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AN EXPERIMENTAL VERIFICATION, WITH KRYPTON,
OF THE THEORY OF THE THERMAL DIFFUSION
COLUMN FOR MULTICOMPONENT SYSTEMS

W. J. Roos

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**AN EXPERIMENTAL VERIFICATION, WITH
KRYPTON, OF THE THEORY OF THE THERMAL
DIFFUSION COLUMN FOR MULTICOMPONENT SYSTEMS**

W. J. Roos

Date: December, 1967

This report of work performed at Mound Laboratory was submitted as a thesis to the University of Dayton School of Engineering in partial fulfillment of the requirements for the degree of Master of Science in Engineering.

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TABLE OF CONTENTS

	<u>Page</u>
TABLE OF NOMENCLATURE	iii
ABSTRACT	viii
INTRODUCTION	1
LITERATURE REVIEW	5
THEORY	26
EQUIPMENT	53
PROCEDURE	66
RESULTS	77
DISCUSSION OF RESULTS	93
CONCLUSIONS AND RECOMMENDATIONS	96
BIBLIOGRAPHY	97
ACKNOWLEDGEMENTS	102
APPENDICES	103

TABLE OF NOMENCLATURE

Symbol

D	Ordinary (self)diffusion coefficient, L^2/t
d_i	Mass difference of component i with respect to the mass of the key component (defined by Equation 60), M
$\underline{g}$	(Vector) acceleration due to gravity, L/t^2
$G^*(r)$	A function related to the convection velocity (defined by Equation 66)
$G(T)$	The function which results when G^* is transformed from a function of r to a function of T .
H	Transport equation coefficient, characteristic of the initial transport in a thermal diffusion column, for a binary system, M/t
$H_{1\ k}$	Transport equation coefficient, characteristic of the initial transport in a thermal diffusion column, for a multicomponent system, M/t
$H'_{1\ k}$	Transport equation coefficient with pressure dependence removed, $M/(t \cdot atm^2)$
H_o	Transport equation coefficient with isotope-pair-dependence removed, $1/t$
$H_{o\ o}$	Transport equation coefficient, related to H_o by Equation 57, M/t
H'_o	Transport equation coefficient with pressure dependence and isotope-pair-dependence removed, $1/(t \cdot atm^2)$
h	Shape factor, defined by Equation 100, dimensionless
$\underline{j}_i$	(Vector) mass flux of component i relative to the mass average velocity (Bird (3)), M/L^2t

Symbol

K	$K_c + K_d$, ML/t
K_c	Transport equation coefficient, characteristic of the convective remixing in a thermal diffusion column, ML/t
K'_c	Transport equation coefficient with pressure dependence removed, ML/(t.atm ⁴)
K_d	Transport equation coefficient, characteristic of diffusive remixing, ML/t
K'_d	Transport equation coefficient, ML ² /t
k	Thermal conductivity, ML/t ³ T
k_c	Shape factor, defined by Equation 101, dimensionless
k_d	Shape factor, defined by Equation 102, dimensionless
k_r^*	Reduced thermal diffusion ratio (Hirschfelder (19)), dimensionless
L	Length of the column, L
M	Mean molecular weight, M/mol
m_i	Molecular weight of species i , M/mol
$\underline{n}_i$	(Vector) mass flux of component i relative to a fixed coordinate system (Bird (3)), M/L ² t
p	Pressure, M/Lt ²
P	Product mass flow rate, M/t
$q_{i,j}$	Separation factor for components i and j , defined by Equation 54b
$\underline{q}$	(Vector) heat flux, M/t ³

Symbol

Q	$2\pi Q$ is the radial heat flow per unit length of column, M/Lt^3
R	Ideal gas law constant, $1.987 \text{ cal g-mol}^{-1} \text{ } ^\circ K^{-1}$
r	Radial coordinate in column; also, the inter-molecular distance in a molecular collision, L
r_c	Cold wall radius, L
r_h	Hot wall radius, L
r_m	Parameter for the Exponential-6 intermolecular potential model, L
T	Absolute temperature, $^\circ K$
T_c	Cold wall absolute temperature, $^\circ K$
T_h	Hot wall absolute temperature, $^\circ K$
T^*	Reduced temperature, defined by $T^* = \frac{\kappa T}{\epsilon}$, dimensionless
$\underline{v}$	(Vector) mass average velocity, defined by $\underline{v} = \left[\frac{\sum_i \rho_i \underline{v}_i}{\sum_i \rho_i} \right], L/t$
$\underline{v}^*$	(Vector) molar average velocity, units L/t , defined by $\underline{v}^* = \left[\frac{\sum_i c_i \underline{v}_i}{\sum_i c_i} \right]$ where c_i is the molar density of component i and has units, mols/L^3
$\underline{v}_i$	(Vector) velocity of component i relative to fixed coordinates, L/t
x_i	Mole fraction of component i , dimensionless

Symbol

z	Longitudinal coordinate in column, L
α	Parameter for the Exponential-6 intermolecular potential model, dimensionless
α_T	Thermal diffusion factor for binary systems, dimensionless
$\alpha_{i,j}$	Thermal diffusion factor for components i and j of a multicomponent system, dimensionless
α_o	Reduced thermal diffusion factor, dimensionless
ϵ	Parameter in Exponential-6 intermolecular potential model, ML^2/t^2
θ	Angular coordinate in column, radians
κ	Boltzmann's constant, ML^2/t^2T
μ	Viscosity, M/Lt
ρ_i	Mass density of component i, M/L ³
ρ	Mass density, M/L ³
τ_i	Mass flow rate of component i in product stream, M/t
ϵ_p	Potential energy of interaction for a collision between two molecules, ML^2/t^2
w_i	Mass fraction of component i, dimensionless
$w_{F,i}$	Mass fraction of component i in the product stream, dimensionless
$\Omega^{(i,j)*}$	Reduced collision integrals (Hirschfelder (19)), dimensionless

Mathematical Symbols

∇ Divergence; in cylindrical coordinates it has the form

$$\left[\frac{\partial}{\partial r} \right] \underline{u}_r + \left[\frac{1}{r} \frac{\partial}{\partial \theta} \right] \underline{u}_\theta + \left[\frac{\partial}{\partial z} \right] \underline{u}_z$$

where $\underline{u}_r$, $\underline{u}_\theta$ and $\underline{u}_z$ are unit vectors in the various coordinate directions.

$\frac{D}{Dt}$ substantial derivative, defined by

$$\frac{D}{Dt} = \left[\frac{\partial}{\partial t} + \underline{v} \cdot \nabla \right]$$

ABSTRACT

The extended form of the Jones and Furry theory, which describes the behavior of a multicomponent heavy isotopic gas in a Clusius-Dickel thermal diffusion column, is tested. Experimental and theoretical values of the thermal diffusion column transport equation coefficients H_{ik} , K_c and K_d , are determined for krypton, a heavy isotopic gas with six isotopes.

The experiments are carried out in a column of the hot-wire type, at three wire temperatures: $T_w = 350^\circ\text{C}$, 500°C and 800°C .

Good agreement is found between the theoretical and experimental values of the coefficients. Seven of nine of the experimentally determined values of the coefficients agree within $\pm 10\%$ with the corresponding theoretical values. The remaining two experimental values agree within $\pm 20\%$ with the corresponding theoretical values.

INTRODUCTION

Thermal Diffusion

The thermal diffusion effect consists of the establishment of a concentration gradient in a liquid or gaseous solution which initially has a uniform concentration, by means of a temperature gradient across the container in which the solution is enclosed. In gaseous solutions, the lighter molecules usually tend to concentrate in the region of higher temperature. The establishment of the concentration gradient, by means of the thermal diffusion flux, is opposed by an ordinary diffusion flux, and a state of dynamic equilibrium is reached when the two opposing fluxes are equal in magnitude.

The thermal diffusion effect can be utilized to separate partially the constituents of a binary or multicomponent mixture of gases. Appendix A has descriptions of two devices which utilize the thermal diffusion effect.

A greater degree of separation can be achieved if the thermal diffusion effect is used in conjunction with a free convection process. This combination of the thermal diffusion effect and the free convection effect is the basis for the operation of the Clusius-Dickel, or thermogravitational, thermal diffusion column.

The theory of the operation of the Clusius-Dickel Column

may be separated into two parts: binary theory and multicomponent theory.

Binary Theory

A number of theories concerning the operation of the thermal diffusion column have been advanced (1, 2, 16, 51). This thesis is concerned specifically with that theory due to Jones, Furry and Onsager (16), and with its extension to multicomponent systems.

The exposition of Jones, Furry and Onsager (16) consists of an analysis of the phenomenological behavior of the thermal diffusion column, where the material contained in the column is a heavy isotopic gas mixture. A heavy isotopic gas mixture is one for which the percentage differences in the masses of the various isotopes are small. The result of the aforementioned analysis is an equation, known as the transport equation, which describes the rate at which one of the components is transported through the column in the longitudinal direction. In addition to giving the form of the transport equation, the theory also gives expressions for the coefficients which appear in the transport equation.

A considerable amount of experimental work has been carried out to test the validity of this theory (42). Until

quite recently, it appeared that the agreement between theoretical predictions and experimental results, as determined by a comparison between theoretical and experimental values of the transport equation coefficients, would only be of a qualitative nature. However, a recent series of experiments (30, 35, 37, 38, 39, 40), carried out with a relatively large number of gases, has shown that reasonably good quantitative agreement between theoretical predictions and experimental results is possible.

Multicomponent Theory

Shortly after the publication of the Jones, Furry and Onsager (16) binary theory, Jones (21) showed that it would be possible to extend the theory to the case of multicomponent heavy isotopic gas mixtures. This extension is important, because some gases have more than two isotopes. The extension results in a system of simultaneous differential equations describing the transport of the various components along the column. As in the binary case, expressions are also given for the coefficients which appear in these equations.

To date, relatively little work has been done in the area of multicomponent systems.

General Objective of This Thesis

The reasonable amount of success achieved by the Jones, Furry and Onsager theory in predicting the behavior of a binary heavy isotopic gas mixture in the thermal diffusion column leads one to surmise that the extended theory might also be successful. It is the purpose of this thesis to examine the theoretical predictions of the multicomponent theory.

The multicomponent theory is tested by comparing the experimentally determined values of the transport equation coefficients with the theoretically predicted values. The experimental determinations are carried out with krypton, a heavy isotopic gas with six stable isotopes (mass numbers 78, 80, 82, 83, 84, 86).

It is necessary to employ numerical methods, both for the calculation of the theoretical values of the transport equation coefficients and also for the reduction of the experimental data.

LITERATURE REVIEW

Thermal Diffusion in Liquids

The thermal diffusion effect in liquids was first observed in 1856 by Ludwig (26), when he noticed that a concentration gradient was established in a sodium sulfate solution which was in a non-uniformly heated vessel. Some years later, Dufour (13, 14) reported the existence of a reverse effect, the diffusion thermoeffect, whereby a temperature gradient resulted from an established concentration gradient. This was the first evidence of a coupling effect between energy and mass. Soret (44, 45, 46, 47) carried out experiments based on Ludwig's work with liquid thermal diffusion. Since that time, much more experimental work has been done. To date, however, attempts at a theoretical explanation of the liquid thermal diffusion effect have met with little success.

Thermal Diffusion in Gases

For the case of gases, the thermal diffusion effect was predicted theoretically before it was observed experimentally. The theoretical prediction of the gaseous thermal diffusion effect came about through the rigorous kinetic theory developed by Enskog (15) and independently by Chapman (6, 7).

Forms of kinetic theory introduced prior to the Chapman-Enskog formulation were not sufficiently sophisticated to predict the thermal diffusion effect. The existence of the effect was actually observed for the first time in an experiment carried out by Chapman and Dootson in 1917 (8).

In 1919, Chapman (9) suggested that the thermal diffusion effect might be useful for separating isotopes. However, in 1922, Mulliken (31) concluded that separation methods based on the thermal diffusion effect could not compete with other separation methods, due to the smallness of the separation brought about by this effect. This conclusion was correct since the two-bulb apparatus (Appendix A) was the only device known at the time to accomplish a separation by thermal diffusion.

Separation of Binary Gas Mixtures by Thermal Diffusion

In 1938 Clusius and Dickel (11) described the thermogravitational thermal diffusion column. This device consists essentially of two concentric vertical tubes, with the inner tube maintained at a high temperature and the outer tube maintained at a low temperature. The horizontal temperature gradient leads to a horizontal concentration gradient, due to the thermal diffusion effect. Simultaneously, natural

convection causes the gas in the cold region to move downward and that in the hot region to move upward, establishing a concentration difference between the top and bottom of the column. This difference is much larger than that attainable by thermal diffusion alone, which points out the importance of the free convection process.

In addition to the mass diffusion flux set up by thermal diffusion, there are two additional mass diffusion fluxes: a horizontal ordinary diffusion flux in a direction opposite to the thermal diffusion flux, and an ordinary diffusion flux in the vertical direction. The various diffusion fluxes, as well as the convection currents, are pictured in Figure 1. The fluxes are depicted for the lighter component, for the case where the lighter component diffuses toward the hot wall.

Within a short period after the publication of Clusius and Dickel's article, Jones, Furry and Onsager (16), as well as Waldmann (51) and Bardeen (1, 2) presented theories to describe the operation of the device.

The theory as developed by Jones, Furry and Onsager (16) is for the separation, in a plane slit, of a binary heavy isotopic gas mixture. While the plane slit model is sufficiently accurate for cylindrical columns in which the ratio of the radius of the outer tube to that of the inner tube is

Figure 1 Thermal diffusion column convection currents and the diffusion fluxes for the lighter component, for the case where the lighter component diffuses toward the hot wall. (1) Thermal diffusion flux. (2) Horizontal ordinary diffusion flux. (3) Vertical ordinary diffusion flux. (4) Convection currents.

nearly unity, it is a poor representation of those cylindrical columns where the radius ratio is significantly larger than unity. In a later paper (23), Jones and Furry carried out a derivation for the cylindrical configuration. In a review article which appeared in 1946, Jones and Furry (22) presented a survey of the results which had been obtained for the binary case.

The result of the derivation of Jones, Furry and Onsager (16) is the binary transport equation.

$$\tau_1 = H\omega_1(1 - \omega_1) - (K_c + K_d) \frac{d\omega_1}{dz} \quad (1)$$

This equation describes the vertical transport of the lighter isotope up the column. A similar equation describes the vertical transport of the heavier isotope down the column. Theoretical expressions for the coefficients H , K_c and K_d are also given by Jones and Furry (22). These expressions, which involve the physical and transport properties of the gas in the column, have the following physical significance. The coefficient H is characteristic of the initial transport in the column, i.e., the transport which occurs before a vertical concentration gradient is present. The coefficient K_c is characteristic of convective remixing, i.e., remixing which takes place between the ascending and descending streams of

gas in the column. The coefficient K_d is characteristic of remixing due to ordinary diffusion in the vertical direction.

Bardeen (1, 2), Saxena and Raman (42), and Reinhold (35) carried out derivations similar to those of Jones and Furry, Bardeen for the plane parallel case and the others for the cylindrical case. Their derivations, which are more satisfying than the derivations of Jones and Furry, lead to a form of the transport equation which differs from that obtained by Jones and Furry. Specifically, the derivations of Saxena and Raman, and Reinhold, lead to the equation

$$\tau_1 = H\omega_1(1 - \omega_1) - (K_c + K_d) \frac{d\omega_1}{dz} + K_d' \frac{d^2\omega_1}{dz^2} \quad (2)$$

The expressions which they obtained for the coefficients H , K_c and K_d are identical to the expressions obtained by Jones and Furry.

The status of experimental work up to about 1962 was reviewed by Saxena and Raman (42). In general, they found that the qualitative agreement between theory and experiment was relatively good, whereas the quantitative agreement was rather poor.

Recently, a series of papers by Rutherford et al. (37, 38, 39, 40) have reported rather good quantitative agreement between theory and experiment. Reinhold (35) and Mueller (30)

have also reported cases in which good agreement was obtained. These results would seem to indicate that the theory is applicable in many cases.

Separation of Multicomponent Gas Mixtures by Thermal Diffusion

Relatively little work has been done in the area of multicomponent systems. Casas et al. (5) have worked with krypton. They have determined both experimental and theoretical values for the quantities $\left[h / (k_c k_d)^{\frac{1}{2}} \right]$ and $\left[k_d / k_c \right]^{\frac{1}{2}}$, where h , k_c and k_d are the shape factors. The shape factors, which are functions of the column geometry, the ratio of hot and cold wall temperatures and the intermolecular potential model, arise because it is possible to separate the expressions for each of the column transport equation coefficients H , K_c and K_d into two factors, one of which is known as the shape factor.

Theoretical values were calculated for the above quantities for both the inverse power model and the Lennard-Jones (12-6) model. Having plotted the theoretical and experimental values, Casas et al. found relatively good qualitative agreement. The quantitative agreement was, however, rather bad. No attempts were made by the authors to extract experimental values of the individual shape factors.

Blumkin and Von Halle (4) have examined experimental data

for the separation of xenon isotopes. Using a method which differs from that used in this thesis, they employed equilibrium data in conjunction with unsteady state (transient) data to determine experimental values for the individual transport equation coefficients. The agreement was reasonably good in a qualitative sense, but quantitative agreement was completely lacking. It should be noted with regard to the work of Blumkin and Von Halle, that the authors apparently were interested mainly in determining an empirical basis from which design of thermal diffusion columns for the separation of xenon isotopes could be carried out. The work apparently was not carried out for the express purpose of testing the quantitative validity of the Jones and Furry theory.

A paper by Mueller (30) treated various methods for determining the individual column transport equation coefficients. He discussed the equations necessary for obtaining the coefficients from both steady state and unsteady state (transient) experiments, and also some of the inherent difficulties, and advantages and disadvantages of the various methods. He compared experimental values of H_{00} and K for the ternary system of argon isotopes with theoretical values calculated from the shape factors of Reinhold (35). Excellent quantitative agreement was found for H_{00} . A discrepancy was

found between the theoretical and experimental values of K . No determination of the individual coefficients K_c and K_d was made.

By way of summary, it appears that there are only two places in the literature where more or less complete comparisons between experimental and theoretical results have been made: Von Halle and Blumkin (4) for xenon and Mueller (30) for argon. In both of these cases, the equations used for determination of the coefficient H_{00} have involved approximations. It does not appear that any comparisons have been made for the case in which the coefficient H_{00} was determined from the exact column transport equations.

Transport Properties

In order to carry out the calculation of the theoretical values of the transport equation coefficients H , K_c and K_d , it is necessary to have values for the transport properties μ , k , D and α_0 . It is best to base the calculation of the coefficients on reliable experimental transport property data, whenever it is available. If reliable data is available, it is smoothed, and the smoothed values are used in calculating the transport equation coefficients.

If reliable data is scarce or nonexistent, another

approach must be taken. This approach consists of calculating the transport properties by means of expressions given by the rigorous kinetic theory, which is not entirely desirable, because an intermolecular potential model must be introduced. Introduction of this model may lead to a certain amount of ambiguity in interpreting the experimental results. Specifically, if agreement is lacking between theoretical and experimental results, it may be impossible to determine whether the lack of agreement is due to incorrect transport property values or to some deficiency in the Jones and Furry theory.

For those temperature ranges where theoretical and experimental transport property values are in good agreement, it makes no difference whether the calculations of the transport equation coefficients are based on smoothed experimental transport property values or values calculated from expressions given by the kinetic theory.

Experimental transport property data

Viscosity Viscosity values have been determined for krypton by a number of workers. The more recent determinations have been made by Clifton (10) and by Rigby and Smith (36). Both of these papers also give experimental results from earlier workers.

Rigby and Smith have plotted a large amount of experimental viscosity data for argon, xenon and krypton, employing the principle of corresponding states. Their plot, which is reproduced in Figure 2, shows that their values agree well with those of other workers, whereas Clifton's values tend to be low at the higher temperatures.

An additional source of data is (34). The recommended values for the viscosity which are listed in this reference are in good agreement with the data of Rigby and Smith.

Because of the good agreement between the results of Rigby and Smith and the results of other workers, it is felt that the results of Rigby and Smith are reliable.

Thermal conductivity Since there is a considerable amount of disagreement among the various workers concerning the values of the thermal conductivity, it is necessary to determine which values are most reliable. In order to do this, use is made of the expression (Bird (3))

$$k = \frac{15}{4} \frac{R}{M} \mu \quad (3)$$

which is given by the rigorous kinetic theory. When the available experimental thermal conductivity values are converted to corresponding viscosity values, by means of Equation 3, it is found that the results of Kannuluik and Carman (24), the

Figure 2. Experimental viscosity values for argon, krypton and xenon, plotted according to the principle of corresponding states.

T_B Boyle temperature

$$B_0 = -B \left|_{T = 0.7 T_B}\right.$$

B second virial coefficient

(Taken from Rigby and Smith (36).)

recommended values from (25, 34) and a number of results from earlier workers, cited in Clifton (10), are consistent with the viscosity values of Rigby and Smith (36) and of (34), whereas the results of Schäfer and Reiter (43), and the high temperature value of von Ubisch (50) are not. For this reason, the former sets of data (10, 24, 25, 34) are thought to be more reliable than the latter sets (43, 50).

Thermal diffusion factor This transport property is usually the most troublesome, from the standpoint of obtaining reliable experimental values, because its measurement is extremely difficult.

Three sets of determinations of the thermal diffusion factor have been made for krypton, by Corbett and Watson (12), by Moran and Watson (28) and by Paul and Watson (33). The results of Paul and Watson are the most recent, and they show the least amount of scatter. The results of Moran and Watson show reasonable agreement with the results of Paul and Watson, except at a few points, whereas the results of Corbett and Watson deviate widely from both of the other sets of results.

Ordinary (self) diffusion coefficient The data for this transport property is rather sparse. The values which are reported (10, 18, 33, 52) exhibit a certain amount of scatter,

and, based solely on the experimental data, it is not clear which values are the most reliable.

The Exponential-6 intermolecular potential model and the rigorous kinetic theory expressions for the transport properties

In certain instances, it is necessary or desirable to calculate values for the transport properties from the expressions given by the rigorous kinetic theory. Calculation of values for the transport properties by this method requires the use of an intermolecular potential model, which represents the potential energy of interaction of two colliding molecules. Such a model is the Modified Buckingham, or Exponential-6, model, which is given by Van Der Valk (48) as:

$$\text{For } r > r_{\text{max}},$$

$$\varphi(r) = \frac{\epsilon}{[1 - (6/\alpha)]} \left[\left(\frac{6}{\alpha} e^{\alpha[1 - (r/r_m)]} \right) - \left(\frac{r_m}{r} \right)^6 \right] \quad (4a)$$

$$\text{For } r \leq r_{\text{max}}$$

$$\varphi(r) = \infty \quad (4b)$$

This model has three adjustable parameters, ϵ , α , r_m , which must be determined from experimental data and which are generally different for different gases.

The expressions given by the rigorous kinetic theory for

the first approximations to the transport properties of a gas composed of spherical monatomic molecules are (Hirschfelder (19))

$$\mu = 2.6693 \times 10^{-5} \frac{\sqrt{MT}}{r_m^2 \Omega^{(2,2)*}} \quad (5)$$

$$k = 1.9891 \times 10^{-4} \frac{\sqrt{T/M}}{r_m^2 \Omega^{(2,2)*}} \quad (6)$$

$$D = 2.6280 \times 10^{-3} \frac{\sqrt{T^3/M}}{Pr_m^2 \Omega^{(1,1)*}} \quad (7)$$

$$\alpha_o = \frac{105}{118} k_T^* = \frac{15(2A^*+5)(6C^*-5)}{2A^*(16A^*-12B^*+55)} \quad (8)$$

Equation 8 is an approximate expression that holds for a heavy isotopic gas mixture. The particular molecular model for the collisions is incorporated in these expressions by computing the collision integrals $\Omega^{(i,j)*}$, using, in this case, the Exponential-6 model.

In Equation 5 the viscosity is in poise, the temperature in °K, r_m in Å and M is the mean molecular weight. Use of the mean molecular weight for the case of krypton should be justified because the ratio of the masses of any two isotopes is reasonably close to unity. The thermal conductivity in Equation 6 is given in cal cm⁻¹ sec⁻¹ °K⁻¹. In Equation 7 the perfect gas law has been assumed to hold for krypton, and D is

given in $\text{cm}^2\text{sec}^{-1}$. The quantities A^* , B^* and C^* in Equation 8 are ratios of various Ω -integrals (19).

The following expression holds (21, 48) for α_{ij} :

$$\alpha_{ij} = \left[\frac{m_i - m_j}{m_i + m_j} \right] \alpha_o \quad (9)$$

where m_i , m_j are the molecular weights of species i and j , respectively.

At this point it is convenient to note that

$$D \propto P^{-1} \quad (10)$$

$$\text{and} \quad \rho \propto P \quad (11)$$

whereas μ , k and α_{ij} are independent of pressure. These results are used in a later section of this thesis.

Smoothing and extrapolation of the transport property data

Smoothing and extrapolation of the viscosity and thermal conductivity data

As stated previously, although experimental data is used, whenever possible, for calculating theoretical values of the transport equation coefficients, it is not used directly. Rather, smoothed values are used. The smoothing procedure for the viscosity and thermal conductivity data consists of plotting the reliable thermal conductivity data, in the form $\frac{4}{15} \frac{M}{R} k$, and the reliable viscosity data, both on the same plot, and passing a smooth curve through this

collection of points. It is not to be expected, and in fact it does not happen, that the curve passes through all of the points. The main requirements are that the curve be smooth and that the experimental values be reasonably close to the curve.

Because experimental data for these two transport properties are not available in the higher temperature range, it is necessary to extrapolate the data that is available. As suggested by Equation 5, the experimental data is plotted versus T on a log-log plot, and the line through this data, which is very nearly straight, is extrapolated to obtain values in the high temperature range.

Smoothing and extrapolation of the thermal diffusion

factor data Paul and Watson (33) have used their thermal diffusion factor data, in conjunction with the viscosity data of Rigby and Smith (36), to determine a set of values for the Exponential-6 parameters α , r_m and ϵ . The values which they determined are tabulated in Table 1. The quantity κ is Boltzmann's constant.

Table 1. Paul and Watson values of the
Exponential-6 parameters for krypton

α	r_m (Å)	ϵ/κ (°K)
16.1 ± 0.6	3.88 ± 0.02	244 ± 13

As is shown in Figure 3, the theoretical curve calculated on the basis of these parameters reproduces their data rather well. Because of the good agreement between the theoretical and experimental values of this property in the range where experimental data is available, the theoretical curve, calculated by use of the Paul and Watson parameters, is used to smooth the experimental values and to extrapolate to the temperatures for which experimental data is not available.

The ordinary (self) diffusion coefficient Because of the uncertainty existing with regard to the experimental data for the ordinary diffusion coefficient, use is made of the expression (19, 52)

$$\frac{\rho D}{\mu} = \frac{6}{5} A^* \quad (12)$$

which is given by the rigorous kinetic theory. The quantity A^* is a slowly varying function of T^* , where $T^* = \kappa T / \epsilon$, and, for the range of temperatures considered in this thesis, is very nearly equal to 1.10.

Thus, the values of D used in calculating the transport equation coefficients are not smoothed experimental values, but rather, are calculated from smoothed values of μ , by means of Equation 12. Corresponding values of ρ are calculated from

Figure 3. Temperature variation of the isotopic thermal diffusion factor for krypton. Calculation of the theoretical values is based on the Exponential-6 model, using the parameters of Paul and Watson.

(Taken from Paul and Watson (33).)

Table 7 Viscosity thermal conductivity and ordinary (self) diffusion coefficient values for krypton

T (K)	Viscosity (μ poise)		Thermal Conductivity ($\times 10^7$) (cal cm ⁻¹ sec ⁻¹ K ⁻¹)		Ordinary Diffusion (at 1 atm) (cm ² sec ⁻¹)
	Expt	Smoothed	Expt	Smoothed	Calculated
100			81.3		
150			119.7		
171.4			136		
194.7			152		
200		175.9b	156.1	156.4b	0.046b
250		216.8b	191.4	192.8b	0.070b
255.4	219.1		195.2		
271.15			207		
273.2			208		
			209		
			212		
291	249.8	250.5			
300		256.0b	225	227.0b	0.099b
310.9	261.1		232.5		
311.2				234	
350		292.0b	257	259.5b	0.132b
363	301.2				
366.5	301.0		268.0		
373.2			272		
400		326.2b	288	290.1b	0.169b
422.0	338.7	340.5	301.6		
450		358.5b	317.9	318.8b	0.208b
453	361.0				
477.6	375		333.4		
491.2			340		
500		390.0b	346	346.8b	0.252b
505	393.4	393.0			
533.2	408		363.6		
550		420.8b		374.2b	0.299b
553	423.9				
575	438.8				
579.1			388		
588.7	441		392.1		
600		451.7b	396.7	400.1b	0.350b
610	456.8	460.0			
644.1	471		418.6		
650		478.2b		425.2b	0.402b
654	480.1				
678	494.0				
700		504.1b	444.6	448.3b	0.456b
725	518.9				
750		528.0b		469.5b	0.512b
775	539.6	540.0			
800		552.5b		491.3b	0.571b
821	564.0				
850		576.2b		512.4b	0.633b
855	579.1				
900		599.3b		532.9b	0.697b
921	608.2				
950		621.0b		552.2b	0.762b
972	610.2				
1000		642.3ab		571.2ab	0.830ab
1050		663.9ab		590.4ab	0.901ab
1100		684.3ab		608.5ab	0.973ab
1150		704.4ab		626.4ab	1.05ab
1200		724.5ab		644.3ab	1.12ab

a - Extrapolated

b - These values were used in calculating the transport equation coefficients

the ideal gas law. The values of D thus obtained are given in Table 2, along with experimental, and smoothed and extrapolated viscosity and thermal conductivity values.

THEORY

Preliminary Considerations

Assumptions

In deriving the thermal diffusion column multicomponent transport equations, use is made of a number of simplifying assumptions. They are listed in this section, for the sake of clarity, and are referred to by number when used in the derivation. It is pertinent to note at this point that the derivation is carried out for a column consisting of two vertical concentric tubes, the inner one of which is heated and the outer one of which is cooled.

The assumptions are:

- (1) The gas used is a heavy isotopic gas mixture.

From this it follows that

$$x_1 = \frac{w_1}{w_1 \left(\frac{m_1}{m_1} \right) + \dots + w_n \left(\frac{m_1}{m_n} \right)} = \frac{w_1}{\sum_1 w_1} = w_1 \quad (13)$$

$$\text{where} \quad \sum_1 w_1 = \sum_1 x_1 = 1, \quad (14)$$

$$\text{and also that} \quad \sum_1 w_1 \underline{v}_1 = \underline{v} = \underline{v}^* = \sum_1 x_1 \underline{v}_1 \quad (15)$$

because $w_1 = x_1$

- (2) The intermolecular force fields for the various

isotopic pairs are identical.

- (3) The transport and physical properties are independent of isotopic composition.
- (4) The system is at steady state and no chemical reactions are occurring.
- (5) The temperature is a function of r only, $T = T(r)$.
- (6) The only nonzero component of the convection velocity is the z -component, which is a function of r only, $v = v_z(r)$, $v_r = v_\theta = 0$.
- (7) In evaluating the properties ρ and D , which are functions of pressure as well as temperature, the pressure in the column is assumed to be constant.
- (8) The gas properties are functions of T only, and hence of r .
- (9) The quantities

$$\frac{\partial w_i}{\partial z}, \frac{\partial^2 w_i}{\partial z^2} \text{ and } w_i w_j$$

are independent of r .

- (10) The mass fractions are functions of r and z , but not of θ , $w_i = w_i(r, z)$.
- (11) The perfect gas law holds.
- (12) The temperature distribution in the column is determined by conduction only.

(13) The flow in the column is laminar.

Saxena and Raman (42) and Reinhold (35) have stated that assumption 12 holds well, except near the ends of the column. They have also stated that assumption 13 is valid under ordinary operating conditions.

The multicomponent molar and mass flux equations

For the case of a heavy isotopic gas mixture, Jones (21) has obtained from the rigorous kinetic theory the multicomponent molar flux equation

$$(\underline{v}_i - \underline{v}^*) = D(-\nabla \ln x_i + (\sum_k \alpha_{i k} x_k) \nabla \ln T) \quad (16)$$

where the quantities $\alpha_{i j}$ satisfy the following relationships

$$\alpha_{i i} = 0 \quad (17a)$$

$$\alpha_{i j} = -\alpha_{j i} \quad (17b)$$

$$\alpha_{i j} + \alpha_{j k} = \alpha_{i k} \quad (17c)$$

Multiplication of Equation 16 by x_i yields

$$x_i (\underline{v}_i - \underline{v}^*) = D(-\nabla x_i + x_i (\sum_k \alpha_{i k} x_k) \nabla \ln T) \quad (18)$$

This equation states that the diffusion flux of component i is composed of an ordinary diffusion flux, described by the ∇x_i term, and a thermal diffusion flux, described by the $\nabla \ln T$ term.

Using assumption 1 and the relation

$$\omega_i = \rho_i / \rho \quad (19)$$

Equation 18 becomes, after some manipulation

$$\underline{n}_i = - \rho D \left[\nabla \omega_i - \omega_i \left(\sum_k \alpha_{i k} \omega_k \right) \nabla \ln T \right] + \omega_i \rho \underline{v} \quad (20)$$

which is the multicomponent mass flux equation. This equation can also be looked upon as a phenomenological relation, which defines the quantities D and $\alpha_{i k}$.

It is easy to show that the quantities D and $\alpha_{i k}$ are measurable quantities. For measuring D , the temperature gradient must be set equal to zero. Then, upon providing a concentration gradient, Equation 20 becomes

$$\underline{n}_i = - \rho D \nabla \omega_i + \rho \omega_i \underline{v} \quad (21)$$

and D can be determined therefrom.

In regard to the measurement of the quantities $\alpha_{i k}$, first write Equation 16 for components i and j

$$(\underline{v}_i - \underline{v}^*) = -D \left[\nabla \ln x_i - \left(\sum_k \alpha_{i k} x_k \right) \nabla \ln T \right] \quad (16)$$

$$(\underline{v}_j - \underline{v}^*) = -D \left[\nabla \ln x_j - \left(\sum_k \alpha_{j k} x_k \right) \nabla \ln T \right] \quad (22)$$

Subtracting Equation 22 from Equation 16, Equation 23 results

$$(\underline{v}_i - \underline{v}_j) = -D \left[\nabla \ln (x_i / x_j) - \left(\sum_k (\alpha_{i k} - \alpha_{j k}) x_k \right) \nabla \ln T \right] \quad (23)$$

At equilibrium $\underline{v}_i = \underline{v}_j = 0$, and making use of Equation 17c and the fact that $D \neq 0$, Equation 23 becomes

$$\nabla \ln \left(\frac{x_i}{x_j} \right) = \alpha_{i,j} \left(\sum_k x_k \right) \nabla \ln T = \alpha_{i,j} \nabla \ln T \quad (24)$$

This equation can be used to determine values for the quantities $\alpha_{i,j}$.

Derivation of the Thermal Diffusion Column Transport Equations for Multicomponent Systems

In addition to the multicomponent mass flux equation, Equation 20, the multicomponent equation of continuity is also required for the derivation. Under assumption 4, the multicomponent equation of continuity for species i is

$$\nabla \cdot \underline{n}_i = 0 \quad (25)$$

Equation 20 is used for $\underline{n}_i$. Then, in cylindrical coordinates and under assumptions 5, 6, 8 and 10, Equation 25 becomes

$$\begin{aligned} \nabla \cdot \underline{n}_i = & - \frac{1}{r} \frac{\partial}{\partial r} \left(r \rho D \frac{\partial \omega_i}{\partial r} \right) - \rho D \frac{\partial^2 \omega_i}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left[r \rho D \omega_i \left(\sum_k \alpha_{i,k} \omega_k \right) \frac{d \ln T}{dr} \right] \\ & + \rho v_z \frac{\partial \omega_i}{\partial z} = 0 \end{aligned} \quad (26)$$

Multiplication of Equation 26 by r , integration of the resulting equation with respect to r between the limits r_H and r , and application of assumption 9 yields

$$\begin{aligned} & - r \rho D \frac{\partial \omega_i}{\partial r} - \frac{\partial^2 \omega_i}{\partial z^2} \int_{r_H}^r \xi \rho D d\xi + r \rho D \omega_i \left(\sum_k \alpha_{i,k} \omega_k \right) \frac{d \ln T}{dr} \\ & + \frac{\partial \omega_i}{\partial z} \int_{r_H}^r \xi \rho v_z d\xi - r_H \left[- \rho D \frac{\partial \omega_i}{\partial r} \right]_{r_H} + \rho D \omega_i \left(\sum_k \alpha_{i,k} \omega_k \right) \frac{d \ln T}{dr} \Big|_{r_H} \Big] = 0 \end{aligned} \quad (27)$$

At this point the boundary condition $[n_{1,r}|_{r_H} = 0]$ can be applied by noting that the term in brackets in Equation 27 is equal to $n_{1,r}|_{r_H}$. Therefore, Equation 27 becomes, after solving for $\frac{\partial w_1}{\partial r}$,

$$\begin{aligned} \frac{\partial w_1}{\partial r} = - \left[\frac{\partial^2 w_1}{\partial z^2} \frac{1}{r \rho D} \int_{r_H}^r \xi \rho D d\xi - w_1 \left(\sum_k \alpha_{1,k} w_k \right) \frac{d \ln T}{dr} \right. \\ \left. - \frac{\partial w_1}{\partial z} \frac{1}{r \rho D} \int_{r_H}^r \xi \rho v_z d\xi \right] \end{aligned} \quad (28)$$

Equation 28 is needed later in the derivation.

Consider now the z-component of the flux

$$n_{1,z} = - \rho D \frac{\partial w_1}{\partial z} + \rho v_z w_1 \quad (29)$$

If it be supposed that a product is being removed from the column at a rate of P gm/sec and that the concentration of component 1 in the product stream is $w_{f,1}$, then

$$\tau_1 = P w_{f,1} = \int_{r_H}^{r_c} \int_0^{2\pi} n_{1,z} r dr d\theta = 2\pi \int_{r_H}^{r_c} n_{1,z} r dr \quad (30)$$

This equation holds at any level in the column, as is shown by consideration of Equation 25.

Substitution of Equation 29 into Equation 30, and use of assumption 9, yields

$$\tau_1 = - 2\pi \frac{\partial w_1}{\partial z} \int_{r_H}^{r_c} r \rho D dr + 2\pi \int_{r_H}^{r_c} r \rho v_z w_1 dr \quad (31)$$

The second term on the right is integrated by parts to obtain

$$2\pi \int_{r_H}^{r_o} r \rho v_z \omega_1 dr = 2\pi \omega_1(r_o, z) \int_{r_H}^{r_o} r \rho v_z dr - 2\pi \int_{r_H}^{r_o} \left[\int_{r_H}^r \xi \rho v_z d\xi \right] \frac{\partial \omega_1}{\partial r} dr \quad (32)$$

Now, note that

$$P = 2\pi \int_{r_H}^{r_o} r \rho v_z dr \quad (33)$$

Therefore, using Equations 32 and 33, Equation 31 can be rewritten as

$$\begin{aligned} \tau_1 = P \omega_{r_1} = P [\omega_1(r_o, z)] - 2\pi \int_{r_H}^{r_o} \left[\int_{r_H}^r \xi \rho v_z d\xi \right] \frac{\partial \omega_1}{\partial r} dr \\ - 2\pi \frac{\partial \omega_1}{\partial z} \int_{r_H}^{r_o} r \rho D dr \end{aligned} \quad (34)$$

Substitution of the expression for $\frac{\partial \omega_1}{\partial r}$, Equation 28, into Equation 34, use of assumption 9, and expansion of the resulting equation yields, after some manipulation,

$$\begin{aligned} \tau_1 = - 2\pi \omega_1 \left\{ \sum_k \omega_k \left[\int_{r_H}^{r_o} \alpha_{1k} \frac{d \ln T}{dr} \left[\int_{r_H}^r \xi \rho v_z d\xi \right] dr \right] \right\} \\ - 2\pi \left[\int_{r_H}^{r_o} \frac{1}{r \rho D} \left[\int_{r_H}^r \xi \rho v_z d\xi \right]^2 dr \right] \frac{\partial \omega_1}{\partial z} - 2\pi \left[\int_{r_H}^{r_o} r \rho D dr \right] \frac{\partial \omega_1}{\partial z} \\ + 2\pi \left[\int_{r_H}^{r_o} \frac{1}{r \rho D} \left[\int_{r_H}^r \xi \rho D d\xi \right] \left[\int_{r_H}^r \xi \rho v_z d\xi \right] dr \right] \frac{\partial^2 \omega_1}{\partial z^2} \\ + P \omega_1(r_o, z) \end{aligned} \quad (35)$$

This is the thermal diffusion column transport equation for

component i of a multicomponent heavy isotopic mixture. The convection velocity v_z , which is an unknown quantity at this point in the derivation, is treated in a later portion of the Theory section.

In order to describe the behavior of an n -component gas in the column, n independent equations are needed. Equation 35 is one of a set of $(n-1)$ independent simultaneous nonlinear differential equations, all of which have the same form. The n^{th} independent equation is Equation 14.

Two simplifications are now made in Equation 35. The first simplification is to write total instead of partial derivatives. This leads to

$$\tau_1 = P\omega_{r_1} = \omega_1 \left[\sum_k H_{1k} \omega_k \right] - (K_o + K_d) \frac{d\omega_1}{dz} + P\omega_1 + K_d' \frac{d^2 \omega_1}{dz^2} \quad (36)$$

where

$$H_{1k} = - 2\pi \int_{r_H}^{r_o} \alpha_{1k} \frac{d \ln T}{dr} \left[\int_{r_H}^r \xi \rho v_z d\xi \right] dr \quad (37)$$

$$K_o = 2\pi \int_{r_H}^{r_o} \frac{1}{r \rho D} \left[\int_{r_H}^r \xi \rho v_z d\xi \right]^2 dr \quad (38)$$

$$K_d = 2\pi \int_{r_H}^{r_o} r \rho D dr \quad (39)$$

$$K_d' = 2\pi \int_{r_H}^{r_o} \frac{1}{r \rho D} \left[\int_{r_H}^r \xi \rho D d\xi \right] \left[\int_{r_H}^r \xi \rho v_z d\xi \right] dr \quad (40)$$

The quantities defined by Equations 37-40 are known as the multicomponent transport equation coefficients.

This first simplification is equivalent to assuming that ω_1 is independent of r . This is a modification of assumption 10 and it should be understood that this is nothing more than a convenient assumption, one which simplifies the numerical calculations. It is not mathematically exact, but it is justifiable on physical grounds. To see that it is justifiable, it is necessary only to note that the separation in the radial direction at a given height z is due to thermal diffusion, and as such, is quite small. Thus,

$$\omega_1(r_H, z) \doteq \omega_1(r_0, z) \doteq \omega_1(z) \quad (41)$$

This assumption could not have been made at the beginning of the derivation because it would have led to incorrect results.

The second simplification is the deletion of the term

$$K_d \frac{d^2 \omega_1}{dz^2}$$

Very little work has been done with this term; there are only two places in the literature where it has been considered (2, 42). In both of these cases, which are by the way for binary systems, calculations have indicated that neglect of this term should lead to errors on the order of 1%.

It is conceivable that this term could be of significance in precise work. Therefore it would be desirable to undertake a more extensive investigation of it.

With the introduction of the second simplification, Equation 36 reduces to

$$P(\omega_{f_1} - \omega_1) = \omega_1 \sum_k H_{1,k} \omega_k - (K_o + K_d) \frac{d\omega_1}{dz} \quad (42)$$

At this point the theoretical treatment separates into two branches. The first branch deals with putting Equation 42 into a form suitable for use in reducing the experimental data, i.e., for determining the experimental values of the transport equation coefficients. The second branch deals with putting Equations 37-39 into forms suitable for making theoretical calculations of the transport equation coefficients.

Transport Equation Coefficients: Experimental and Theoretical

Derivation of the equations necessary for experimental determination of the transport equation coefficients

In order to experimentally determine the values of the transport equation coefficients, it is necessary to carry out two types of experiments. The first type is a static experiment and the second type may be either a transient (unsteady state) experiment, or a flow experiment. In the work reported in this thesis, flow experiments were performed.

Static experiments Consider first the case of a static experiment (i.e., the case where the net flow P is zero). Then Equation 42 reduces to

$$\sum_k H_{i k} \omega_k - K \frac{d \ln \omega_i}{dz} = 0 \quad (43)$$

where $K = K_o + K_d$. Rewriting Equation 43 for component j yields

$$\sum_k H_{j k} \omega_k - K \frac{d \ln \omega_j}{dz} = 0 \quad (44)$$

Subtraction of Equation 44 from Equation 43, and combination of like terms leads to

$$\sum_k (H_{i k} - H_{j k}) \omega_k - K \frac{d \ln (\omega_i / \omega_j)}{dz} = 0 \quad (45)$$

Using the definitions of $H_{i k}$ and $H_{j k}$, and Equation 17c and Equation 14, Equation 45 becomes

$$H_{i j} - K \frac{d \ln (\omega_i / \omega_j)}{dz} = 0 \quad (46)$$

or

$$\frac{d \ln (\omega_i / \omega_j)}{dz} = \frac{H_{i j}}{K} \quad (47)$$

Integration of Equation 47 between the limits $z = 0$ and $z = L$ yields

$$\frac{H_{i j} L}{K} = \ln \left[\frac{(\omega_i / \omega_j)|_{z=L}}{(\omega_i / \omega_j)|_{z=0}} \right] \quad (48)$$

Now, from Equations 10 and 11 it is known that

$$D \propto p^{-1} \quad (10)$$

$$\rho \propto p \quad (11)$$

It can be shown from a consideration of the transport equation coefficients that

$$H_{1,j} \propto p^2 \quad (49)$$

$$K_o \propto p^4 \quad (50)$$

$$K_d \propto p^0 \quad (51)$$

Therefore it is possible to introduce quantities $H'_{1,j}$ and K'_o , which are defined by the following expressions

$$H_{1,j} = H'_{1,j} p^2 \quad (52)$$

$$K_o = K'_o p^4 \quad (53)$$

The quantities $H'_{1,j}$ and K'_o are thus seen to be independent of pressure.

Using Equations 52 and 53, it is possible to rewrite Equation 48 in the following form

$$\ln q_{1,j} = \frac{Lp^2}{ap^4 + b} \quad (54a)$$

where

$$q_{1,j} = \left[\frac{(w_1/w_1) \big|_{z=L}}{(w_j/w_j) \big|_{z=0}} \right] \quad (54b)$$

$$a = \left[K'_o / H'_{1,j} \right] \quad (54c)$$

$$b = \left[K_d / H'_{1,j} \right] \quad (54d)$$

The experimentally determined compositions at the top and bottom of the column are used to calculate values for $\ln q_{1,j}$. Then, using Equations 54a, b, c, d, a nonlinear least squares fit is made of the experimental data (40). This fit yields

the experimental values of the ratios $(K'_o/H'_{1,j})$ and $(K_d/H'_{1,j})$.

Flow experiments Those experiments in which a non-zero net flow through the column exists, i.e., $P \neq 0$, are known as flow experiments. The purpose of flow experiments is to determine experimental values of the transport equation coefficient $H_{1,j}$. The purpose of the present section is to develop the procedure and equations needed to determine experimental values of $H_{1,j}$ from the experimental data.

The theoretical expression for $\alpha_{1,j}$ is given by Equation 9. Since, for a given gas, the quantity α_o is a function of T only, it follows that the dependence of $\alpha_{1,j}$ on any particular isotope pair is due solely to the factor $\left[\frac{m_i - m_j}{m_i + m_j} \right]$. Since $H_{1,j}$ depends on $\alpha_{1,j}$, this is also true for $H_{1,j}$. A quantity H_{oo} , which is defined by Equation 55 may be introduced

$$H_{1,j} = \left[\frac{m_i - m_j}{m_i + m_j} \right] H_{oo} \quad (55)$$

The quantity H_{oo} is the same for all pairs of isotopes of a particular gas, for a given set of hot and cold wall temperatures and radii. Now, from assumption 1

$$m_i + m_j = 2M \quad (56)$$

Introducing a quantity H_o , defined by

$$H_o = \frac{H_{oo}}{2M} = \frac{H_{oo}}{m_i + m_j} = \frac{H_{1,j}}{m_i - m_j} \quad (57)$$

it is possible to rewrite Equation 42 as

$$P(\omega_{f_1} - \omega_1) = \omega_1 H_0 \sum_k (m_1 - m_k) \omega_k - K \frac{d\omega_1}{dz} \quad (58)$$

In order to further modify Equation 58, the concept of a key component is introduced. The key component is some component, arbitrarily chosen, with respect to which mass-differences are to be calculated. Thus, for the case of krypton, if the mass 86 isotope is chosen as the key component, the mass differences for the isotopes with mass numbers 78, 80, 82, 83, 84 and 86 are -8, -6, -4, -3, -2 and 0, respectively. Designating the mass of the key component by m_o , it is possible to write

$$(m_i - m_j) = (m_i - m_o) - (m_j - m_o) \quad (59)$$

Introduction of a quantity d_i defined by

$$d_i = (m_i - m_o) \quad (60)$$

enables Equation 58 to be rewritten, after some manipulation, as

$$\frac{K}{H_0} \frac{d\omega_1}{dz} = \omega_1 \left[d_1 - \sum_k d_k \omega_k \right] - \frac{P}{H_0} \left[\omega_{f_1} - \omega_1 \right] \quad (61)$$

Now define

$$y = \frac{H_0 z}{K} \quad (62)$$

and

$$n = \frac{P}{H_0} \quad (63)$$

Then

$$\frac{dw_1}{dy} = w_1 \left[d_1 - \sum_k d_k w_k \right] - n \left[w_{F_1} - w_1 \right] \quad (64)$$

Since there are n isotopes, there are n differential equations of the form of Equation 64, of which $(n - 1)$ are independent. The n th independent equation is Equation 14.

The experimental data for a single flow run consists of the measured isotopic compositions at the top and bottom of the column, the net flow rate, and the column pressure, which is essentially constant throughout any single run. Generally speaking, a number of flow runs are made for a given hot wall temperature. The column pressure may or may not be the same for all of these runs. Now, it has been shown previously, in Equations 49 and 55, that $H_{1,j}$ is a function of both the column pressure and the particular isotope pair being considered. It has further been shown that the quantity H_0 is independent of any particular isotope pair. It is now convenient to remove the pressure dependence from H_0 by introducing a quantity H'_0 , defined by

$$H_0 = H'_0 p^2 \quad (65)$$

The quantity H'_0 is independent of both the column pressure and the choice of isotope pair. The procedure for determining experimental values of $H_{1,j}$ is now discussed.

The first step in the process is to calculate $\ln q_{1,j}$ for each individual flow run. This is accomplished by use of the measured top and bottom compositions, and Equation 54b. This value of $\ln q_{1,j}$ is designated by $\left[\ln q_{1,j} \right]_{EXP}$. Next, a value is assumed for H_0' . Then, beginning with the measured composition at the bottom of the column, and using the flow rate, the column pressure and the measured top concentration for that particular run, the system of transport equations is integrated numerically to yield a calculated value for the composition at the top of the column. Using this calculated top composition and the measured bottom composition, a value of $\ln q_{1,j}$, designated by $\left[\ln q_{1,j} \right]_{CALC}$ is calculated for each individual flow run. In general, $\left[\ln q_{1,j} \right]_{EXP}$ and $\left[\ln q_{1,j} \right]_{CALC}$, for a given flow run, are not equal. Therefore, a deviation between the two values can be calculated for each flow run. Then, a root-mean-square (RMS) deviation can be calculated for the series of flow runs.

This procedure of choosing a value of H_0' and determining a corresponding RMS deviation, is then repeated for a series of values of H_0' . There results a series of values for the RMS deviations, one value corresponding to each of the assumed values of H_0' . As is illustrated in Figure 4, these RMS deviations are then plotted versus the corresponding values of

Figure 4. Illustration of the method used for determining the experimental value of H_0 . The experimental value is that value which corresponds to the minimum point of the parabola, which has been passed through the three points that bracket this minimum.

H'_0 , and a parabola is passed through the three points which bracket the minimum RMS deviation. The value of H'_0 which corresponds to the minimum point of this parabola is taken as the experimental value of H'_0 . From this quantity, the values of $H'_{1,j}$ and $H_{1,j}$ for any particular column pressure and any particular isotope pair can be found.

Since the value of $H'_{1,j}$ is now known, the values of K'_0 and K_0 can be determined from the experimental values of the ratios $(K'_0/H'_{1,j})$ and $(K_0/H_{1,j})$, which were determined in the static experiments.

Theoretical values of the transport equation coefficients

Representation of the convection velocity in terms of the

function G^*

The starting point for this section is the set of equations, Equations 37-39. Inspection of these equations reveals that an expression for the convection velocity, v_z , is needed in order to evaluate the expressions for $H_{1,k}$ and K_0 . It is possible to simplify the notation in the following treatment by introducing a function $G^*(r)$, defined by

$$G^*(r) = \frac{kQ^3}{\rho D} \int_{r_H}^r \xi \rho v_z d\xi \quad (66)$$

The quantity Q is defined by

$$2\pi Q = - 2\pi k r \frac{dT}{dr} \quad (67)$$

Thus, $2\pi Q$ is the radial heat flow per unit length of column.

Representation of the theoretical expressions for the transport equation coefficients in terms of the function

G Introducing the G^* -function into Equations 37-39 yields

$$H_{1k} = - \frac{2\pi}{Q^3} \int_{r_H}^{r_o} \frac{\alpha_{1k} \rho DG^*(r)}{kT} \frac{dT}{dr} dr \quad (68)$$

$$K_o = \frac{2\pi}{Q^3} \int_{r_H}^{r_o} \frac{D\rho [G^*(r)]^2}{k^2 r} dr \quad (69)$$

$$K_d = 2\pi \int_{r_H}^{r_o} r \rho D dr \quad (70)$$

A change of variables from r to T in Equations 68-70 leads to

$$H_{1k} = \frac{2\pi}{Q^3} \int_{T_o}^{T_H} \frac{\alpha_{1k} D \rho G(T)}{kT} dt \quad (71)$$

$$K_o = \frac{2\pi}{Q^3} \int_{T_o}^{T_H} \frac{D \rho [G(T)]^2}{k} dt \quad (72)$$

$$K_d = \frac{2\pi}{Q} \int_{T_o}^{T_H} r^2 D \rho k dt \quad (73)$$

where $G(T)$ is the function that results when the right hand side of Equation 66 is expressed in terms of the variable T .

Derivation of a differential equation for the G -function

It is now necessary to find an expression from which values of

G(T) can be determined. To do this, consider (Bird (3)) the general equation of motion for Newtonian fluids. Applying assumption 6, the r-, θ - and z-components of this equation reduce to

$$\text{r-component: } \frac{\partial p}{\partial r} = 0 \quad (74)$$

$$\theta\text{-component: } \frac{1}{r} \frac{\partial p}{\partial \theta} = 0 \quad (75)$$

$$\text{z-component: } \frac{1}{r} \frac{\partial}{\partial r} \left[\mu r \frac{\partial v_z}{\partial r} \right] = \frac{\partial p}{\partial z} - \rho g_z \quad (76)$$

Note that Equations 74-76 show that

$$p = p(z) \quad (77)$$

Taking the partial derivative of both sides of Equation 76, with respect to r, yields

$$\frac{\partial}{\partial r} \left[\frac{1}{r} \frac{\partial}{\partial r} \left[\mu r \frac{\partial v_z}{\partial r} \right] \right] = \frac{\partial^2 p}{\partial r \partial z} - \frac{\partial}{\partial r} [\rho g_z] \quad (78)$$

In view of the fact that $p = p(z)$, it follows that

$$\frac{\partial}{\partial r} \left[\frac{\partial p}{\partial z} \right] = 0 \quad (79)$$

Thus Equation 78 reduces to

$$\frac{d}{dr} \left[\frac{1}{r} \frac{d}{dr} \left[\mu r \frac{dv_z}{dr} \right] \right] = \frac{d}{dr} [\rho g] \quad (80)$$

where $g = -g_z$ and where total derivatives have been written instead of partial derivatives because all of the quantities involved are functions of r only.

At this point, refer back to Equation 66. Rearrangement of and differentiation of this equation with respect to r yields

$$v_z = \frac{1}{r\rho} \frac{d}{dr} \left[\frac{D_\rho G^*(r)}{kQ^3} \right] \quad (81)$$

Substitution of Equation 81 into Equation 80 yields

$$\frac{d}{dr} \left[\frac{1}{r} \frac{d}{dr} \left[\mu r \frac{d}{dr} \left[\frac{1}{r\rho} \frac{d}{dr} \left[\frac{D_\rho G^*(r)}{kQ^3} \right] \right] \right] \right] = g \frac{d\rho}{dr} \quad (82)$$

Changing variables from r to T , Equation 82 becomes

$$\frac{d}{dT} \left[\frac{1}{kr^2} \frac{d}{dT} \left[\frac{\mu}{k} \frac{d}{dT} \left[\frac{1}{\rho kr^2} \frac{d}{dT} \left[\frac{D_\rho G(T)}{k} \right] \right] \right] \right] = - g \frac{d\rho}{dT} \quad (83)$$

Since this differential equation is of fourth order, four boundary conditions are needed in order to determine a solution. The boundary conditions can be determined in the following manner. From the defining equation for the G^* -function, the two boundary conditions

$$(1) G^*(r_H) = 0, \text{ which implies that } G(T_H) = 0 \quad (84)$$

$$(2) G^*(r_c) \neq 0, \text{ which implies that } G(T_c) \neq 0 \quad (85)$$

are determined. Boundary condition 1 holds because at $r = r_H$ ($T = T_H$), the limits on the integral in the defining expression for the G^* -function are equal. Boundary condition 2 holds because the integral in the defining expression for the G^* -function is proportional to the net flow through the column. In practice, the net flow rates are either identically zero

(for the case of a column operating under static conditions)

or, when nonzero, are relatively small.

It still remains to find two more boundary conditions.

Note that

$$\frac{d}{dT} \left[\frac{D_{\rho} G(T)}{k} \right] = \frac{d}{dr} \left[\frac{D_{\rho} G^*(r)}{k} \right] \frac{dr}{dT} \quad (86)$$

Now,

$$\frac{D_{\rho} G^*(r)}{k} = Q^3 \int_{r_H}^r \rho v_z r dr \quad (87)$$

and therefore

$$\frac{d}{dr} \left[\frac{D_{\rho} G^*(r)}{k} \right] = Q^3 \rho v_z r \quad (88)$$

Equation 88 is equal to zero at $r = r_c$ and $r = r_H$ because $v_z(r_c) = v_z(r_H) = 0$. This shows that Equation 86 is equal to zero at $r = r_c$ and $r = r_H$.

Now, note that

$$\frac{d}{dT} \left[\frac{D_{\rho} G(T)}{k} \right] = \frac{D_{\rho}}{k} \frac{d}{dT} [G(T)] + G(T) \frac{d}{dT} \left[\frac{D_{\rho}}{k} \right] = 0 \quad (89)$$

at $r = r_c$ and $r = r_H$. Therefore, since $G(T_H) = 0$, it follows that

$$\left. \frac{d}{dT} [G(T)] \right|_{T = T_H} = 0 \quad (90)$$

This result is exact, whether a net flow exists or not. For $r = r_c$ ($T = T_c$), it is necessary to examine the term

$$G(T) \frac{d}{dT} \left[\frac{D_{\rho}}{k} \right]$$

Since $G(T_c) \neq 0$, the above term will be small, provided that the quantity

$$\frac{d}{dT} \left[\frac{D_{\rho}}{k} \right]$$

is not too large. Examination of Equations 6 and 7 shows that the quantity $\left[\frac{D_{\rho}}{k} \right]$ is almost a constant for the temperature range of interest. Therefore, the approximation

$$\left. \frac{d}{dT} \left[\frac{D_{\rho}}{k} \right] \right|_{T = T_c} \doteq 0 \quad (91)$$

is a good one, and, to a good approximation,

$$\left. \frac{d}{dT} [G(T)] \right|_{T = T_c} \doteq 0 \quad (92)$$

Equation 83 can be solved subject to the boundary conditions given in Equations 84, 85, 90, 92 by numerical methods. With the values of $G(T)$ thus calculated, it is possible to evaluate the expressions for $H_{1,k}$, K_o and K_d , provided that the transport properties are known as functions of temperature and also that the temperature distribution in the column is known. (Note, that when the temperature distribution in the column is known, the quantity Q can be evaluated from Equation 67.) The method of determining the temperature distribution in the column is discussed in the next section.

Calculation of the temperature profile in the column

It was stated previously that conduction is assumed to be the only heat transfer mechanism of importance in establishing the temperature profile. Thus, Fourier's Law is applicable:

$$\underline{q} = - k \nabla T \quad (93)$$

By assumption (5), Fourier's Law reduces to

$$q_r = - k \frac{dT}{dr} \quad (94)$$

It is convenient at this point to let

$$Q = r q_r \quad (95)$$

Then, Fourier's Law may be written as

$$Q = -kr \frac{dT}{dr} \quad (96)$$

It should be noted that the quantity Q defined by Equation 95 is identical to the quantity Q appearing in the immediately preceding section.

Rearranging Equation 96 and integrating from the cold wall to the hot wall leads to

$$- Q \ln \left[\frac{r_h}{r_c} \right] = \int_{T_c}^{T_h} k dT \quad (97)$$

Equation 96 may also be integrated from the cold wall to some arbitrary point in the column. Thus

$$- Q \ln \left[\frac{r}{r_c} \right] = \int_{T_c}^T k dT \quad (98)$$

Division of Equation 98 by Equation 97 leads to

$$\frac{\ln \left[\frac{r}{r_c} \right]}{\ln \left[\frac{r_H}{r_c} \right]} = \frac{\int_{T_c}^T k dT}{\int_{T_c}^{T_H} k dT} \quad (99)$$

From this expression, using numerical integration, it is possible to determine T as a function of r .

The Shape Factors

Until relatively recently, the task of calculating the thermal diffusion column transport equation coefficients was extremely formidable. Because of this, it was desirable to have a method which would reduce the number of calculations necessary to cover the range of conditions met with in the actual operation of thermal diffusion columns. A method which met this requirement was the one which made use of shape factors.

In general, it is possible to write the expressions for the transport equation coefficients as products of two factors. The first factor is a function of the gas properties at the cold wall temperature and the prevailing column pressure, and of the cold wall radius. This factor is independent of any particular intermolecular potential model which may be used to calculate the transport equation coefficients.

The second factor, which is known as the shape factor, is

dependent on the particular intermolecular potential model which is being used to carry out the calculations. For the case of the inverse power model, the shape factors are functions of the ratios T_H/T_c and r_c/r_H (Jones (22)). For the Lennard-Jones (12-6) model, the shape factors are functions of T_H/T_c , r_c/r_H and also T_c^* (McInteer (27)). For the Exponential-6 model, the shape factors are functions of T_H/T_c , r_c/r_H , T_c^* and also α (Saviron et al. (41)). α should not be confused with the thermal diffusion factor α_T .

By way of illustration, the expressions for $H_{1,1}$, K_c and K_d , for the case where the Exponential-6 model is used, are given by

$$H_{1,1} = \frac{2\pi}{6!} \left[\frac{\alpha_{1,1} \rho^2 g r^4}{k} \right]_{T=T_c} \cdot h(\alpha, T_c^*, T_H/T_c, r_c/r_H) \quad (100)$$

$$K_c = \frac{2\pi}{9!} \left[\frac{\rho^3 g^2 r^8}{k^2 D} \right]_{T=T_c} \cdot k_c(\alpha, T_c^*, T_H/T_c, r_c/r_H) \quad (101)$$

$$K_d = 2\pi \left[r^2 \rho D \right]_{T=T_c} \cdot k_d(\alpha, T_c^*, T_H/T_c, r_c/r_H) \quad (102)$$

The quantities h , k_c and k_d are the shape factors. The defining expressions for these quantities are given in Equations 20-22 of McInteer (27). It should be noted that the defining expressions have the same form for both the Lennard-Jones (12-6) model and the Exponential-6 model. However, the quantities involved in these expressions, such as the Ω -integrals, have different

values for different models.

At the present time, due mainly to the existence of high speed digital computers, the task of calculating the shape factors is not as formidable as it previously was. Since a computer and program are available at Mound Laboratory for calculating these quantities, the present practice is to calculate the values of the shape factors as they are needed. Strictly speaking, since this program is available, the shape factor approach does not offer much of an advantage, i.e., the program could equally well have been written to calculate the transport equation coefficients without separating the expressions for these coefficients into two parts. However, there is at least one advantage to using the shape factor approach. Since the values of the shape factors depend on the intermolecular potential model, the shape factors can be used to compare the influence of the various models on the values of the transport equation coefficients.

EQUIPMENT

This section is divided into two parts. The first deals with the thermal diffusion column and the second deals with accessory equipment.

Figure 5 is a schematic flow diagram of the system showing the relative location of the thermal diffusion column and the accessory equipment. The names and addresses of the manufacturers of the more specialized pieces of equipment are given in the text. Pieces of equipment which were fabricated at Mound Laboratory are denoted by the abbreviation ML.

Thermal Diffusion Column

The thermal diffusion column is built around a type 304L stainless steel tube. The tube, which is approximately 24 feet in length has an inside diameter of $3/4$ " and an outside diameter of $1-1/4$ ". Manifolds (ML) shown in Figure 6, permit access to the stainless steel gas tube and provide support for the brass water jacket (ML). They are located at 4 feet intervals along the column. The machined manifolds are slipped onto the stainless steel gas tube and then welded in place. The holes depicted in the walls of the tube are drilled after the manifolds have been welded in place.

Figure 5. Schematic flow diagram of the system, showing the relative location of the thermal diffusion column and accessory equipment.

Figure 6. A figure, showing a manifold mounted on the stainless steel tube, and also, the brass water jacket. (a) Top view of the manifold, showing the holes through which cooling water passes from one section of the water jacket to the next. (b) Side view.

The individual sections of the brass water jacket are then slid into place. The ends of the sections overlap the ends of the manifolds and are sealed by O-rings located on the outside ends of the manifolds, as depicted in Figure 6. The water passes from one section of the water jacket to the next through vertical holes drilled in the manifolds.

Cover plates (ML) with O-ring seals, shown in Figure 7, are used to close the openings to the gas tube in the manifold.

Removal of samples of gas from the column is accomplished through a sample port (ML), shown in Figure 7. The sample port is connected to a valve located on a cover plate. All valves, unless specifically stated to be otherwise, are Hoke H4171M4B valves, manufactured by Hoke Incorporated, Cresskill, New Jersey.

A drawing of the items located at the top of the column is given in Figure 8. The nylon plug (ML) electrically insulates the wire support stud from the stainless steel tube. Seals are maintained by O-rings. The top of this steel stud is connected by means of a brass connector to the power supply and the bottom of the stud is fastened to the 1/16" electrically heated nichrome wire by means of the ferrule and wire nut. This wire is 1/16" Nichrome V, obtainable from Driver-Harris Co.,

Figure 7. Illustration of various types of cover plates and other related items. (a) Cover plate with valve and sample port. (b) Sample bottle. (c) Finger stay cover plate, with aligning finger. (c') A drawing showing the end of an aligning finger. (d) Peephole with neoprene washer and glass window. The washer provides a cushion between the glass and the cover plate.

Not shown is a blank cover plate, which is identical to the finger stay cover plate except that it has no recessed hole.

Figure 8. Exploded view of the items located at the top of the column. These items, after being assembled, fit into the top of the column, and are held down in place by a flange (not shown) which is then fastened with screws to the bracket (not shown) which supports the column.

Harrison, New Jersey. Aligning fingers, shown in Figure 7, are used to keep the hot wire centered in the gas tube.

At the bottom of the column, as shown in Figure 9, the end of the nichrome wire is connected to a steel rod by a Swagelok fitting. Swagelok fittings are manufactured by Crawford Fitting Co., Cleveland, Ohio. The steel rod extends through an electrically insulating nylon plug (ML), which is sealed in the same manner as the nylon plug at the top of the column. The steel rod moves freely through the nylon plug as the length of the nichrome wire changes, due to changes in the temperature of the wire. At the bottom of the rod, a brass weight is attached by means of a threaded stud. A flexible braided copper wire connects the brass weight to electrical ground.

Accessory Equipment

Three Wallace and Tiernan differential pressure gauges, which are converted to absolute pressure gauges by evacuating the static side of the gauge, are associated with the system. These gauges are manufactured by Wallace and Tiernan Co., Belleville, New Jersey.

One gauge, a model number FA145 with a pressure range of 0 to 1500 torr is connected to the column. The other two

Figure 9. Exploded view of the items located at the bottom of the column. They are held in place by a flange (not shown) which is fastened with screws to a second flange (not shown) located at the bottom of the column.

gauges are connected to the tubing in such a way that one, a model number FA145 with a pressure range of 0 to 5080 torr, measures the pressure in the feed tank, while the other, a model number FA160 with a pressure range of 0 to 50 torr, measures the pressure on the downstream side of the variable leak. The variable leak is an adjustable restriction, which is used to vary flow rates through a line. The unit used is a Model 5001-51 Adjustable Restriction, manufactured by Andonian Associates Inc., Waltham, Massachusetts.

The compressors used for circulating the gas are Frigidaire #5901285 Sealed Unit Compressors, manufactured by Frigidaire Division GMC, Dayton, Ohio.

The flowmeter used is a Model 10A4137A, manufactured by Fischer and Porter, Warminster, Pennsylvania.

The gauge used to measure wire elongation is a Model 25-441 gauge, with graduations of 0.001", manufactured by the Starrett Company, Athol, Massachusetts.

The pressure sensing device (ML), which is shown in Figure 10, centers around a mercury manometer. One leg of the manometer is open to the column and the other, which is evacuated, contains a glass tube in which two wires have been sealed. The tube enters the leg through a fitting (ML) at the top of the leg, and an O-ring inside the fitting provides a

Figure 10. Simplified drawing of the pressure sensing device, showing the features of the metal fitting at the top of the manometer leg.

seal between the fitting and the glass tube. The wires, which have bare ends of different lengths, extend beyond the end of the tube and into the mercury. At the other end of the tube, the wires are connected to an Ultra-Sensitive Electronic Relay, model number ST-511-2, manufactured by Servo-Tek Products Co., Hawthorne, New Jersey. When the bare ends of the wire are both in contact with the mercury, the relay is closed which in turn closes a solenoid valve. (Skinner Valve No. V52DB2100, manufactured by Skinner Electric Valve Division, Skinner Precision Industries, Inc., New Britain, Connecticut.) This shuts off the gas to the column and surge tank. When the column pressure drops to the point where the shorter bare wire is no longer in contact with the mercury, the relay opens, and gas is admitted into the surge tank and column. The desired operating pressure is set by sliding the glass tube up and down in the manometer. The tube is held in position by tightening a set screw in a small metal collar which surrounds the tube and which rests on top of the fitting at the top of the manometer leg.

An arrangement to permit purification of the gas in the column is depicted at the top of the column in Figure 5. The arrangement consists of a gas circulating loop, containing an electric pump (ML), a hydrogen diffusion apparatus (ML) and a large evacuated cylinder. The hydrogen diffusion apparatus

consists of a piece of large copper tubing, into which protrudes a palladium thimble. The large copper tubing is wound in the vicinity of the palladium thimble with a small calrod heating element, which permits the temperature of the palladium thimble to be raised. The hydrogen diffusion apparatus is connected into the circulating loop in such a way that the gas can be circulated past the heated palladium thimble. The hydrogen diffuses through the thimble as the gas flows past it, and from there the hydrogen passes into the evacuated tank.

The power supply to the column provides DC current and has a maximum rating of 7.5 KW at 150 volts.

A Lab-Chron 1401 timer, manufactured by Lab-Line Instruments, Inc., Melrose Park, Illinois, is used for measuring elapsed time when determining flow rates.

The sample bottle (ML), shown in Figure 7, consists of a male standard (10/30) brass taper, a Poly-flo fitting, and two Hoke H4171M4B valves, connected by fittings and a piece of copper tubing. The Poly-flo tubing and fittings used in these experiments are manufactured by Imperial-Eastman Corporation, Chicago, Illinois. All of the copper tubing used is 1/4" outside diameter.

The leak detector used for leak checking the system is a

Model 24-101A Leak Detector, manufactured by Consolidated
Electrodynamics Corporation, Pasadena, California.

The gas analyses are performed on a CEC Model 620 Mass
Spectrometer, manufactured by Consolidated Electrodynamics
Corporation, Pasadena, California.

PROCEDURE

This section is divided into three parts, general procedures, static experiments and flow experiments.

General Procedures

This portion of the procedure section is devoted to consideration of a number of topics which are pertinent to both static and flow experiments, or which must be carried out prior to the initial startup of the column.

Leak checking

The initial step in the experimental procedure is checking the system to make certain that it is either vacuum-or pressure-tight, depending on whether the experiments are to be carried out at pressures below or above atmospheric. The experiments described in this thesis are all run at pressures well below atmospheric. Therefore, the system is checked for vacuum tightness.

The checking procedure consists, first of all, of isolating a portion of the system and pumping on this section with a vacuum pump for a period which is long enough to allow a significant amount of out-gassing to occur. Out-gassing is a term used to describe the evacuation of adsorbed materials,

such as grease or solvents, which are present in the system. It generally takes considerably longer to remove such materials than it does to remove air or other gases. If this material is not removed, it will vaporize, causing a pressure rise that will interfere with the leak-checking process. Also, a sufficient amount of this material can cause contamination of the experimental gas. After evacuation, the section is isolated and the rate of pressure rise in this section is measured. If the section is vacuum-tight, the pressure will rise slightly and then remain at a constant value. This is due to normal outgassing by the small amount of residual adsorbed material. A pressure rise due to a leak will continue until atmospheric pressure is reached.

If a section is found to have a leak, the exact location of the leak can ordinarily be found by a number of methods. One method, which is usually quite effective, is to put helium, under pressure, into the section under scrutiny and then to "sniff" the outside of the section with a helium leak detector.

Wire oxidation

When the system is completely vacuum-tight, the next step is to oxidize the surface of the wire which serves as the column hot wall. It is desirable to do this, because it has

been found by experience that if this were not done, the surface of the wire would become oxidized in spots, due to the presence of impurities in the gas. Because the wire temperature is lower at oxidized spots, due to higher radiation losses, a nonuniformity of temperature along the length of the wire would result. Oxidation of the surface of the wire insures a more nearly uniform wire temperature.

The oxidation is accomplished by introducing high purity oxygen into the evacuated column, and setting the wire temperature at about 800°C. The oxygen pressure is then adjusted to about 500 torr absolute and the apparatus is allowed to remain undisturbed for 16 hours. During this period, the column pressure drops due to the reaction of the oxygen with the metal of the wire.

Determination of wire temperature

The next topic to be discussed is methods for determining the wire temperature.

At high temperatures (above 750°C) an optical pyrometer can be used to determine the wire temperature. At lower temperatures, however, another method must be used. A rather convenient method is measurement of the amount of elongation which occurs in the wire as the temperature is increased. A

calibration chart is prepared (Figure 11), which gives the elongation as a function of temperature. Since the calibration chart is prepared for a 6 ft. (at room temperature) wire it is necessary to determine the ratio of the elongation of the wire in the experimental column to the elongation of the 6 ft. wire. This is done by measuring the amount of elongation which occurs when the temperature of the wire in the column is raised from room temperature to 800°C. Since this temperature is in the optical range, it is measured by an optical pyrometer. The calibration chart is then consulted and the elongation for the 6 ft. wire at the same temperature is ascertained. The elongation for the wire in the experimental column is then divided by the elongation for the 6 ft. wire. This ratio, when multiplied by the elongation for the 6 ft. wire at any other temperature, yields the elongation for the wire in the experimental column at the same temperature.

Sampling procedure

Another topic of general interest is the procedure by which a sample of gas is removed from the column. This is accomplished through the sample ports which are located at various places along the column. In the experiments described in this thesis, the samples are taken at sample ports located,

Figure 11. Calibration chart giving the elongation, as a function of temperature, for a Nichrome V wire which is 6 ft. long at room temperature.

respectively, 4 ft. from the top and 4 ft. from the bottom of the column. This procedure is followed because it has been found in previous experiments that end effects in the column could lead to incorrect results if samples are taken too close to the ends.

The procedure, which is quite simple, consists of inserting a sample bottle, into the sample port (see Figure 7). This operation aligns three valves; one on the column and two on the sample bottle. Opening both valves on the sample bottle allows a vacuum to be drawn up to the valve on the column. The vacuum is then shut off with the third valve. The column valve is opened to allow the sample to enter the bottle and is then closed. The second valve on the sample bottle is now closed, isolating the sample in the sample bottle. The samples are then analyzed.

Static Experiments

For the static experiments, there is no net flow of material through the column and the only gas withdrawn is that used for samples.

A quantity of gas, sufficient to give a desired column pressure, is introduced into the column, and the separation process is allowed to proceed until concentration equilibrium

is established throughout the column. Samples are then taken at the appropriate locations.

It is usually most convenient to begin at the highest desired pressure and then, after the samples have been taken, lower the pressure by removing some of the gas from the column. By repeated application of this procedure a complete series of values for q_1 , the separation factor, as a function of pressure, can be obtained.

Flow Experiments

The experimental setup for the flow experiments, which are more complex than the static experiments, is depicted in Figure 12. The flow experiments are begun in the following manner (see Figure 12). With the draw-off line closed, a flow is started in the loop consisting of the feed tank, the solenoid and throttle (A) valves, the surge tank, the bottom of the column, throttle valve (B), the flow meter and the Frigidaire compressor (F). The flow rate, as measured by the flow meter, is controlled by means of throttle valves (A) and (B), and by the solenoid valve, which is controlled by a pressure-sensing device attached to the column. The pressure is kept very nearly constant during each individual flow run.

The wire is then heated to the operating temperature.

Figure 12. Simplified flow diagram of the system, showing the setup for the flow experiments.

This causes the convection currents to be established in the column. When the operating temperature is attained, the draw-off line is opened and a stream of gas exits at the top of the column. The gas passes through valve (D), through the variable leak, through valve (C), through the compressor (G) and back to the feed tank. The flow rate of this stream of gas is regulated by means of the variable leak. It may be necessary, after starting the draw-off, to readjust the throttle valves in order to keep the column pressure and the two flow rates at the desired values. When the flow rates and column pressure are steady at the desired values, the system is allowed to come to concentration equilibrium. After concentration equilibrium is established, samples are taken. The flow rate for that particular experimental run is determined by closing valve (C) and measuring the rate of pressure rise in the volume included between the variable leak and valve (C). This volume must be calibrated beforehand. While it is true that the flow rate decreases as the pressure builds up on the downstream side of the variable leak, this decrease can be shown to be negligible, provided that the downstream pressure does not become too large. In the experiments reported in this thesis, care was taken not to allow the downstream pressure to become too large.

The calibration of the above-mentioned volume can be carried out in the following manner: close valves (C) and (D) tightly. Through valve (E), evacuate the volume between valve (C) and valve (D). This volume includes the volume of the pressure side of the gauge. Now, close the variable leak as tightly as possible and expand air at atmospheric pressure, from a vessel whose volume is accurately known, into the volume to be calibrated. The final pressure, after the expansion has taken place, is then determined from the gauge, and this pressure, together with the known atmospheric pressure and known volume of the vessel, can be used to determine the desired volume.

When a given flow experiment is concluded, the draw-off flow rate is readjusted to a new valve by changing the setting of the variable leak. It may also be necessary to adjust valves (A) and (B) slightly in order to maintain the column pressure and the flow rate in the other loop at the desired values.

The occurrence of hydrogen in the column caused a serious problem with regard to the purity of the gas used in the experiments. Specifically, over an extended period of time, the hydrogen concentration in the upper 4 feet of the column became rather large, and hydrogen began to appear in the

product stream. The origin of this hydrogen could not be ascertained and, therefore, in order to correct this situation, use was made of the setup depicted at the top of the column in Figure 5, and described in the Equipment Section. This procedure proved to be quite successful in reducing the hydrogen concentration.

RESULTS

The raw data, which consists of isotopic compositions for each of the samples, as well as the other pertinent information, such as the column pressures, hot wire temperatures and flow rates, is given in Tables 13-21, which are located in Appendix B. The flow rates are expressed in terms of "standard cc per hour," that is, cc at standard conditions of temperature and pressure (0°C, 760 torr). It should be noted that the volume flow rate units are directly related to mass flow rate units, because one mole of any gas occupies 22.4 liters at standard conditions. Each sample is assigned a number, in order that the raw data corresponding to any of the results reported in this section may be easily located.

In all cases, for both static and flow experiments, the distance between sample ports (L) is 487.68 cm, the hot and cold wall radii are 0.0794 cm and 0.9525 cm, respectively, and the cold wall temperature is 288°K.

Static Data

In Figures 13-15, theoretical values of (H_o/K) are plotted versus the column pressure, for $T_w = 350^\circ\text{C}$, 500°C and 800°C , respectively. On each of these figures, experimental values of (H_o/K) , as determined for each of the three isotope pairs

Figure 13. Plot of the quantity $|H_0/K|$ as a function of pressure, for three isotope pairs, at $T_H = 350$ C.

Figure 14. Plot of the quantity $|H_0/K|$ as a function of pressure for three isotope pairs, at $T_H = 500^\circ\text{C}$.

Figure 15. Plot of the quantity $|H_0 K|$ as a function of pressure, for three isotope pairs, at $T_H = 800$ C.

^{80}Kr - ^{86}Kr , ^{80}Kr - ^{84}Kr and ^{82}Kr - ^{86}Kr , by use of Equations 48 and 57, are also plotted. The experimental and theoretical values which are plotted in Figures 13-15, are tabulated in Tables 3-5. Tables 3-5 also list the numbers of the samples used to determine the experimental values, and the corresponding column pressures.

Flow Data

In Tables 6-11, the values of $\ln q_{1,j}$, calculated from the experimentally determined top and bottom compositions, for the above-mentioned isotope pairs are given, for two sets of flow experiments, one set at relatively low pressures and the other set at higher pressures, for each value of hot wall temperature (T_H). Also given are the corresponding calculated values of $\ln q_{1,j}$. The calculated values of $\ln q_{1,j}$ are determined from a numerical integration of Equation 14 and the $(n-1)$ equations of the form of Equation 64, using the value of H'_0 which corresponds to the minimum RMS deviation. The flow rates and column pressures, as well as the sample numbers corresponding to each $\ln q_{1,j}$ value are also listed in the tables.

Theoretical and Experimental Values of the Coefficients H'_0 , K'_0 and K_d

In Table 12 the theoretical and experimental values of H'_0 ,

Table 3. Experimental and theoretical values of (H_0 , K), for the three isotope pairs ^{80}Kr - ^{86}Kr , ^{80}Kr - ^{84}Kr and ^{82}Kr - ^{86}Kr . The column length and hot and cold wall temperatures and radii are as follows:

$$\begin{aligned} r_H &= 0.0794 \text{ cm} & T_H &= 350^\circ\text{C} \\ r_C &= 0.9525 \text{ cm} & T_C &= 15^\circ\text{C} \\ L &= 487.68 \text{ cm} \end{aligned}$$

Sample Numbers	Theoretical ($\times 10^4$)	Experimental ($\times 10^4$)			Column Pressure (torr)
		^{80}Kr - ^{86}Kr	^{80}Kr - ^{84}Kr	^{82}Kr - ^{86}Kr	
1T,B ^{a)}	2.30	2.40	2.38	2.40	234.2
2T,B	2.93	3.05	3.06	3.11	200.3
3T,B	4.00	4.14	4.08	4.33	149.0
4T,B	4.18	4.33	4.26	4.54	136.0
5T,B	4.21	4.33	4.34	4.44	125.0
6T,B	4.13	4.30	4.26	4.38	115.4
7T,B	3.77	4.00	3.99	4.09	100.0

a) - T designates upper sample port, B designates lower sample port.

Table 4. Experimental and theoretical values of (H_0/K) , for the three isotope pairs ^{80}Kr - ^{86}Kr , ^{80}Kr - ^{84}Kr and ^{82}Kr - ^{86}Kr . The column length and hot and cold wall temperatures and radii are as follows:

$$\begin{aligned} r_H &= 0.0794 \text{ cm} & T_H &= 500^\circ\text{C} \\ r_C &= 0.9525 \text{ cm} & T_C &= 15^\circ\text{C} \\ L &= 487.68 \text{ cm} \end{aligned}$$

Sample Numbers	Theoretical ($\times 10^4$)	Experimental ($\times 10^4$)			Column Pressure (torr)
		^{80}Kr - ^{86}Kr	^{80}Kr - ^{84}Kr	^{82}Kr - ^{86}Kr	
8T,B	2.43	2.47	2.43	2.51	304.2
9T,B	3.38	3.57	3.57	3.55	252.4
10T,B	4.80	4.87	4.90	4.83	201.1
11T,B	6.01	6.05	6.04	6.04	162.4
12T,B	6.37	6.48	6.46	6.45	142.2
13T,B	5.70	5.84	5.97	5.85	105.6
14T,B	5.70	5.78	5.75	5.74	105.6
15T,B	4.20	4.34	4.36	4.38	82.6
16T,B	4.20	4.24	4.28	4.23	82.6

Table 5. Experimental and theoretical values of (H_0/K) , for the three isotope pairs ^{80}Kr - ^{86}Kr , ^{80}Kr - ^{84}Kr and ^{82}Kr - ^{86}Kr . The column length and hot and cold wall temperatures and radii are as follows:

$$\begin{aligned} r_H &= 0.0794 \text{ cm} & T_H &= 800^\circ\text{C} \\ r_C &= 0.9525 \text{ cm} & T_C &= 15^\circ\text{C} \\ L &= 487.68 \text{ cm} \end{aligned}$$

Sample Numbers	Theoretical ($\times 10^4$)	Experimental ($\times 10^4$)			Column Pressure (torr)
		^{80}Kr - ^{86}Kr	^{80}Kr - ^{84}Kr	^{82}Kr - ^{86}Kr	
17T,B	5.48	5.76	5.81	5.75	304.5
18T,B	6.09	6.44	6.43	6.43	286.4
19T,B	7.86	8.37	8.47	8.29	241.2
20T,B	8.75	9.04	9.06	9.01	221.5
21T,B	9.45	9.97	10.04	9.82	206.2
22T,B	10.31	10.43	10.52	10.34	182.2
23T,B	10.61	10.56	10.52	10.66	162.7
24T,B	10.60	10.68	10.72	10.71	161.5
25T,B	10.50	10.46	10.80	10.20	148.0
26T,B	10.28	9.96	10.01	9.97	141.0
27T,B	10.03	9.60	9.53	9.77	136.2
28T,B	8.80	8.24	8.24	8.29	117.2
29T,B	8.40	7.93	7.94	7.93	112.5
30T,B	8.30	7.50	7.53	7.42	110.5

Table 6. Experimental values of $\frac{1}{2}[\ln q_{ij}]$, at low pressures, for the three isotope pairs ^{80}Kr - ^{86}Kr , ^{80}Kr - ^{84}Kr and ^{82}Kr - ^{86}Kr , and corresponding values calculated by numerical integration of Equation 14 and the (n-1) equations of the form of Equation 64, using the experimental value of H_0 . The column length and hot and cold wall temperatures and radii are as follows:

$$\begin{aligned} r_H &= 0.0794 \text{ cm} & T_H &= 350^\circ\text{C} \\ r_C &= 0.9525 \text{ cm} & T_C &= 15^\circ\text{C} \\ L &= 487.68 \text{ cm} \end{aligned}$$

Sample Numbers	[ln q _{ij}]						Column Pressure (torr)	Flow Rate (Std cc/hr)
	^(80Kr-86Kr) Exp.		^(80Kr-84Kr) Exp.		^(82Kr-86Kr) Exp.			
	^(80Kr-86Kr) Calc.	^(80Kr-84Kr) Calc.	^(80Kr-84Kr) Calc.	^(82Kr-86Kr) Calc.				
31T,B	0.382	0.401	0.243	0.253	0.263	0.284	131.7	14.9
32T,B	0.520	0.534	0.334	0.336	0.362	0.380	131.7	10.2
33T,B	0.664	0.675	0.423	0.426	0.458	0.481	132.1	7.0
34T,B	0.893	0.845	0.561	0.538	0.660	0.599	131.9	4.2
35T,B	0.947	0.973	0.600	0.626	0.677	0.685	132.1	2.7

Table 7. Experimental values of $[\ln q_{ij}]$ at high pressures, for the three isotope pairs ^{80}Kr - ^{86}Kr , ^{80}Kr - ^{84}Kr and ^{82}Kr - ^{86}Kr , and corresponding values calculated by numerical integration of Equation 14 and the (n-1) equations of the form of Equation 64, using the experimental value of H_0 . The column length and hot and cold wall temperatures and radii are as follows:

$$\begin{aligned} r_H &= 0.0794 \text{ cm} & T_H &= 350^\circ\text{C} \\ r_C &= 0.9525 \text{ cm} & T_C &= 15^\circ\text{C} \\ L &= 487.68 \text{ cm} \end{aligned}$$

Sample Numbers	[$\ln q_{ij}$]						Column Pressure (torr)	Flow Rate (Std cc/hr)
	$(^{80}\text{Kr}-^{86}\text{Kr})_{\text{Exp.}}$	$(^{80}\text{Kr}-^{84}\text{Kr})_{\text{Exp.}}$	$(^{82}\text{Kr}-^{86}\text{Kr})_{\text{Exp.}}$	$(^{80}\text{Kr}-^{86}\text{Kr})_{\text{Calc.}}$	$(^{80}\text{Kr}-^{84}\text{Kr})_{\text{Calc.}}$	$(^{82}\text{Kr}-^{86}\text{Kr})_{\text{Calc.}}$		
	$(^{80}\text{Kr}-^{86}\text{Kr})_{\text{Calc.}}$	$(^{80}\text{Kr}-^{84}\text{Kr})_{\text{Calc.}}$	$(^{82}\text{Kr}-^{86}\text{Kr})_{\text{Calc.}}$					
36T,B	0.385	0.379	0.237	0.246	0.272	0.257	227.0	41.1
37T,B	0.384	0.395	0.259	0.255	0.257	0.268	210.8	35.8
38T,B	0.482	0.458	0.312	0.298	0.327	0.313	225.8	27.7
39T,B	0.455	0.483	0.291	0.313	0.314	0.330	210.8	24.6
40T,B	0.574	0.530	0.358	0.346	0.390	0.364	226.5	18.4
41T,B	0.545	0.568	0.366	0.369	0.365	0.390	210.8	16.3
42T,B	0.609	0.650	0.419	0.424	0.417	0.447	210.5	10.0
43T,B	0.725	0.704	0.463	0.465	0.504	0.488	210.6	6.1

Table 8. Experimental values of $[\ln q_{ij}]$, at low pressures, for the three isotope pairs ^{80}Kr - ^{86}Kr , ^{80}Kr - ^{84}Kr and ^{82}Kr - ^{86}Kr , and corresponding values calculated by numerical integration of Equation 14 and the (n-1) equations of the form of Equation 64, using the experimental value of H_0 . The column length and hot and cold wall temperatures and radii are as follows:

$$\begin{aligned} r_H &= 0.0794 \text{ cm} & T_H &= 500 \text{ C} \\ r_C &= 0.9525 \text{ cm} & T_C &= 15 \text{ C} \\ L &= 487.68 \text{ cm} \end{aligned}$$

Sample Numbers	[$\ln q_{ij}$]						Column Pressure (torr)	Flow Rate (Std cc hr)
	$(^{80}\text{Kr}-^{86}\text{Kr})_{\text{Exp.}}$	$(^{80}\text{Kr}-^{84}\text{Kr})_{\text{Exp.}}$	$(^{82}\text{Kr}-^{86}\text{Kr})_{\text{Exp.}}$	$(^{80}\text{Kr}-^{86}\text{Kr})_{\text{Calc.}}$	$(^{80}\text{Kr}-^{84}\text{Kr})_{\text{Calc.}}$	$(^{82}\text{Kr}-^{86}\text{Kr})_{\text{Calc.}}$		
	$(^{80}\text{Kr}-^{86}\text{Kr})_{\text{Calc.}}$	$(^{80}\text{Kr}-^{84}\text{Kr})_{\text{Calc.}}$	$(^{82}\text{Kr}-^{86}\text{Kr})_{\text{Calc.}}$					
44T,B	0.587	0.541	0.365	0.339	0.419	0.387	134.2	15.0
45T,B	0.667	0.660	0.402	0.411	0.499	0.474	134.7	11.8
46T,B	0.801	0.785	0.500	0.488	0.577	0.565	134.7	9.3
47T,B	0.903	0.939	0.563	0.585	0.640	0.675	134.7	7.0
48T,B	1.066	1.098	0.669	0.689	0.757	0.784	134.7	5.2
49T,B	1.088	1.102	0.676	0.691	0.769	0.787	135.1	5.2
50T,B	1.246	1.263	0.812	0.800	0.880	0.894	134.7	3.7
51T,B	1.345	1.361	0.855	0.868	0.940	0.956	134.7	3.0

Table 9. Experimental values of $[\ln q_{ij}]$, at high pressures, for the three isotope pairs ^{80}Kr - ^{86}Kr , ^{80}Kr - ^{84}Kr and ^{82}Kr - ^{86}Kr , and corresponding values calculated by numerical integration of Equation 14 and the (n-1) equations of the form of Equation 64, using the experimental value of H_0 . The column length and hot and cold wall temperatures and radii are as follows:

$$\begin{aligned} r_H &= 0.0794 \text{ cm} & T_H &= 500^\circ\text{C} \\ r_C &= 0.9525 \text{ cm} & T_C &= 15^\circ\text{C} \\ L &= 487.68 \text{ cm} \end{aligned}$$

Sample Numbers	[ln q _{ij}]						Column Pressure (torr)	Flow Rate (Std cc/hr)
	⁽⁸⁰ Kr- ⁸⁶ Kr) _{Exp.}		⁽⁸⁰ Kr- ⁸⁴ Kr) _{Exp.}		⁽⁸² Kr- ⁸⁶ Kr) _{Exp.}			
	⁽⁸⁰ Kr- ⁸⁶ Kr) _{Calc.}		⁽⁸⁰ Kr- ⁸⁴ Kr) _{Calc.}		⁽⁸² Kr- ⁸⁶ Kr) _{Calc.}			
52T,B	0.332	0.309	0.216	0.196	0.231	0.219	238.4	86.5
53T,B	0.388	0.405	0.222	0.256	0.304	0.287	238.7	62.1
54T,B	0.524	0.540	0.335	0.342	0.366	0.381	238.4	40.4
55T,B	0.697	0.692	0.453	0.442	0.477	0.482	237.7	24.8
56T,B	0.849	0.842	0.560	0.544	0.560	0.578	238.2	13.9
57T,B	0.927	0.959	0.608	0.627	0.626	0.649	238.2	7.2

Table 10. Experimental values of $[\ln q_{ij}]$, at low pressures, for the three isotope pairs ^{80}Kr - ^{86}Kr , ^{80}Kr - ^{84}Kr and ^{80}Kr - ^{86}Kr , and corresponding values calculated by numerical integration of Equation 14 and the (n-1) equations of the form of Equation 64, using the experimental value of H_0 . The column length and hot and cold wall temperatures and radii are as follows:

$$\begin{aligned} r_H &= 0.0794 \text{ cm} & T_H &= 800^\circ\text{C} \\ r_C &= 0.9525 \text{ cm} & T_C &= 15^\circ\text{C} \\ L &= 487.68 \text{ cm} \end{aligned}$$

Sample Numbers	[ln q _{ij}]						Column Pressure (torr)	Flow Rate (Std cc/hr)
	(⁸⁰ Kr- ⁸⁶ Kr) _{Exp}	(⁸⁰ Kr- ⁸⁴ Kr) _{Exp.}	(⁸² Kr- ⁸⁶ Kr) _{Exp.}					
	(⁸⁰ Kr- ⁸⁶ Kr) _{Calc.}	(⁸⁰ Kr- ⁸⁴ Kr) _{Calc.}	(⁸² Kr- ⁸⁶ Kr) _{Calc.}					
58T,B	0.501	0.473	0.309	0.291	0.352	0.335	158.0	31.6
59T,B	0.736	0.692	0.436	0.413	0.543	0.502	158.0	21.0
60T,B	0.753	0.712	0.451	0.424	0.560	0.517	160.5	21.0
61T,B	1.132	1.075	0.662	0.624	0.827	0.796	160.8	12.8
62T,B	1.112	1.069	0.662	0.621	0.814	0.792	158.0	12.4
63T,B	1.476	1.520	0.889	0.890	1.074	1.130	159.0	7.4
64T,B	1.922	2.027	1.158	1.229	1.415	1.480	160.0	4.0
65T,B	2.290	2.365	1.422	1.479	1.635	1.688	160.0	2.4

Table II. Experimental values of $[\ln q_{ij}]$, at high pressures, for the three isotope pairs $^{80}\text{Kr}-^{86}\text{Kr}$, $^{80}\text{Kr}-^{84}\text{Kr}$ and $^{82}\text{Kr}-^{86}\text{Kr}$, and corresponding values calculated by numerical integration of Equation 14 and the (n-1) equations of the form of Equation 64, using the experimental value of H_0 . The column length and hot and cold wall temperatures and radii are as follows:

$$\begin{aligned} r_H &= 0.0794 \text{ cm} & T_H &= 800^\circ\text{C} \\ r_C &= 0.9525 \text{ cm} & T_C &= 15^\circ\text{C} \\ L &= 487.68 \text{ cm} \end{aligned}$$

Sample Numbers	[ln q _{ij}]						Column Pressure (torr)	Flow Rate (Std cc/hr)
	⁽⁸⁰ Kr- ⁸⁶ Kr) _{Exp.}		⁽⁸⁰ Kr- ⁸⁴ Kr) _{Exp.}		⁽⁸² Kr- ⁸⁶ Kr) _{Exp.}			
	⁽⁸⁰ Kr- ⁸⁶ Kr) _{Calc.}		⁽⁸⁰ Kr- ⁸⁴ Kr) _{Calc.}		⁽⁸² Kr- ⁸⁶ Kr) _{Calc.}			
66T,B	0.415	0.432	0.250	0.260	0.304	0.305	278.0	116.4
67T,B	0.547	0.542	0.341	0.323	0.338	0.385	279.0	90.7
68T,B	0.989	1.010	0.608	0.607	0.716	0.723	278.0	37.7
69T,B	1.161	1.191	0.717	0.729	0.812	0.844	282.0	27.3
70T,B	1.391	1.330	0.823	0.824	0.975	0.937	279.0	20.6

Table 12. Theoretical and experimental values of the coefficients H_o' , K_c' and K_d .

Theoretical	T_H (°C)		$H_o' \times 10^5$	K_c'	$K_d \times 10^3$	
	350		3.31	1.37	1.13	
	500		4.90	1.19	1.23	
	800		6.73	0.70	1.42	
Experimental	T_H (°C)	Isotope Pair	$H_o' \times 10^5$	K_c'	$K_d \times 10^3$	Calculated from data in Tables
I. Low pressure flow runs	350	80-86	3.81	1.57	1.21	13 & 16
	350	80-84	3.81	1.58	1.21	13 & 16
	350	82-86	3.83	1.53	1.18	13 & 16
II. High pressure flow runs	350	80-86	4.10	1.68	1.30	13 & 17
	350	80-84	4.15	1.72	1.32	13 & 17
	350	82-86	3.92	1.56	1.21	13 & 17
Average			3.94	1.61	1.24	
III. Low pressure flow runs	500	80-86	4.98	1.21	1.21	14 & 18
	500	80-84	5.10	1.24	1.22	14 & 18
	500	82-86	4.99	1.22	1.21	14 & 18
IV. High pressure flow runs	500	80-86	5.06	1.22	1.22	14 & 19
	500	80-84	5.04	1.23	1.21	14 & 19
	500	82-86	5.17	1.26	1.25	14 & 19
Average			5.06	1.23	1.22	
V. Low pressure flow runs	800	80-86	6.36	0.61	1.47	15 & 20
	800	80-84	6.40	0.61	1.48	15 & 20
	800	82-86	6.29	0.61	1.45	15 & 20
VI. High pressure flow runs	800	80-86	6.95	0.67	1.61	15 & 21
	800	80-84	6.72	0.64	1.55	15 & 21
	800	82-86	6.91	0.67	1.60	15 & 21
Average			6.60	0.64	1.53	

K'_0 and K_4 are tabulated. Also given, for the experimental values, are the numbers of the tables which contain the raw data from which each set of experimental values of H'_0 , K'_0 and K_4 are calculated.

DISCUSSION OF RESULTS

As can be seen by an examination of Table 12, the agreement between theory and experiment is rather good in all cases. In order to illustrate this fact, and also to facilitate the following discussion, the ratios of the theoretical values of each of the coefficients to the average experimental values at the corresponding temperatures are tabulated in Table 12a.

Table 12a.

Ratios of theoretical to average experimental values of the transport equation coefficients

T_H (°C)	$\frac{(H'_O)_{T_H}}{(H'_O)_{EXP, AVG}}$	$\frac{(K'_C)_{T_H}}{(K'_C)_{EXP, AVG}}$	$\frac{(K_d)_{T_H}}{(K_d)_{EXP, AVG}}$
350	0.84	0.85	0.91
500	0.97	0.97	1.01
800	1.02	1.09	0.93

The quantities tabulated in Table 12a show that in seven of nine cases the experimental values of the coefficients are within $\pm 10\%$ of the theoretical values. In the remaining two cases, the experimental values are within $\pm 20\%$ of the theoretical values. An attempt is now made to explain the discrepancies which exist between the theoretical and experimental values of the coefficients.

First of all, the agreement is so good at $T_H = 500^\circ\text{C}$ that it is reasonable to attribute the discrepancies to experimental and analytical error. At $T_H = 350^\circ\text{C}$ and $T_H = 800^\circ\text{C}$, however, the agreement is not as good, and another possible source of error must be considered. This is the set of values for the ordinary diffusion coefficient which was used to calculate the theoretical values of the column coefficients.

Consider first the results at $T_H = 800^\circ\text{C}$. The agreement is good for the coefficient H'_0 . However, the theoretical value of the coefficient K'_0 is high and the theoretical value of the coefficient K_d is low. An examination of Equations 37, 38 and 39 shows that the coefficients K'_0 and K_d depend on the ordinary diffusion coefficient, D , whereas the coefficient H'_0 does not. Furthermore, the theoretical expression for the coefficient K'_0 contains D in the denominator of the integrand, whereas the theoretical expression for K_d contains D in the numerator. Thus, it can be seen that low values for the ordinary diffusion coefficient, in the temperature range $\sim 750^\circ\text{K} \sim 1100^\circ\text{K}$, would lead to the observed situation. Because data for the ordinary diffusion coefficient is non-existent in this temperature range, it is not possible at present to determine whether or not this is the cause of the observed discrepancies. However, there is a very distinct possibility that it is.

For the results at $T_w = 350^\circ\text{C}$, the discrepancies exhibit a different type of behavior. For this case, all of the theoretical values are lower than the corresponding average experimental values. This behavior indicates that the average experimental value for H_0' is low. Also, the fact that the ratio of the theoretical value of K_c' to the average experimental value is lower than the corresponding ratio for K_a is indicative of high values for D in the temperature range $\sim 275^\circ\text{K}$ $\sim 650^\circ\text{K}$. However, the major parts of the discrepancies are undoubtedly due to the low average experimental value for H_0' , and hence, to experimental and analytical error. It is to be expected that the analytical error will have its most serious effect at low values of the hot wall temperature, because in these cases the separations achieved are small and the values of the separation factors are correspondingly more sensitive to small errors in the values of the isotopic concentrations.

CONCLUSIONS AND RECOMMENDATIONS

From a study of the theoretical predictions and experimental results, it is concluded that the extended Jones and Furry theory, which deals with multicomponent heavy isotopic gases, gives a rather good quantitative description of the behavior of such gases in a Clusius-Dickel thermal diffusion column.

For future work, it is recommended that additional comparisons between theory and experiment be made for hot wire temperatures in the lower temperature range ($\sim 500^{\circ}\sim 650^{\circ}\text{K}$). These comparisons should serve to pinpoint the cause or causes of the discrepancies reported in this thesis, for $T_{\text{H}} = 350^{\circ}\text{C}$.

It is also recommended that more work be done in the area of the transport properties of krypton, with particular attention to the ordinary diffusion coefficient and the thermal-diffusion factor, with the aim of providing a reliable set of values for these properties over a wide range of temperatures.

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APPENDIX A
DEVICES UTILIZED FOR EXPERIMENTAL
DETERMINATION OF THE THERMAL DIFFUSION FACTOR

DEVICES UTILIZED FOR EXPERIMENTAL DETERMINATION OF THE THERMAL DIFFUSION FACTOR

This section is devoted to a qualitative discussion of the "two-bulb" apparatus and the "Trennschauckel," or, "Swing Separator." These devices are utilized in making experimental determinations of the thermal diffusion factor. They are not used for separating large quantities of material. Separation of large quantities of material is achieved by means of the Clusius-Dickel column, which is described in the Literature Review and Equipment sections.

Two-Bulb Apparatus

The first device to be discussed is the two-bulb apparatus. The two-bulb apparatus, which is shown in Figure 16, consists of two glass or metal bulbs joined by a connecting tube. During operation, the two bulbs are held at different temperatures. Then, because of the existence of the thermal diffusion effect, a concentration difference is established, which is usually such that the lighter constituent is enriched in the high temperature bulb and the heavier constituent is enriched in the low temperature bulb. When this behavior holds, i.e., when the lighter constituent concentrates in the hot bulb and the heavier constituent concentrates in the cold

Figure 16. Simplified drawing of the two-bulb apparatus. Other valves located in the connecting tube, for removal of gas between expansions, are not shown.

bulb, the thermal diffusion factor α_T is, by convention, taken to be positive. When the opposite behavior holds, the thermal diffusion factor is taken to be negative.

The establishment of the concentration difference by the thermal diffusion flux is opposed by an ordinary diffusion flux in the opposite direction. Since the thermal diffusion flux and the ordinary diffusion flux are vectors which are oppositely directed, a state of equilibrium is attained when their magnitudes become equal.

It is possible to further increase the concentration of one or the other of the constituents by closing the valve in the middle of the connecting tube, removing the gas which is enriched in the undesired component from the system (by means of additional valves in the connecting tube, which are not shown), and then allowing the gas which is enriched in the desired constituent to fill both bulbs. This will result in further separation. However, only one half of the original amount of gas is now present. This procedure can be carried out repeatedly. However, although this results in increased separation, it also leads to a reduction in the amount of gas in the system. Thus, although the final separation achieved after a number of expansions is greater than after a single expansion, the amount of gas remaining is likely to be quite

small. This is perhaps the chief drawback of the two-bulb apparatus.

Trennschauckel

The other device to be discussed is the Trennschauckel, or, "swing separator" (48). This device, a simplified drawing of which appears in Figure 17, consists essentially of a number of cells which are connected serially. The tops and bottoms of these cells are maintained at, respectively, high and low temperatures. The temperatures are the same for all cells. The first and last cells are connected to two bellows, which cause the gas to be "rocked" or "swung" back and forth. When equilibrium has been established, the separation q_n which has been effected between the top of the n^{th} cell, where n is the number of cells, and the bottom of the first cell is very nearly equal to $(q_1)^n$, where q_1 is the separation which would be produced in a single two-bulb apparatus operating between the same two temperatures. This device finds considerable application in making experimental determinations of the thermal diffusion factor α_T .

Figure 17 Simplified drawing of the Trennschauckel or 'Swing Separator' (Van Der Valk (48)).

APPENDIX B

RAW DATA

Table 13. Compositions of samples, expressed as mass fractions, for static experiments. The corresponding column pressures are also given. The column length and hot and cold wall temperatures and radii are as follows:

$$\begin{aligned} r_H &= 0.0794 \text{ cm} & T_H &= 350^\circ\text{C} \\ r_C &= 0.9525 \text{ cm} & T_C &= 15^\circ\text{C} \\ L &= 487.68 \text{ cm} \end{aligned}$$

Sample Numbers	Mass Fraction						Column Pressure (torr)
	78	80	82	83	84	86	
1T ^a	0.0046	0.0237	0.1271	0.1186	0.5773	0.1452	234.2
1B	0.0023	0.0174	0.1022	0.1067	0.5848	0.1865	234.2
2T	0.0038	0.0231	0.1160	0.1130	0.5846	0.1595	200.3
2B	0.0015	0.0128	0.0855	0.0965	0.5882	0.2155	200.3
3T	0.0046	0.0275	0.1275	0.1192	0.5819	0.1392	149.0
3B	0.0015	0.0126	0.0843	0.0965	0.5909	0.2143	149.0
4T	0.0051	0.0287	0.1333	0.1232	0.5786	0.1311	136.0
4B	0.0015	0.0128	0.0870	0.0994	0.5920	0.2073	136.0
5T	0.0056	0.0310	0.1380	0.1240	0.5732	0.1282	125.0
5B	0.0018	0.0137	0.0910	0.1014	0.5909	0.2012	125.0
6T	0.0057	0.0323	0.1398	0.1247	0.5727	0.1248	115.4
6B	0.0017	0.0145	0.0939	0.1033	0.5897	0.1969	115.4
7T	0.0061	0.0338	0.1435	0.1252	0.5700	0.1214	100.0
7B	0.0020	0.0161	0.0992	0.1055	0.5908	0.1863	100.0

a - T designates upper sample port, B designates lower sample port.

Table 14. Compositions of samples, expressed as mass fractions, for static experiments. The corresponding column pressures are also given. The column length and hot and cold wall temperatures and radii are as follows:

$$\begin{aligned} r_H &= 0.0794 \text{ cm} & T_H &= 500^\circ\text{C} \\ r_C &= 0.9525 \text{ cm} & T_C &= 15^\circ\text{C} \\ L &= 487.68 \text{ cm} \end{aligned}$$

Sample Numbers	Mass Fraction						Column Pressure (torr)
	78	80	82	83	84	86	
8T	0.0052	0.0218	0.1296	0.1191	0.5716	0.1464	304.2
8B	0.0028	0.0177	0.1030	0.1086	0.5780	0.1899	304.2
9T	0.0061	0.0327	0.1391	0.1233	0.5679	0.1309	252.4
9B	0.0024	0.0167	0.1010	0.1073	0.5825	0.1901	252.4
10T	0.0078	0.0392	0.1531	0.1302	0.5552	0.1145	201.1
10B	0.0022	0.0158	0.1000	0.1083	0.5818	0.1919	201.1
11T	0.0096	0.0468	0.1684	0.1349	0.5448	0.0955	162.4
11B	0.0022	0.0155	0.1009	0.1094	0.5862	0.1858	162.4
12T	0.0112	0.0523	0.1785	0.1337	0.5378	0.0865	142.2
12B	0.0020	0.0162	0.1047	0.1113	0.5872	0.1786	142.2
13T	0.0106	0.0512	0.1782	0.1383	0.5348	0.0869	105.6
13B	0.0024	0.0177	0.1088	0.1131	0.5920	0.1660	105.6
14T	0.0108	0.0505	0.1749	0.1377	0.5395	0.0866	105.6
14B	0.0042	0.0179	0.1096	0.1152	0.5868	0.1663	105.6
15T	0.0069	0.0384	0.1570	0.1324	0.5592	0.1061	82.6
15B	0.0024	0.0173	0.1072	0.1129	0.5901	0.1701	82.6
16T	0.0069	0.0381	0.1561	0.1312	0.5608	0.1069	82.6
16B	0.0023	0.0174	0.1081	0.1132	0.5902	0.1688	82.6

Table 15. Compositions of samples, expressed as mass fractions, for static experiments. The corresponding column pressures are also given. The column length and hot and cold wall temperatures and radii are as follows:

$$\begin{aligned} r_H &= 0.0794 \text{ cm} & T_H &= 800^\circ\text{C} \\ r_C &= 0.9525 \text{ cm} & T_C &= 15^\circ\text{C} \\ L &= 487.68 \text{ cm} \end{aligned}$$

Sample Numbers	Mass Fraction						Column Pressure (torr)
	78	80	82	83	84	86	
17T	0.0057	0.0337	0.1442	0.1261	0.5692	0.1211	304.5
17B	0.0011	0.0112	0.0843	0.0980	0.5882	0.2173	304.5
18T	0.0059	0.0350	0.1485	0.1282	0.5668	0.1155	286.4
18B	0.0009	0.0103	0.0820	0.0981	0.5852	0.2235	286.4
19T	0.0077	0.0436	0.1695	0.1377	0.5496	0.0919	241.2
19B	0.0007	0.0090	0.0803	0.0981	0.5925	0.2194	241.2
20T	0.0090	0.0486	0.1779	0.1389	0.5445	0.0812	221.5
20B	0.0007	0.0091	0.0809	0.0987	0.5965	0.2141	221.5
21T	0.0111	0.0568	0.1934	0.1432	0.5257	0.0699	206.2
21B	0.0007	0.0091	0.0843	0.1022	0.5967	0.2071	206.2
22T	0.0050	0.0368	0.1674	0.1407	0.5658	0.0844	182.2
22B	0.0002	0.0050	0.0641	0.0898	0.5980	0.2429	182.2
23T	0.0092	0.0486	0.1813	0.1399	0.5434	0.0776	162.7
23B	0.0005	0.0068	0.0697	0.0922	0.5919	0.2389	162.7
24T	0.0138	0.0683	0.2151	0.1486	0.5031	0.0511	161.5
24B	0.0007	0.0103	0.0913	0.1084	0.6139	0.1754	161.5
25T	0.0086	0.0491	0.1801	0.1423	0.5373	0.0825	148.0
25B	0.0002	0.0066	0.0706	0.0922	0.5937	0.2367	148.0
26T	0.0157	0.0739	0.2240	0.1494	0.4905	0.0466	141.0
26B	0.0010	0.0131	0.1045	0.1163	0.6130	0.1521	141.0
27T	0.0073	0.0414	0.1673	0.1372	0.5553	0.0915	136.2
27B	0.0004	0.0068	0.0677	0.0904	0.5854	0.2493	136.2
28T	0.0032	0.0260	0.1378	0.1287	0.5865	0.1179	117.2
28B	0.0002	0.0052	0.0609	0.0858	0.5852	0.2627	117.2
29T	0.0085	0.0469	0.1759	0.1382	0.5457	0.0847	112.5
29B	0.0008	0.0109	0.0886	0.1026	0.5965	0.2005	112.5
30T	0.0169	0.0775	0.2250	0.1497	0.4857	0.0452	110.5
30B	0.0023	0.0219	0.1343	0.1298	0.5969	0.1148	110.5

Table 16. Compositions of samples, expressed as mass fractions, for flow experiments at low pressures. The corresponding column pressures and net flow rates are also given. The column length and hot and cold wall temperatures and radii are as follows:

$$\begin{aligned} r_H &= 0.0794 \text{ cm} & T_H &= 350^\circ\text{C} \\ r_C &= 0.9525 \text{ cm} & T_C &= 15^\circ\text{C} \\ L &= 487.68 \text{ cm} \end{aligned}$$

Sample Numbers	Mass Fraction						Column Pressure (torr)	Flow Rate (Std cc/hr)
	78	80	82	83	84	86		
31T	0.0045	0.0271	0.1264	0.1182	0.5757	0.1482	131.7	14.9
31B	0.0032	0.0214	0.1124	0.1113	0.5801	0.1715	131.7	14.9
32T	0.0052	0.0295	0.1315	0.1205	0.5725	0.1408	131.7	10.2
32B	0.0033	0.0214	0.1117	0.1114	0.5803	0.1719	131.7	10.2
33T	0.0058	0.0321	0.1373	0.1231	0.5695	0.1321	132.1	7.0
33B	0.0032	0.0214	0.1125	0.1119	0.5798	0.1712	132.1	7.0
34T	0.0070	0.0363	0.1503	0.1283	0.5622	0.1159	131.9	4.2
34B	0.0033	0.0215	0.1124	0.1114	0.5837	0.1678	131.9	4.2
35T	0.0074	0.0381	0.1524	0.1272	0.5612	0.1137	132.1	2.7
35B	0.0033	0.0217	0.1137	0.1119	0.5824	0.1670	132.1	2.7

Table 17. Compositions of samples, expressed as mass fractions, for flow experiments at high pressures. The corresponding column pressures and net flow rates are also given. The column length and hot and cold wall temperatures and radii are as follows:

$$\begin{aligned} r_H &= 0.0794 \text{ cm} & T_H &= 350^\circ\text{C} \\ r_C &= 0.9525 \text{ cm} & T_C &= 15^\circ\text{C} \\ L &= 487.68 \text{ cm} \end{aligned}$$

Sample Numbers	Mass Fraction						Column Pressure (torr)	Flow Rate (Std cc/hr)
	78	80	82	83	84	86		
36T	0.0039	0.0248	0.1208	0.1154	0.5800	0.1552	227.0	41.1
36B	0.0029	0.0196	0.1069	0.1088	0.5814	0.1804	227.0	41.1
37T	0.0042	0.0267	0.1245	0.1173	0.5749	0.1524	210.8	35.8
37B	0.0032	0.0208	0.1101	0.1108	0.5808	0.1743	210.8	35.8
38T	0.0045	0.0267	0.1258	0.1177	0.5761	0.1492	225.8	27.7
38B	0.0029	0.0197	0.1084	0.1100	0.5807	0.1783	225.8	27.7
39T	0.0048	0.0277	0.1276	0.1188	0.5745	0.1467	210.8	24.6
39B	0.0032	0.0209	0.1108	0.1107	0.5799	0.1745	210.8	24.6
40T	0.0050	0.0290	0.1301	0.1196	0.5752	0.1412	226.5	18.4
40B	0.0031	0.0204	0.1100	0.1111	0.5790	0.1764	226.5	18.4
41T	0.0052	0.0298	0.1318	0.1198	0.5722	0.1411	210.8	16.3
41B	0.0032	0.0210	0.1112	0.1110	0.5819	0.1716	210.8	16.3
42T	0.0058	0.0319	0.1378	0.1209	0.5662	0.1374	210.5	10.0
42B	0.0031	0.0215	0.1126	0.1117	0.5807	0.1704	210.5	10.0
43T	0.0064	0.0339	0.1417	0.1225	0.5686	0.1269	210.6	6.1
43B	0.0033	0.0218	0.1136	0.1117	0.5811	0.1685	210.6	6.1

Table 19. Compositions of samples, expressed as mass fractions, for flow experiments at high pressures. The corresponding column pressures and net flow rates are also given. The column length and hot and cold wall temperatures and radii are as follows:

$$\begin{aligned} r_H &= 0.0794 \text{ cm} & T_H &= 500^\circ\text{C} \\ r_C &= 0.9525 \text{ cm} & T_C &= 15^\circ\text{C} \\ L &= 487.68 \text{ cm} \end{aligned}$$

Sample Numbers	Mass Fraction						Column Pressure (torr)	Flow Rate (Std cc/hr)
	78	80	82	83	84	86		
52T	0.0039	0.0248	0.1217	0.1171	0.5754	0.1571	238.4	86.5
52B	0.0028	0.0201	0.1092	0.1113	0.5789	0.1776	238.4	86.5
53T	0.0040	0.0254	0.1269	0.1202	0.5723	0.1512	238.7	62.1
53B	0.0029	0.0204	0.1108	0.1130	0.5740	0.1790	238.7	62.1
54T	0.0044	0.0282	0.1303	0.1209	0.5733	0.1429	238.4	40.4
54B	0.0029	0.0204	0.1104	0.1118	0.5799	0.1746	238.4	40.4
55T	0.0055	0.0313	0.1379	0.1237	0.5696	0.1319	237.7	24.8
55B	0.0023	0.0203	0.1115	0.1125	0.5814	0.1719	237.7	24.8
56T	0.0068	0.0364	0.1459	0.1262	0.5623	0.1224	238.2	13.9
56B	0.0028	0.0214	0.1145	0.1143	0.5788	0.1682	238.2	13.9
57T	0.0078	0.0393	0.1522	0.1277	0.5561	0.1168	238.2	7.2
57B	0.0031	0.0222	0.1162	0.1148	0.5770	0.1668	238.2	7.2

Table 20. Compositions of samples, expressed as mass fractions, for flow experiments at low pressures. The corresponding column pressures and net flow rates are also given. The column length and hot and cold wall temperatures and radii are as follows:

$$\begin{aligned} r_H &= 0.0794 \text{ cm} & T_H &= 800^\circ\text{C} \\ r_C &= 0.9525 \text{ cm} & T_C &= 15^\circ\text{C} \\ L &= 487.68 \text{ cm} \end{aligned}$$

Sample Numbers	Mass Fraction						Column Pressure (torr)	Flow Rate (Std cc/hr)
	78	80	82	83	84	86		
58T	0.0041	0.0264	0.1266	0.1189	0.5781	0.1459	158.0	31.6
58B	0.0026	0.0195	0.1085	0.1097	0.5818	0.1779	158.0	31.6
59T	0.0049	0.0295	0.1366	0.1242	0.5749	0.1298	158.0	21.0
59B	0.0027	0.0193	0.1084	0.1106	0.5817	0.1773	158.0	21.0
60T	0.0051	0.0300	0.1370	0.1246	0.5748	0.1286	160.5	21.0
60B	0.0028	0.0194	0.1074	0.1097	0.5840	0.1766	160.5	21.0
61T	0.0064	0.0366	0.1533	0.1314	0.5675	0.1048	160.8	12.8
61B	0.0027	0.0194	0.1103	0.1115	0.5837	0.1724	160.8	12.8
62T	0.0063	0.0365	0.1529	0.1306	0.5665	0.1072	158.0	12.4
62B	0.0027	0.0194	0.1095	0.1112	0.5839	0.1733	158.0	12.4
63T	0.0086	0.0450	0.1716	0.1382	0.5500	0.0865	159.0	7.4
63B	0.0027	0.0197	0.1122	0.1134	0.5862	0.1657	159.0	7.4
64T	0.0122	0.0598	0.1982	0.1447	0.5216	0.0635	160.0	4.0
64B	0.0030	0.0212	0.1166	0.1166	0.5887	0.1539	160.0	4.0
65T	0.0176	0.0766	0.2188	0.1468	0.4892	0.0510	160.0	2.4
65B	0.0029	0.0222	0.1220	0.1190	0.5879	0.1460	160.0	2.4

Table 21. Compositions of samples, expressed as mass fractions, for flow experiments at high pressures. The corresponding column pressures and net flow rates are also given. The column length and hot and cold wall temperatures and radii are as follows:

$$\begin{aligned} r_H &= 0.0794 \text{ cm} & T_H &= 800^\circ\text{C} \\ r_C &= 0.9525 \text{ cm} & T_C &= 15^\circ\text{C} \\ L &= 487.68 \text{ cm} \end{aligned}$$

Sample Numbers	Mass Fraction						Column Pressure (torr)	Flow Rate (Std cc/hr)
	78	80	82	83	84	86		
66T	0.0040	0.0251	0.1244	0.1171	0.5790	0.1503	278.0	116.4
66B	0.0028	0.0196	0.1086	0.1105	0.5806	0.1779	278.0	116.4
67T	0.0045	0.0269	0.1279	0.1200	0.5772	0.1436	279.0	90.7
67B	0.0028	0.0193	0.1076	0.1095	0.5827	0.1782	279.0	90.7
68T	0.0062	0.0348	0.1480	0.1285	0.5680	0.1146	278.0	37.7
68B	0.0025	0.0195	0.1089	0.1116	0.5847	0.1727	278.0	37.7
69T	0.0075	0.0400	0.1584	0.1313	0.5599	0.1028	282.0	27.3
69B	0.0028	0.0203	0.1140	0.1141	0.5822	0.1667	282.0	27.3
70T	0.0083	0.0440	0.1613	0.1314	0.5651	0.0898	279.0	20.6
70B	0.0028	0.0201	0.1117	0.1125	0.5879	0.1650	279.0	20.6