered and the increase in pressure due to the extra gas let in measured.

The volumes of the 'dead space' and adsorption bulb required when calculating the actual quantity of nitrogen adsorbed on the oxide were determined by expanding a small measured quantity of gas successively into each and applying Boyles law to the P-V data obtained. Considerable trouble was experienced in getting consistent results due to errors in both the pressure and volume readings, but satisfactory values were ultimately obtained which agreed well with those found later by filling the parts with mercury and weighing the amount held in each.

Calculation of results.

The B.E.T. equation is:-

$$\frac{p}{v(p_o - p)} = \frac{1}{V_m c} + \frac{(c-1)p}{V_m c\ p_o} \qquad (1)$$

where p_o is the liquefaction pressure of the adsorbate, c a constant of large value, V_m is the volume of molecules in a monolayer and p, v are experimental values of the pressure and volume of gas adsorbed*. The latter are calculated from the results as follows:-

The temperature of the liquid nitrogen surrounding the oxide bulb is obtained from the observed oxygen vapour pressure p' by using [13]:-

$$\lg p' = -419.30/T_o + 8.1173 - 0.00648\ T_o \qquad (2)$$

and p_o then calculated from the corresponding equation for nitrogen:-

$$\lg p_o = -334.64/T_o + 7.5778 - 0.00476\ T_o \qquad (3)$$

Knowing p_o, v' the volume at T:-

v' = (vol. in burette) + (dead volume)

v" the volume of the bulb in liquid nitrogen, and V, the total volume of nitrogen present (at N.T.P.), the adsorbed volume is now given by:-

$$v(ads) = V - v' \cdot \frac{p}{760} \cdot \frac{273}{T} - v'' \frac{p}{760} \cdot \frac{273}{T_o} [1 + 5p/76000] \qquad (4)$$

the last term being the corroction required for the gas laws (5%) at the temperature of liquid nitrogen.

* Pressures are in mm. Hg. - volumes in cc.

It is evident from (1) that a plot of $p/v(p_o-p)$ vs (p/p_o) should give a straight line (this was the case for both MgO and ZnO for (p/p_o) up to 0.30). The theory used for deriving (1) and explaining the divergence from linearity of actual results is still a highly controversial topic. Since the constant c is large, the slope of the B.E.T. plot is $(1/V_m)$, and substitution of a suitable value for the area of an adsorbed nitrogen molecule (16.2 sq.Å) leads to the simple formula:-

$$\text{Surface area} = 4.38\ V_m/(\text{weight of solid})\ m^2/g \qquad (5)$$

The B.E.T. line obtained for magnesium oxide is shown in Figure VII, and the results for both this and zinc oxide are as follows:-

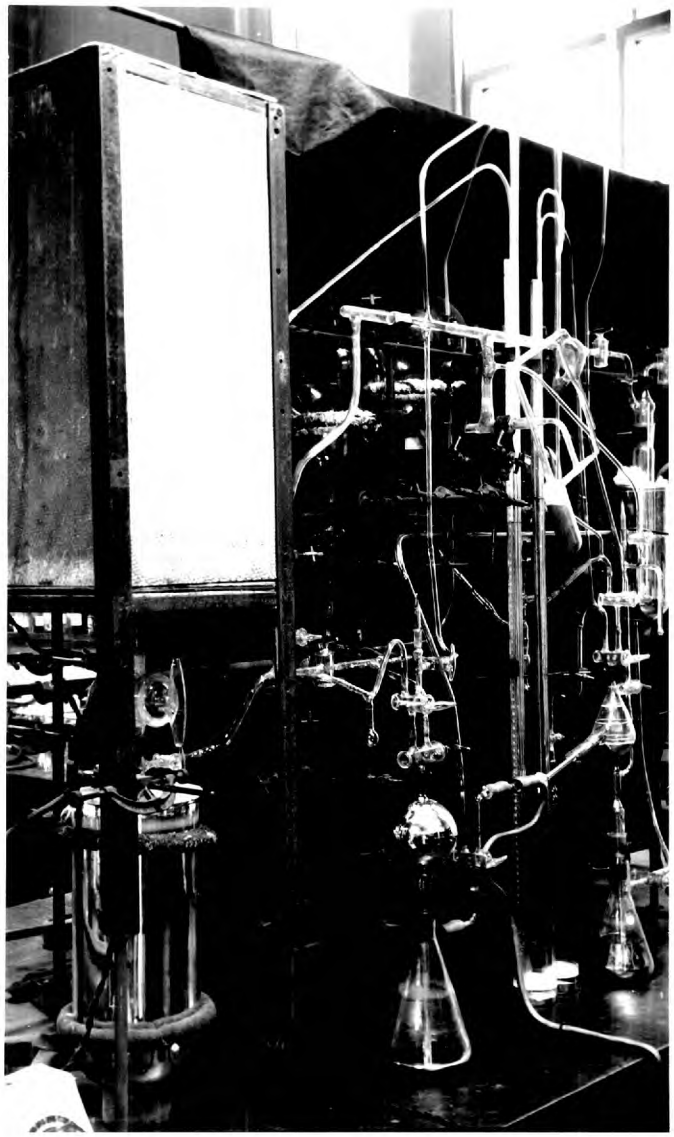
Surface areas of Oxides

	Magnesium oxide	Zinc oxide*
V_m(oc/g)	2.5	0.127
Surface area (m^2/g)	13.7	0.518

* Determined by Dr. E.R.S. Winter.

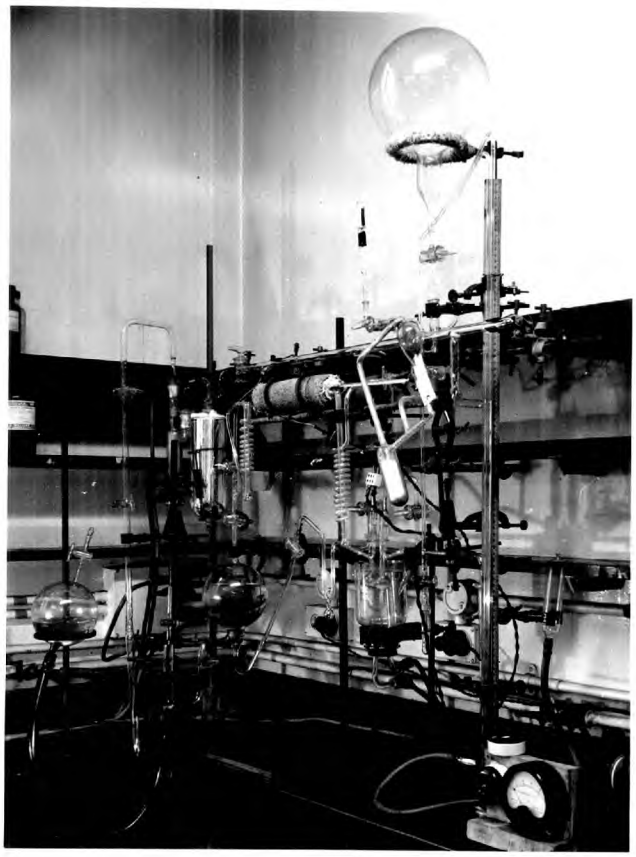
REFERENCES

1.	"Heterogeneous Catalysis"	Farad.Soc.Discussion, No.8,	(1950)
2.	"Semi-conducting Materials"	Butterworth's	(1951)
3.	Garner, Gray and Stone	Proc.Roy.Soc. A197 294	(1949)
4.	Whalley	Ph.D. Thesis, London	(1949)
5.	Whalley and Winter	J.Chem.Soc. 1175	(1950)
6.	Winter	ibid. p.1170	
7.	Houghton and Winter	Nature 164 1130	(1949)
8.	Winter	ref (1) p.231 ff.	
9.	Singleton	Ph.D. Thesis, London	(1949)
10.	Paterson	Proc.Phys.Soc. 59 50	(1947)
11.	Barrer	Trans.Farad.Soc.45 358	(1949)
12.	Bugge and Kerlogue	J.Soc.Chem.Ind. 66 377	(1947)
13.	Farkas and Melville		
	"Experimental Methods in Gas Reactions"	MacMillan	(1939)



TWO BULB SYSTEM

used for thermal diffusion constant determinations (see Figure 2). The methane sample combustion apparatus (Figure 7) is at the bottom right hand corner.



ELECTROLYSIS APPARATUS

(see Figure 1)

