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RICE UNIVERSITY

THE DIFFUSION OF KRYPTON-85
IN DENSE GASES

by

Leonel D. Durbin

A THESIS
SUBMITTED TO THE FACULTY
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN CHEMICAL ENGINEERING

Houston, Texas
June, 1961

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ACKNOWLEDGEMENTS

The author would like to express his appreciation to the many persons and organizations that have contributed to this endeavor by their advice, support, and assistance. More specifically, I am very grateful to the following:

Dr. Riki Kobayashi for his advice, assistance and whole-hearted support;

Dr. T. W. Leland for his advice and assistance;

Mr. Sam Pollard and Mr. Hugh Hales for their assistance with the construction of the experimental equipment;

Mr. Walter Ruska for his advice concerning the construction of equipment;

Mr. John Giddings for his assistance with the mercury resistance measurements;

Mr. David Cardner for his advice and generous help with the computer reductions;

Messrs. Antonio Faillace, T. K. Wong, and Ronald Darby for their photographic endeavors;

Miss Leona Hoop for her diligence at typing the final copy;

The Chemical Engineering Department for research funds;

Lane-Wells Co. for advice concerning high pressure ionization chambers;

Cook's Heat Treating Co. for performing needed metal heat treating;

American Oil Co. for fellowship grant (1958-59);

National Science Foundation for fellowship grant (1969-60);

Celanese Corporation of America for fellowship grant (1960-61);

My Parents and Family for their encouragement and support.

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I. INTRODUCTION

The process by which matter is transported from one part of a system to another as a result of the random motion of the molecules is termed "diffusion". Although the direction of motion of each molecule is random, the bulk motion of the molecules is from a region of high concentration (number) to a region of low concentration. Diffusion is known as a "transport" phenomenon because of this transfer of matter (mass). The analysis of the motion of the molecules as individual units is termed a microscopic analysis, whereas that which follows the bulk movement of the molecules is called a macroscopic analysis.

Because experimental observations of bulk properties are readily carried out, the macroscopic (phenomenological) analysis of diffusion processes was developed at an early date. The prediction of the rate of transfer of matter involved the definition of a diffusion coefficient to characterize the system and conditions of study. Many attempts were made at empirically correlating this coefficient with system and observation conditions.

The kinetic theory of gases was developed to explain the familiar physical properties of gases and of gaseous phenomenon on the basis of molecular interaction among the molecules and with system boundaries. By the application of the classical mechanical conservation laws of mass, momentum, and energy to the interactions with an averaging process in accordance with statistical averaging methods the theory seeks to explain bulk properties and phenomenon. This theory has progressed to the extent that a quantitative description of diffusion processes can be made within ordinary experimental accuracy for relatively simple gas systems at near atmospheric pressure and moderate temperatures. Theoretical developments along these

lines have not been successful in predicting diffusion behavior at higher densities. This has not been accomplished because the description of the molecular interactions and their relation to transport phenomena becomes exceedingly complex.

In order to advance the understanding of diffusion phenomena and the methods of study the experimental developments, procedures, observations, and analysis recorded in this dissertation were formulated and carried out.

The objectives of the experimental investigation were as follows:

1. to obtain absolute values of diffusion coefficients at high pressures by an accurate description of quasi-stationary diffusion cell geometry;
2. to study the effect on the diffusion coefficient of mixing in quasi-stationary state diffusion cell chambers;
3. to compare the results of measurements by ionization and scintillation detection for a quasi-stationary state diffusion cell;
4. to study the diffusion process of krypton-85 in a varied assortment of dense gases of well known state properties with a wide reduced temperature range.

In order to initiate the realization of these stated research purposes experimental equipment was designed and constructed for studying diffusion processes. The important items of the experimental equipment that were specially designed and constructed for utilization in this investigation are as follows:

1. a high pressure ionization detection quasi-stationary state diffusion cell with stirred chambers and in-cell valves.
2. an electrode assembly which permitted the use of a vibrating reed electrometer to measure the ionization currents of the

ionization cell with oil bath temperature control and stirring of the chambers.

3. a high pressure scintillation detection quasi-stationary state diffusion cell with magnetically stirred chambers and in-cell valves.

4. a glass capillary tube bundle diffusion path for which the area to length ratio was very accurately determined.

For the purpose of furthering the realization of the stated objectives of this investigation experimental determinations were made of the Fick's law diffusion coefficients for krypton-85 (Kr^*) diffusing in various gases under varied experimental conditions for which no previous experimental data existed. The systems studied with the conditions of study indicated are as follows:

1. Ionization Cell System;

- a. Kr^* - A at $35^\circ C$ to 15 moles per liter,
- b. Kr^* - N_2 at $35^\circ C$ to 14 " " " ,
- c. Kr^* - He at $35^\circ C$ to 14 " " " ,
- d. Kr^* - CO_2 at $35^\circ C$ to 14 " " " ,
- e. Kr^* - C_2H_4 at $25^\circ C$ to 13 " " " ,
- f. Kr^* - K_r at $35^\circ C$ to 12 " " " ,

2. Scintillation Cell Systems;

- a. Kr^* - A at $35^\circ C$ to 5 moles per liter ,
- b. Kr^* - A at $-25^\circ C$ to 10 " " " ,
- c. Kr^* - N_2 at $-25^\circ C$ to 10 " " " ,

Finally, to complete the objective study the experimental results were:

- 1. analyzed with respect to consistency among themselves in particular with respect to the mixing effect and

detection method,

2. compared to the dilute gas theory and previous experimental observations in the extrapolation limit to low densities,
3. compared to the available dense gas theory with modifications suggested by the literature and this investigation.

II. HISTORICAL AND THEORETICAL BACKGROUND OF DIFFUSION WORK

The body of literature relating to experimental and theoretical investigations of the various aspects of the diffusion process is quite extensive and will not be reviewed in its entirety here. Only the important phenomenological and kinetic theory results which may find application to this investigation are displayed and discussed. Considerable attention is given to the assumptions inherent in a particular theoretical development. The discussion of prior experimental work is limited to those investigations of the same or similar gas systems as well as those investigations which have advanced the methods of experimentally studying diffusion particularly if these are similar to the methods and procedures of this investigation. Emphasis is placed on the comparison of the various methods as to reliability of results. Now investigations of diffusion processes in gases at elevated pressures are limited to such an extent that all known investigations of this nature have been indicated and discussed.

The early research carried out by Fick⁽²³⁾ provided the basis for the formal description of diffusion by the so-called phenomenological relations. Early theoretical work to relate diffusion to molecular properties were pursued by Stefan⁽⁸²⁾, Maxwell⁽⁴⁸⁾ and Meyer⁽⁵¹⁾. Further refinements and development of the theory in a more rigorous fashion were made by Langevin⁽⁴²⁾, Chapman⁽¹²⁾ and Enskog⁽²¹⁾. Jeans⁽³⁵⁾ gives a very good account of the development of the theory by these early workers. The most complete development and evaluation of the rigorous theory of dilute non-uniform gases, commonly known as the Chapman-Enskog theory, is presented by the now classic monograph "The Mathematical Theory of Non-Uniform Gases" by Chapman and Cowling⁽¹³⁾.

Arnold⁽¹⁾ and Gilliland⁽²⁵⁾ employed the early rigid sphere theoretical equations with empirically evaluated constants derived from available ex-

perimental data to develop their equations for predicting binary diffusion coefficients. A brief summary of the equations and methods available for estimating diffusion coefficients are given by Reid and Sherwood⁽⁷⁰⁾.

Mathematical descriptions of the more common geometrical systems encountered in diffusion processes are developed and evaluated in the monograph by Jost⁽³⁸⁾ and Crank⁽¹⁷⁾.

PHENOMENOLOGICAL RELATIONS

The diffusion flow, flux, or current J of a gaseous component in a mixture with other components is defined as the amount of this component which passes perpendicularly through a reference surface of unit area during unit time. With a volume velocity of zero for two components the phenomenological equations of the fluxes, J_1 and J_2 , for ordinary isothermal mutual diffusion are given by (2)

$$-J_1 = L_{11} \nabla \mu_1 + L_{12} \nabla \mu_2, \quad (1)$$

and

$$-J_2 = L_{21} \nabla \mu_1 + L_{22} \nabla \mu_2 \quad (2)$$

where μ_1 and μ_2 are the chemical potentials for components, 1 and 2, respectively, while L_{11} , L_{12} , L_{21} , and L_{22} are the phenomenological coefficients.

When the pressure is constant and uniform throughout the system Fick's first law⁽²³⁾ diffusion is the diffusion process. When the Gibbs-Duhem equation,

$$C_1 \left(\frac{\partial \mu_1}{\partial C_1} \right)_{T,P} + C_2 \left(\frac{\partial \mu_2}{\partial C_1} \right)_{T,P} = 0, \quad (3)$$

is used to rearrange Equation (1) it is found that

$$-J_1 = \frac{1}{C_2} \left(\frac{\partial \mu_1}{\partial C_1} \right)_{T,P} [C_2 L_{11} \nabla C_1 - C_1 L_{12} \nabla C_1]. \quad (4)$$

Here, C_1 and C_2 are the molar concentrations of components 1 and 2, respectively. Now Equation (4) may be rearranged to give Fick's first law

$$-J_1 = D_{12} \nabla C_1 \quad (5)$$

where

$$D_{12} = \frac{1}{C_2} \left(\frac{\partial \mu_1}{\partial C_1} \right)_{T,P} [C_2 L_{11} - C_1 L_{12}]. \quad (6)$$

When the formalism of irreversible thermodynamics⁽¹⁸⁾ is applied to this case it can be shown that⁽¹⁸⁾,

$$\begin{aligned} L_{11} + L_{12} &= 0, & L_{21} + L_{22} &= 0, \\ L_{11} + L_{21} &= 0, & L_{12} + L_{22} &= 0, \end{aligned} \quad (7)$$

so that

$$J_1 = -J_2. \quad (8)$$

Actually, this result is obvious because the volume velocity is zero which requires that the net flux across a reference plane be zero. Thus, for this case no Onsager reciprocal relations exist in accordance with the singularity of the mutual diffusion phenomenon, that is, there are no cross effects.

Now, $C_1 + C_2 = 1$, therefore

$$D = \frac{1}{C_2} \left(\frac{\partial \mu_1}{\partial C_1} \right)_{T,P} L_{11}, \quad (9)$$

and the diffusion coefficient derived from Equation (2) in a similar fashion may be equated to this coefficient under the assumption that the volume velocity is zero. For other frames of reference this will not be the case, as shown by Bennett⁽⁷⁾.

For a constant diffusivity in a binary system Fick's second law is given by⁽³⁸⁾

$$\frac{\partial C_1}{\partial t} = D_{12} \nabla^2 C_1 \quad (10)$$

where t is the time. This equation is widely applied to unsteady state diffusion processes.

DILUTE GAS THEORY

The early theories of transport were developed for the so-called rigid sphere model of a molecule. This model although unrealistic served to clarify many points of concern in the general problem of predicting transport

properties by consideration of parameters related to the gas. In this manner it was determined that the coefficient of diffusion varies as the three-halves power of the temperature and is inversely proportional to the pressure and the square of the molecular diameter as well as the square root of the molecular weight.

The most sophisticated dilute gas theory available at the present time is the so-called Chapman-Enskog theory⁽¹³⁾ and within the utility of the assumptions made it is a rigorous theory. It is important here to point out the main assumptions and conditions of development associated with this theory. The theory is based on the Boltzman integro-differential equation written in terms of the distribution function $f(\underline{r}, \underline{v}, t)$ which represents the number of molecules in the volume element about point $\underline{r}$ which have velocities within a range about $\underline{v}$ at time t . The f of this integro-differential equation reduces to the Maxwell distribution for systems at equilibrium. It is only when the system is slightly disturbed from the equilibrium configuration that the derivatives of the flux vectors are linear consistent with the usual definition of transport coefficients. For this case the Boltzman equation is solved by a perturbation technique developed by Chapman and Enskog.

The transport coefficients are expressed in terms of a set of integrals $\Omega^{(l,s)}$ which result from consideration of the molecular collisions so that they involve the intermolecular force laws acting between the molecules. Collisions of higher order than binary are excluded from consideration. Consequently the theory is not applicable at densities where higher order collisions become important. Quantum effects are not considered in the theory because it is based solely on classical mechanics. The solution of the Boltzman equation is a series approximation to the distribution function. The first approximation in this series results from small gradients in the

constants of motion. In this approximation the resulting equations in the first derivatives of the mass, velocity, and temperature are commonly known as the Navier-Stokes equations or the "equation of change". The theory assumes that the dimensions of the containing vessel are large compared to the mean free path so that surface effects are negligible.

The Chapman-Enskog theory applies only to monatomic gases but in general it has been successful in predictions of diffusion of reasonably spherical polyatomic molecules. The theory assumes that the potential energy of interaction between two molecules is spherically symmetric. For non-polar molecules the Lennard-Jones⁽⁶⁻¹²⁾ potential is commonly employed. This potential between two molecules is

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (11)$$

Here the parameter ϵ is the depth of the potential well and σ is the radius at the point of zero potential. At large separations the molecules attract according to the inverse $\frac{1}{6}$ th power and at close distances they repulse each other by the inverse $\frac{1}{12}$ th power. This type of interaction has been quite successful in describing the behavior of many gases and it is expected that it will be useful for the gases considered in this investigation. This potential is convenient in many cases because of the ease with which certain integrals embodying it may be solved.

The development of the rigorous kinetic theory has shown that the first approximation to the mutual diffusion coefficient of a binary gas mixture is given by⁽³¹⁾

$$D_{12})_1 = 2.628 \times 10^{-3} \frac{(T^3 (M_1 + M_2) / 2 M_1 M_2)^{\frac{1}{2}}}{P \sigma_{12}^2 \int_{12}^{(1,1)} \cdot} \quad (12)$$

Now for the case of self-diffusion this reduces to

$$D_{11})_1 = \frac{2.628 \times 10^{-3} (T^3/M)^{\frac{1}{2}}}{P \sigma_1^2 \Omega_{11}^{(1,1)*}} \quad (13)$$

In these equations

$D_{12})_1$ and $D_{11})_1$ are the mutual and self-diffusion coefficients, cm^2/sec , respectively,

P is the pressure in atmospheres,

T is the temperature in $^{\circ}\text{K}$,

M_1 and M_2 are the molecular weights of species 1 and 2, respectively, and

σ_2 and σ_1 are the collision diameters in $\text{\AA}$ for 1-2 interactions and 1-1 interactions, respectively.

Now the collision integrals $\Omega_{12}^{(1,1)*}$ and $\Omega_{11}^{(1,1)*}$ are functions of the reduced temperatures $T_{12}^* = (kT/\epsilon_{12})$ and $T_1^* = (kT/\epsilon_1)$ where $\frac{\epsilon_{12}}{k}$ and $\frac{\epsilon_1}{k}$ are the molecular potential force parameters in $^{\circ}\text{K}$ for 1-2 and 1-1 interactions, respectively.

In this investigation the usual combining laws; namely,

$$\epsilon_{12} = (\epsilon_1 \epsilon_2)^{\frac{1}{2}} \quad \text{and} \quad \sigma_{12} = (\sigma_1 + \sigma_2)/2, \quad (14)$$

are employed for the calculations involving interactions between pairs of molecules of different species. The molecular parameters of the pure gases used in this investigation are given in Appendix H.

The Chapman-Enskog second approximation⁽¹³⁾ to the diffusion coefficient is given by

$$D_{12})_2 = \frac{D_{12})_1}{1 - \Delta}, \quad (15)$$

where the factor $(1-\Delta)$ is a function of the molecular weights, the mole fractions, and the viscosities of the two components as well as the temperature. In general the correction $(1-\Delta)$ approaches unity but if there are wide differences in the molecular weights of the components, it will be significant. Eerkens and Grossman⁽²⁰⁾ plot Δ as a function of M_2/M_1 and KT/ϵ_{12} for pure component 2. For a system such as $Kr^{85}-He$, Δ amounts to 0.032 so that an increase of slightly more than three per cent in the calculated diffusivity is indicated.

The self-diffusion coefficient of Equation (13) is the diffusivity of molecules of species one in a system of these same molecules and strictly speaking cannot be measured. The usual practice is to approximate the coefficient of self-diffusion by measurements of tracer molecules in a system of very similar molecules. If a radioactive isotope is used for this purpose, the intermolecular force parameters are assumed to be the same as those for the bulk gas because they are not affected to any great extent by the presence of the neutrons in the atomic nuclei. However, a correction for the differences in molecular weights must be made to convert the diffusion coefficient of a tracer gas to the self-diffusion coefficient. Thus the ratio of diffusivities is given by

$$\frac{D_{11}}{D_{11}^*} = \left(\frac{M_1^* + M_1}{2 M_1^* M_1} \right)^{\frac{1}{2}} \quad (16)$$

where D_{11}^* is the diffusion coefficient of the radioactive tracer gas in the bulk gas of the same species and M_1^* is the molecular weight of the tracer gas. It is immediately obvious that the ratio of the diffusivity of component 1 in another component 2 to the diffusivity of radioactive component 1* in the same component 2 is given by Equation (16) also.

DENSE GAS THEORY

In dense gas systems certain of the assumptions of the Chapman-Enskog theory are no longer valid. These are the assumptions that the molecular encounters are solely between pairs of molecules and that the molecules may be considered to be point masses. Any dense gas theory must contain a consideration of these assumptions and an evaluation of their effect.

In a dense gas two effects which become important because of the finite size of the molecules are (1) "collisional transfer" of momentum and energy and (2) change in the frequency of collisions. In the dilute gas theory the transfer of molecular properties was considered to be due only to the free motion (kinetic) of the molecules between collisions. However, it is easy to visualize the transfer of momentum or energy between two rigid spheres upon collision. To a greater or lesser extent this would be evident in a real gas. For diffusion it is not expected that any collisional transfer of mass would be important so that the main factor to be considered is the change in the frequency of collisions. The frequency of collision is increased because the molecular diameter is not negligible when compared with the average distance between molecules. On the other hand, the frequency of collision is decreased because the molecules are close enough together to shield each other from collisions.

In a somewhat qualitative manner Enskog⁽²¹⁾ developed a dense gas theory for rigid spheres that accounted for the collisional transfer and frequency change effects. The rigorous development of this theory is given by Chapman and Cowling⁽¹³⁾. Enskog considered a rigid sphere gas with molecules of diameter, σ . For a rigid sphere there are essentially only two body collisions and the collisions are instantaneous so that the "molecular chaos" assumption is valid no matter how great the density.

Enskog's derivation for self-diffusion in a system of identical molecules is represented as the ratio of the high density-diffusivity product, ρD , to the low density (generally 1 atm.) product $(\rho D)^0$ such that

$$\frac{\rho D}{(\rho D)^0} = \frac{1}{Y}, \quad (17)$$

where Y is a correction factor related to the probability of collisions. Now Y is identical to the virial expansion in the rigid sphere equation of state,

$$\frac{P}{\rho RT} = 1 + b_0 \rho Y \quad (18)$$

or

$$Y = \frac{1}{\rho b_0} \left[\frac{P}{\rho RT} - 1 \right], \quad (19)$$

where $b_0 = \frac{2}{3} \pi N \sigma^3$ is the rigid sphere second virial coefficient. The factor

$$y = \left(\frac{P}{\rho RT} - 1 \right) \quad (20)$$

is recognized as the rigid sphere compressibility factor and is usually equated to a dimensionless number y which may be written in the rigid sphere virial form as

$$y = b_0 \rho + \frac{5}{8} b_0^2 \rho^2 + 0.2869 b_0^3 \rho^3 + \dots \quad (21)$$

When these equations are substituted in Equation (17) above, the density-diffusivity product ratio is obtained in the form

$$\frac{\rho D}{(\rho D)^0} = \frac{\rho b_0}{y}. \quad (22)$$

Thus, according to this theory the predictions of diffusivities at elevated densities requires only a knowledge of the rigid spherical molecular model.

For real gases Enskog suggested that the pressure P of Equation (20) be replaced by the thermal pressure,

$T \left(\frac{\partial P}{\partial T} \right)_\rho$. This is equivalent to setting the internal pressure $\left(\frac{\partial U}{\partial V} \right)_T$ in the thermodynamic equation of state,

$$P = T \left(\frac{\partial P}{\partial T} \right)_\rho - \left(\frac{\partial U}{\partial V} \right)_T, \quad (23)$$

equal to zero. The thermodynamic equation of state is an expression of the fact that for a real fluid the attractive forces decrease the pressure because of the decrease of the internal energy, U , with density.

When the thermal pressure replaces the pressure P in Equation (20), it is found that

$$\gamma = \left[\frac{1}{\rho R} \left(\frac{\partial P}{\partial T} \right)_\rho - 1 \right]. \quad (24)$$

In order for this form to be used with Equation (22), it is apparent that b_0 must now become an empirical parameter because as $\rho \rightarrow \rho^0$ it is required that

$$\rho b_0 \rightarrow \gamma, \quad (25)$$

in order for both sides of the equation converge to unity.

Now, when the statistical mechanical virial expression,

$$\frac{P}{\rho R T} = 1 + B\rho + C\rho^2 + \dots, \quad (26)$$

is differentiated with respect to temperature T at constant density ρ then it is apparent that in the limit of small densities approaching zero the b_0 of Equation (25) becomes

$$b_0 = \left(B + T \frac{dB}{dT} \right) \quad (27)$$

where B is the usual statistical mechanical second virial coefficient as defined by the virial expansion of Equation (26).

Thus, if the temperature derivatives of the pressure of a given gas at constant density can be obtained, the diffusivity at high densities can be calculated from Equation (22) with y determined by Equation (24) and b_0 determined by Equation (27).

Enskog's⁽²¹⁾ equation for the ratio of the viscosity, μ , of a rigid sphere fluid at high density to its viscosity at low density, μ^0 , is given by

$$\frac{\mu}{\mu^0} = \rho b_0 (\gamma^{-1} + 0.8 + 0.761\gamma). \quad (28)$$

Again the substitution of thermal pressure for pressure in Equation (24) may be made for real gases. Consequently, b_0 may be eliminated between Equations (22) and (28) to give

$$\frac{\rho D}{(\rho D)^0} = \frac{\mu}{\mu^0} (1 + 0.8\gamma + 0.761\gamma^2)^{-1}. \quad (29)$$

In order to determine the self-coefficient of a gas at a high density by Equation (29), it is required that the ratio of the viscosity at this density to that at the low density (atmospheric pressure) be known as well as the temperature derivative of the pressure for this density at the given temperature.

The Enskog equation for viscosity accurately describes some of the data for non-polar compressed gases such as nitrogen⁽¹³⁾. However, it will not predict viscosity density data on methane, ethylene or propane unless b_0 decreases (non-linearly) with pressure⁽¹¹⁾.

Thorne⁽⁸⁷⁾ has generalized Enskog's dense gas theory for application to dense gas mixtures. The result for diffusion in dense gas binary mixtures

may be written as

$$\frac{\rho D_{12}}{(\rho D_{12})} = \frac{1}{Y_{12}}, \quad (30)$$

where the frequency factor Y_{12} is given by

$$Y_{12} = 1 + \frac{\pi}{12} n_1 \sigma_1^3 (8 - 3\sigma_1/\sigma_{12}) + \frac{\pi}{12} n_2 \sigma_2^3 (8 - 3\sigma_2/\sigma_{12}) + \dots \quad (31)$$

and n_1 and n_2 are the partial number density molecules of components 1 and 2, respectively, in the mixture.

Within recent years several theories of transport in dense media have been developed from non-equilibrium statistical mechanics. Rice⁽⁷³⁾ gives a very good review of the various theories with their inherent assumptions and shortcomings. This so-called Kirkwood theory⁽⁷³⁾ is based in part upon analogies with Brownian motion theory. The principal problem is the evaluation of the non-equilibrium pair distribution function. Along these lines theoretical verification of Enskog's dense gas equations have been made by several investigators^(44,71). For a dense rigid sphere fluid the non-equilibrium pair distribution function is identical with the Y of the Enskog theory. Other than this verification the development of the theory has not proceeded to the degree that useful calculations may be made.

CORRESPONDING STATES THEORIES

The principle of corresponding states is based on the concept that physical properties of different substances obey the same laws in terms of certain reduced variables. In general there are two methods of obtaining the reduced variables (1) the well-known reduction based on critical constants and (2) the reduction based on molecular force constants.

Intuitively, this idea was extended to transport properties with the

basis made in a straightforward dimensionless grouping attack. However, recently Rice⁽⁷³⁾ has shown that with the spherically symmetric intermolecular form necessary for correspondence of equilibrium properties the law of corresponding states can be derived for transport properties. His method utilizes the quantum mechanical expressions for the transport coefficients in terms of the autocorrelation functions. However, in the limit as Planck's constant h vanishes the classical results are obtained. Self-diffusion in the strict sense is only classical, but by considering it as the mutual diffusion of a tagged species the formulation may be made so that the reduced self-diffusion coefficient D^* is determined to be a function of the form

$$D^* = \frac{D}{\sigma} \left(\frac{M}{\epsilon} \right)^{\frac{1}{2}} = f(T^*, \rho^*) , \quad (32)$$

where

$$T^* = (kT/\epsilon) ,$$

and

$$\rho^* = \rho \sigma^3 .$$

It is quite obvious that this is dimensionally consistent.

For spherical non-polar molecules obeying the Lennard-Jones⁽⁶⁻¹²⁾ potential the critical constants can be related to the molecular parameters. Thus, a reduction with critical constants readily follows from Equation (32) and the reduced self-diffusion coefficient D_R is given by

$$D_R = D M^{\frac{1}{2}} \rho_c^{\frac{1}{2}} T_c^{-\frac{1}{2}} = D_R(P_r, T_r) , \quad (33)$$

where

$$P_r = P/\rho_c ,$$

$$T_r = T/T_c ,$$

and P_c and T_c are the critical pressure and temperature, respectively, of the gas.

Slattery and Bird⁽⁷⁸⁾ applied Equation (33) to most of the available data for self-diffusion and binary diffusion coefficients of dilute gases excepting mixtures containing air. Mixtures containing helium and hydrogen (quantum effects) and water vapor (non-polar) did not correlate with the bulk of the data so that they were not included in the correlation. This correlation is in the form of Equation (33) and

$$(D_{12})_r = \frac{3.882 \times 10^{-4}}{P_r} (T_r)^{1.823}, \quad (34)$$

where

$$(D_{12})_r = D_{12} M_{12}^{\frac{1}{2}} P_{c12}^{\frac{1}{2}} T_{c12}^{-\frac{5}{6}},$$

$$M_{12} = 2 M_1 M_2 / (M_1 + M_2),$$

$$P_{c12} = (P_{c1} P_{c2})^{\frac{1}{2}}, \quad T_{c12} = (T_{c1} T_{c2})^{\frac{1}{2}}.$$

This equation represents the experimental data of the systems studied as accurately as the Chapman-Enskog Equation (13) with Lennard-Jones viscosity parameters. If the Lennard-Jones collision integral $\Omega^{(1,1)*}$ is plotted vs. $\frac{KT}{\epsilon}$ the slope varies from about -0.1 to about -0.5 over the normal range of moderate temperatures⁽²²⁾. Consequently, Equation (13) shows that D_{12} varies as the temperature T to the 1.6 - 2.0 power in agreement with the Slattery correlation.

Other corresponding states reduction schemes involve dividing the diffusion coefficient by its critical value. Since a critical diffusivity is not readily measured this method has little practical application. However, techniques⁽²²⁾ which define critical diffusivities on the basis of the dilute gas theory have been developed to correlate a large amount of dilute gas experimental data.

The only available development of a corresponding states treatment for dense gas diffusion coefficients is that due to Slattery and Bird⁽⁷⁸⁾ for self-diffusion coefficients. This development utilizes the Enskog dense gas theory discussed above. The defining equation is Equation (28) written as

$$\frac{PD}{(PD)^0} = \frac{\mu}{\mu^0} Z (1 + 0.8\gamma + 0.761\gamma^2)^{-1}, \quad (35)$$

where Z is the compressibility factor. With the compressibility factor of the generalized corresponding states theory the dimensionless number γ defined by Equation (24) may be written as

$$\gamma = Z \frac{1 + (\partial \ln Z / \partial \ln T_r)_r}{1 + (\partial \ln Z / \partial \ln P_r)_r} - 1. \quad (36)$$

Thus, Slattery and Bird⁽⁷⁸⁾ were able to prepare a generalized self-diffusion chart for $\frac{PD}{(PD)^0}$ as a function of reduced pressure and reduced temperature. This required a knowledge of Z with its temperature and pressure derivatives, and the viscosity ratio, $\frac{\mu}{\mu^0}$. These factors were determined from enlarged generalized charts such as the Hougen and Watson⁽³³⁾ charts.

It should be emphasized that the Slattery chart is not based on experimental data. Secondly, because P_r was used as a parameter, the main variation in the chart may be attributed to the compressibility factor.

DILUTE GAS EXPERIMENTAL WORK

In this section a brief review is made of the prior low pressure experimental investigations that are important to the understanding and development of the research recorded here. In the main a fairly large body of ex-

perimental diffusion results exists for various gas pairs at or about room temperature and at or below one atmosphere total pressure. Eerkens and Grossman⁽²⁰⁾ have tabulated a large number of these results which they compiled from other sources such as Hirschfelder, et al.⁽³¹⁾ and Wilke and Lee⁽⁹⁰⁾.

In general two types of diffusion measurement apparatus, each based on a statement of Fick's law, have been commonly used. The "quasi-stationary" method is based on Fick's first law Equation (5). The unsteady state method is based on Fick's second law Equation (10) and involves a solution of this partial differential equation with suitable boundary conditions pertinent to the particular experiment. Jost⁽³⁸⁾ and Crank⁽¹⁷⁾ give rather complete summaries of the mathematical description of the various geometrical diffusion assemblies with various initial distribution functions of concentration with respect to time. With certain qualifications a quasi-stationary system has a much more simpler mathematical description than an unsteady state assembly.

The more common types of unsteady state methods are variations of one of the oldest types, the Loschmidt type⁽⁴⁵⁾. This equipment usually consists of two cylinders, one containing a high concentration of the diffusion gas, and the other a low concentration. Means are provided for bringing the tube faces together or a valve is opened between them so that diffusion may occur. Concentration measurements may be in the form of a detection device say at one end of the tube or the total amount of the diffusing material in one of the tubes may be determined by mass spectrometer or other means. In the first case the usual Fourier power series solution⁽¹²⁾ of the concentration in terms of the diffusivity, length of tubes and time may be used to evaluate the diffusion coefficient. In the second case the integration of the power series solution over the length of the tube provides the defining equation.

The theory of the quasi-stationary state diffusion cell that is of interest here is given in several places^(34,38). The physical system may be described as two chambers separated by a porous diaphragm or a capillary path. Initially a concentration difference of the diffusing species 1 is produced between the chambers A and B. After the initial transients die out it is assumed that a linear gradient in concentration of species 1 is maintained in the plug. Also, it is assumed that the chambers are well mixed so that all of the resistance to diffusion occurs in the capillary.

With these assumptions the concentration of species 1 in the capillary is given by

$$\frac{dC}{dx} = \frac{C_A - C_B}{L} \quad (37)$$

where C_A and C_B are the concentrations of species 1 in the well mixed cell chambers A and B, respectively, and L is the length of the capillary between the chambers and along x . Now the amount of the diffusing component crossing the plane normal to the opening between the chambers is given by Fick's first law Equation (5). Thus, for the A side

$$\frac{dC_A}{dt} = \left(\frac{C_A - C_B}{L} \right) \left(- \frac{DA}{V_A} \right), \quad (38)$$

and for the B side

$$\frac{dC_B}{dt} = \left(\frac{C_A - C_B}{L} \right) \left(\frac{DA}{V_B} \right), \quad (39)$$

where V_A and V_B are the chamber volumes of the A and B sides, respectively, A is the cross-sectional area of the diffusion path, and D is the diffusion coefficient.

When Equation (39) is substituted from Equation (38) the defining differential equation,

$$\frac{d(C_A - C_B)}{dt} = - \frac{DA}{L} \left(\frac{1}{V_A} + \frac{1}{V_B} \right) (C_A - C_B), \quad (40)$$

results. The integrated form of the equation is

$$\log_e (C_A - C_B) = - K D t + R_1 \quad (41)$$

where

$$K = \frac{A}{L} \left(\frac{1}{V_A} + \frac{1}{V_B} \right). \quad (42)$$

Equations (41) and (42) are the equations which are important in diffusion investigations with the quasi-stationary state type diffusion cell. The cell constant, K , may be determined from the physical dimensions of the cell if these can be determined. For the case of a capillary as the connecting path between the chambers this is possible and A is the average cross-sectional area of the tube of length L . For a plug of porous media, A and L are the effective cross-sectional area and length, respectively. The normal procedure is to calibrate such cells with a system of known diffusivity.

From an historical standpoint the Northrup-McBain^(49,62) type of cell corresponding to the description above was first applied to diffusion measurements in liquids. Ney and Armistead⁽⁶²⁾ were the first to apply the quasi-stationary method to gaseous diffusion measurements in their investigation of the self-diffusion coefficient of uranium hexafluoride vapor. Samples were continuously withdrawn to a mass spectrometer. Other sampling procedures used for this type of cell have included the taking of samples at preset times and analyzing for radioactive tracer⁽⁷⁶⁾ or taking micro-samples at various times and analyzing by thermal conductivity means

for a gas component⁽⁸⁰⁾.

Hutchinson⁽³⁴⁾ employed a quasi-stationary cell which did not require sampling. Each chamber of the cell was operated as an ionization chamber to measure the ionization current resulting from argon-41 radiation in a bulk gas of argon-40 and thus, follow the progress of diffusion. This cell is the low pressure forerunner of the high pressure ionization cell of this investigation as well as others^(10,64,61) used in recent years. The analysis of a cell of this type requires a knowledge of the relationship between the ionization current and the concentration of the radioactive species. Usually, it is found that the ionization current is proportional to the radioactive species concentration. When this is the case Equation (41) can be rewritten as

$$\log_e (I_A - f I_B) = -KDt + R_z \quad (43)$$

where I_A and I_B are the ionization currents from the A and B sides, respectively. Here, f is the ratio of the A side current to the B side current for the same radioactive species concentration within the range of interest. A correction term in the time is made if the half-life of the radioactive species is short enough with respect to the time for diffusion as to cause appreciable error.

Schäfer and Schuhmann⁽⁷⁶⁾ determined the self-diffusion coefficient of krypton and mutual coefficient of argon in krypton between 200°K and 473°K and also the diffusion coefficient of neon in argon between 90°K and 473°K. All measurements were carried out at pressures less than one atmosphere. The apparatus was of the Ney-Armistead type with provision for removing samples at given times to analyze either by mass spectrometer for the binaries or by Geiger counter for Kr-85 in the self-diffusion determina-

tion. These investigators did not take many samples as a function of time but merely one at the beginning of an experimental run and one at a preset time after opening the stopcock between the diffusion chambers. It is doubtful that the initial non-linearity of the concentration gradient in the tube greatly affected the results because of the large chamber volume to tube volume ratio. The diameter of the interconnecting tube was two tenths of a centimeter with an apparent significance of at best two figures. However, convection may have played an important role with this size tube because of the poor temperature regulation ($\pm 1^\circ\text{C}$).

For the above or other reasons the results of Schafer and Schulmann⁽⁷⁶⁾ for the argon-krypton system were considerably higher than a determination made by Srivastava and Srivastava⁽⁸⁰⁾. These investigators used a Ney-Armistead type diffusion cell with microsample withdrawal at different times for thermal conductivity analysis. They studied the mutual diffusion of binary gas mixtures of argon, helium, and xenon in one case⁽⁸¹⁾ and argon, neon, and krypton in the other case⁽⁸⁰⁾ over the temperature range $0-45^\circ\text{C}$. The data of Srivastava and Srivastava⁽⁸⁰⁾ is believed to be more accurate than that of Schäfer and Schuhmann⁽⁷⁶⁾ in view of the fact that they obtained excellent representation of the concentration versus time data according to the theory of the experiment, also the bore diameter of the tube was determined with greater accuracy and the temperature control of $\pm 0.01^\circ\text{C}$ was much better.

Groth and Harteck⁽²⁶⁾ used a Loschmidt diffusion cell to determine the self-diffusion coefficient of krypton. In Table I a comparison of the three determinations of atmospheric pressure diffusivities applicable to this investigation are given for 273°K in the binary cases and 293°K in the krypton self-diffusion case. Shown also are the results for the Ne-A binary which provides further comparison. It is interesting to note that there is

better agreement for this system. The Kr-Kr coefficient determined with Lord Kelvin's method⁽¹³⁾ by Srivastava and Srivastava may be error due to the assumptions in determining self diffusivities in this manner.

TABLE I
COMPARISON OF EXPERIMENTAL ATMOSPHERIC
DIFFUSIVITIES OF SYSTEMS OF INTEREST

System - - - - -	<u>Kr-Kr</u>	<u>A-Kr</u>	<u>Ne-A</u>
Temperature °K	293	273	273
Investigator:			
Grath and Harteck ⁽²⁶⁾	0.09 ± 0.004	---	---
Schafer and Schulmann ⁽⁷⁶⁾	0.090	0.197	0.285
Srivastava and Srivastava ⁽⁸⁰⁾	0.096*	0.119	0.276

* Determined by Lord Kelvin's method⁽¹³⁾

Schäfer and Schuhman⁽⁷⁶⁾ found that the product PD of pressure and diffusivity was not constant over the pressure range 250 to 700 mm Hg. for the case of the neon-argon system at -183°C. The product increased about 66% over this range. Schäfer⁽⁷⁷⁾ also found marked increases of this product for binary diffusivities of several gases in sulphur dioxide at or below 1 atmosphere.

DENSE GAS EXPERIMENTAL INVESTIGATIONS

There are relatively few recorded investigations of high pressure gaseous diffusion. The first studies in this direction were undertaken by

Timmerhaus and Drickamer^(88,89) and Robb and Drickamer⁽⁷⁴⁾. These investigators measured the diffusion coefficient for carbon-14 dioxide diffusion in carbon dioxide to determine the self diffusion coefficient of carbon dioxide. The equipment used was of the Loschmidt type modified for application at high pressures. At the low concentration end of the diffusion tube an anthracene crystal was mounted at the end of a light pipe and window combination that could withstand the pressure encountered. Thus, the amount of radioactivity reaching the end could be determined by the count rate of the scintillations as amplified through a photomultiplier-ratameter circuit. The diffusion tube was filled with a porous material so that a calibration procedure was indicated. This was accomplished by using a low pressure cell (long diffusion tube) and using the Chapman-Enskog theory prediction of the low pressure self-diffusion coefficient to calibrate the cell. An intermediate cell overlapped the pressure range of the low pressure cell in order that it could be calibrated against it. Another higher pressure cell which was employed at pressures up to 1,000 atmospheres was calibrated against the intermediate cell.

A density-diffusivity product versus density plot of the Drickamer^(74,88,89) carbon dioxide data shows very high scatter ranging to ± 20 per cent. The very high scatter of this data contrasts sharply with the carbon dioxide self-diffusion coefficient data obtained by O'Hern^(64,65) with a high pressure ionization cell. This data was of remarkably good precision (± 1 per cent). The density-diffusivity product for the 35°C isotherm increased slightly in the low density region and then gradually dropped to a few per cent lower than the 1 atmosphere value at the higher densities up to 16 moles per liter. The density-diffusivity product for the 100°C isotherm increased to five per cent over the low pressure value

at six moles per liter and then gradually decreased again. The Enskog dense rigid sphere gas theory with Lennard-Jones collision diameters would not predict the results.

The diffusion cell used by O'Hern^(64,65) was the first application of an ionization detection method to a high pressure diffusion cell. This cell consisted of two high pressure ionization chambers separated by a porous bronze plug. Another cell with the interconnection consisting of four 0.037" drilled holes performed reasonably well below 20 atmospheres, but at higher pressures the rate of transfer was accelerated possibly by convection. The ionization currents were of the order of 10^{-13} to 10^{-10} amperes.

Jeffries and Drickamer⁽³⁶⁾ measured the self-diffusion of methane to 300 atmospheres using tritiated methane as the tracer and the Drickamer equipment described above. They found good agreement with the rigid sphere Enskog theory to moderate densities. The carbon dioxide-methane system was also investigated by these authors⁽³⁷⁾ with carbon-14 dioxide as the tracer.

Becker, Vogell, and Zigan⁽⁶⁾ found that the density-diffusivity product for nitrogen self-diffusion was essentially constant with pressure in the range 20 to 90 atmospheres at 20°C. However, a 30 per cent increase in the self-diffusion coefficient-density product for carbon dioxide was obtained for the pressure range 15 to 52 atmospheres at 20°C. This increase was attributed to coagulation of the CO₂ molecules in this pressure range. A quasi-stationary cell was employed with mass spectrometer analysis of nitrogen-15 and carbon-13 dioxide.

Chou and Martin⁽¹⁴⁾ employed the O'Hern equipment to study the diffusion of carbon-14 dioxide in carbon dioxide-hydrogen mixtures at 35°C and 100°C at densities up to 10 moles per liter. Also, they studied the diffu-

sion of carbon-14 dioxide in carbon dioxide-propane mixtures at 37.8°C to 4 moles per liter and at 100°C to 10 moles per liter. The density-diffusivity product increased slightly with density and then decreased for the majority of the mixture isotherms. In the other cases the density-diffusivity product was essentially constant for varying density. The carbon dioxide-hydrogen system diffusivities could be correlated by a function which included the mole fraction of hydrogen in the mixture with a temperature dependence directly proportional to the absolute temperature raised to the 1.27 power.

Mifflin and Bennett⁽⁶¹⁾ used an ionization quasi-stationary state diffusion cell to measure self-diffusion coefficients for argon at 49.4°C and up to 11 mole/liter. The current measuring device, a Lindemann electrometer, and the weak radiation of the argon-37 tracer may well have accounted for the very high scatter in this data. It was stated that the Enskog theory based on FVT data was more successful than the rigid sphere correction for predicting the data. However, a critical interpretation could not be made because of the scatter of the data.

Berry and Keeller⁽⁸⁾ studied the diffusion in the binary systems hydrogen-nitrogen and methane-ethane at temperatures of 40°C, 60°C and 77°C to 18 moles per liter and of the binary systems nitrogen-methane and nitrogen-ethane at 40°C to 8.5 moles per liter. The diffusion cell was of the Loschmidt type with mass spectrometric analysis. For all the cases the density-diffusivity product predicted by the Thorne⁽⁸⁷⁾ dense gas mixture correction with Lennard-Jones collision diameters diverged below the experimental data in the high density region. However, the density-diffusivity product decreased rather markedly with density for all cases. For the methane-nitrogen and ethane-nitrogen systems where it could be applied, the Slattery-Bird reduced state self-diffusion correlation used with combined

critical constants gave somewhat better agreement with the data. The temperature dependence of the results was best described by an exponential form of the type

$$D = b e^{-E/RT} \quad (44)$$

which has been successful for liquid diffusion characterization.

A modification of the O'Hern⁽⁶¹⁾ cell was used by Bray⁽¹⁰⁾ to determine the diffusion coefficient of tritiated hydrogen through hydrogen and in mixtures of hydrogen and carbon dioxide and in mixtures of hydrogen and argon at 35° and 100°C up to densities in the 12 mole per liter range. In general the density-diffusivity product decreased with density although not to the extent predicted by the Enskog dense gas theories. This correction when calculated using PVT data more nearly predicted the hydrogen self-diffusion than the calculation based on the solid sphere model. The density-diffusivity products calculated by the Thorne binary solid sphere theory diverged well below the experimental values for the mixtures studied.

A study of the various high pressure investigations shows that for the Loschmidt unsteady state type cells the density-diffusivity product decreases with density to a much greater extent than determinations made by quasi-stationary type cells. Another difference occurs in the temperature dependence of the results. In general unsteady state investigations have shown the exponential form of Equation (44) peculiar to liquid theories. Whereas, the ionization quasi-stationary state studies appear to favor a power law form such as

$$D = a T^n, \quad (45)$$

predicted by the dilute gas theory. It should be emphasized, however, that these equations are based on only a couple of isotherms in most cases.

III. DESCRIPTION OF EXPERIMENTAL EQUIPMENT

The primary units of equipment for this investigation were the ionization and scintillation diffusion cells. The associated equipment consisted of high pressure generating and measuring equipment, constant temperature baths, the electronic instrumentation necessary for measuring the output of the diffusion cells and regulating the various components. The general layout of this equipment for the purpose of making diffusion runs is shown by Figure 1. The diffusion cells and temperature baths were inside the floor to ceiling hood as a safety precaution should a leak of the radioactive gas occur. The instrumentation was on one side of the hood and the pressure measurement and generation equipment was on the other side. The description of the equipment given here proceeds with a description of the ionization cell proper, the porous plug inserts, the electronic circuitry for measuring the ionization currents. Attention is then focused on the scintillation cell and the necessary electronic circuitry for measuring the counting rates. Finally the service equipment is described.

FIGURE 1: THE UNIT

THE IONIZATION CELL

Before the ionization cell of this investigation is described a brief description of the working of an idealized ionization cell is in order. A quasi-stationary state diffusion ionization cell consists basically of two ionization chambers separated by a porous membrane or capillary. Each ionization chamber consists of a center electrode insulated from the chamber wall which is usually the other electrode. An electric field is maintained between these electrodes by the application of a potential across them. With radioactive gas in the chamber a current passes between the electrodes because of the electric field induced electron and ion flow which results from the ionization of the gas by the radiation from the decay of the radioactive species. A diffusion experiment is carried out by introducing a high concentration of radioactive tracer in one side of the cell and obtaining the time rate of change of the ionization currents from the sides with time. The diffusion coefficient of the radioactive tracer is obtained from Equation (43).

The important features of the high pressure ionization cell used in this experimental investigation are shown by Figure 2. Because each half of the cell is essentially a mirror image of the other half, a half-sectioned diagram is presented. The right side is shown in sectional form so that the layout of the inner construction is apparent. In this discussion the porous plug inserts are discussed separately because of their application in both cells and singular design characteristics.

The ionization cell consisted essentially of two (6" dia. x $2\frac{1}{2}$ ") 416 stainless steel flanges each with an ion chamber (1" dia. x 1" deep) bored in it and bolted across a steel encased porous plug insert of nominal one inch width. Thirteen one-half inch carbon steel bolts fastened the flanges

FIGURE 2
THE IONIZATION CELL

(A and B sides) together. This cell featured quarter inch stem in-cell valves, a stirrer mechanism, and a unique electrode and current pickup assembly. Axle attachments and axle housing mounts provided the means for rocking (stirring) the cell. Figure 3 is a photograph of the cell in a disassembled condition.

The heart of an ionization cell is the electrode and current pickup assembly. The major components of the type of assembly used in this ionization cell are numbered in Figure 2. The stainless steel center electrode 1 is separated from the guard ring 2 by Kel-F insulation. This guard ring is in turn insulated by a Kel-F sleeve from the outer electrode concentric shell 3 which is insulated from the cell body by a polycarbonate resin plastic (Lexan). All of these electrodes are machined with shoulders at 60° and pressed into the coned chamber opening so that they protrude at the outside end of the cell body flange. The electrode holding assembly 4 is designed to hold the electrodes in place with sufficient force to maintain low pressures. A design of this type gives even better pressure tightness as the pressure increases. The outer electrode sleeve is held by a separate Teflon insulated holding nut. The guard sleeve has a steel washer which is insulated from the outer electrode holding nut and the center electrode holding nut but is free to move. The final hold and fastening is provided by the center electrode holding nut. Kel-F washers are used as insulators. The pickup electrode 5 consists of a length of 1/16" stainless steel rod which is inserted through the axle hole to impinge upon the indented end of the center electrode. The pickup electrode is insulated from the axle by Teflon bushings and is forced inward by the spring assembly 6. A hollow 1/8" pipe plug houses the spring which acts on the pickup electrode through a Kel-F bushing. A copper sleeve 7 about the pickup electrode

transmits the current to the Teflon pickup cable and current measuring circuitry. A detachable springloaded high voltage input assembly (not shown) provided the means of introducing negative voltage to the outer electrode.

Certain design and development procedures used in the construction of the electrode assembly are of interest. The center electrode was machined from 303 stainless steel and polished to a high degree. The guard ring has a lip on it to prevent the outward extrusion of the Kel-F insulation when the assembly is tightened. The Kel-F was forced into the guard ring under vice pressure at an elevated temperature. After this intrusion the center electrode hole was machined into the solid Kel-F center of the guard ring unit. The other Kel-F and Lexan sleeves were machined with 60° flares. Polycarbonate resin (Lexan) was selected for the outer insulation because of its superior resistance to deformation. Here, electrical resistance is not of high importance but structural properties are. The outer electrode was machined from 416 stainless steel with a concentric wall thickness of 1/32" at a spacing of 5/64" from the cell body wall.

The design of an electrode assembly for a high pressure ionization chamber entails many problems. However, the chief problem is concerned with the insulation of the electrodes. For the small currents encountered it is readily apparent that surface leakage and insulation stress current effects could easily mask any measurements made. For this reason only Teflon and Kel-F insulators have been used because of their excellent electrical resistance properties and low water absorption. Because the best operating characteristics of the vibrating reed electrometer are for the case of the input at or near ground potential the outer negative electrode was introduced. Now center electrode potential was obtainable with ground zero cell body advantages. At no place except within the ion chamber itself could current pass from one electrode to the other without being grounded by a

FIGURE 3: IONIZATION CELL PHOTOGRAPH

guard ring or shield. Each electrode could have substantial leakage to ground but only for ionization in the chamber could current flow from one electrode to the other⁽⁴¹⁾.

A $2\frac{1}{2}$ " diameter by 1" nominal width stainless steel insert housed the porous plug. In each face $1\frac{1}{4}$ " I.D. by $1/8$ " thick Teflon O'rings sealed against the well polished surfaces of the insert cavities of the cell body flanges.

As far as is known the ionization cell used in this investigation was the first such cell to employ chamber stirring. The stirring mechanism used consisted of a pendulum within the cell chamber. The pendulum was actuated by rocking the cell about its axis. The arrangement is shown by Figure 2. The porous plug insert supported the stirrers. A stirrer pin (0.039 ") protruded into the top of the facing chamber from each face of the porous plug insert. On each pin the pendulum stirrer for that chamber was hung. A stirrer consisted of a $1/16$ " diameter by $7/8$ " long stainless steel rod upon which (at $\frac{1}{4}$ " from the top) a shorter rod was silver soldered on each side to flare out at 30° and down. Thus, a three pronged pendulum was the result. A hole near the top provided the means of hanging the stirrer on the pin protruding from the porous plug face. Also, in the cell chamber between the outer electrode and the chamber wall a $1/16$ " diameter glass rod was inserted. When the cell was rocked about its axis the rolling motion of the glass rod provided additional stirring.

Another difference between this cell and other high pressure ionization cells is that in-cell valves were used to obtain complete isolation of the cell chambers. A $\frac{1}{4}$ " file hardened valve stem with 30° cone provided closure against the seat close to the cell chamber. The $1/8$ " hole into the chamber was somewhat larger than desired but it should have provided an area large enough so that no capillary diffusion paths due to in-

complete mixing were present. The valve stem was packed with graphite impregnated Teflon packing. A packing gland and nut with internal stem threads completed the assembly. A $1/16$ " hole leading into the stem area provided the gas inlet. A specially designed cell body tubing fitting with a hardened cone 60° tubing flare seal was necessary in order to make the sharp tubing bends at the inlet.

Over the electrode holding assembly at each end a stainless steel axle attachment was fastened to provide coverage of the holding assembly as well as provide the axle necessary for rocking the cell. This axle was a $13/16$ " diameter 416 stainless steel rod. Over the axle the brass axle housing was fitted. The axle housing contained the signal outlet port and also the center line hole for the spring loading assembly. These were both $1/8$ " pipe threaded holes. A ($3/16$ " flare to $1/8$ " pipe) copper tubing fitting allowed the threading of the Teflon output cable (0.10 ") into the housing assembly. About the axle three Teflon packing rings with packing gland provided the axle to housing seal.

POROUS PLUG INSERTS

Three different porous plugs were used in this investigation. Each plug was mounted in the $2\frac{1}{2}$ " diam. by 1" nominal width 303 stainless steel insert mentioned previously. This insert was provided with a $1\frac{1}{4}$ " I.D. Teflon O'ring seal in each face. The O'ring was fitted so that it very nearly fitted its cavity. Thus, metal to metal contact at the plug to cell body interface could be obtained in order to eliminate any diffusion paths into the O'ring groove. The three porous plugs used in this investigation are identified by the porous mediums used as well as by the cell application. Porous Plug A was a porous plug made up of a bundle of 67 glass

capillaries which was used in the ionization cell. Porous Plug B was a 10 micron porous ceramic filter used in the ionization cell. Porous Plug C was a 25 micron retention porous ceramic filter used in the scintillation cell.

The preparation of the glass capillary porous plug involved a considerable amount of endeavor. Because it was desired to obtain diffusion coefficients on an absolute basis, it was necessary to have a plug with known geometrical characteristics. For this purpose seven redrawn Pyrex (Corning Glass) capillaries twelve inches long and approximately 0.025 cm bore diameter were purchased. The average cross-sectional area of these long capillaries was determined by filling them with mercury and weighing this volume of mercury. The length was determined by "shooting" with a cathetometer. Each of the long capillaries was broken up into ten short capillaries. The ends of these capillaries were sanded smooth, cleaned, and placed in an assembly which allowed mercury to be threaded through the capillary into a bulk reservoir at each end. The resistance of the thread of mercury was measured with a Mueller resistance bridge. The lengths were determined by measuring with a micrometer. From this the average cross-sectional area for each of the short capillaries was obtained. Both of these calibrations are given in Appendix F. For the 67 short capillaries used the total cross-sectional area for the plug as obtained by the two methods agreed to within 0.1 per cent.

After the resistance measurements were made the outside of each capillary was lightly sanded and both ends were capped off by a small application of epoxy paste. The epoxy used in the mounting of the glass capillaries was a low-coefficient of expansion, high temperature epoxy. Several days were allowed for the slow room temperature set-up of the epoxy capping the ends. After this the 67 capillaries were placed side by side on a strip of Teflon

sheet and a hot solution of the epoxy was poured over them. The ends of the strip were very quickly brought up and the capillaries formed into a bundle and wired together. After this had set-up the plug was placed in the steel plug insert and bonded in place with more of the epoxy in the usual fashion. The protruding ends of the capillaries were sanded down beginning with a coarse paper and ending with a fine (600 grain) wet carborundum paper. The final length of the capillaries in the plug was 0.9618 inches.

In order to prepare the porous ceramic plugs for setting in the steel insert the plug was first coated with a layer of epoxy resin in such a manner that seepage into the plug did not occur. In order to do this a high temperature (150°C) curing epoxy mixture was allowed to almost set up by keeping at 100°C for a given length of time. Immediately this was applied to the surfaces of the porous ceramic plug. The epoxy cooled quickly to form a paste so that practically no seepage occurred. The epoxy was allowed to continue setting up at room temperature for several days. The plug was then mounted in the stainless steel plug and bonded in place with more epoxy in the usual manner. After the epoxy resin was cured the porous plug was faced off by a diamond cutting tool. A solution of Dri-Film and benzene was filtered through the plug and it was baked out at 150°C. For the ionization cell plug (Porous Plug B) a small hole (0.039"dia.) was drilled into each face directly opposite each other and right above the epoxy resin about the porous plug. A small bent pin which supports one of the pendulum stirrers was secured in each hole.

The ionization cell porous ceramic plug (Porous Plug B) was a nominal 3/4" dia. 10 micron retention porous ceramic filter (Corning Glass) which had a mean particle size of 25 microns. The plug was 0.963 inches wide.

For the scintillation cell the porous plug (Porous PlugC) was a nominal 3/4" dia. 25 micron retention porous ceramic filter with a mean particle size of 52 microns diameter. The plug was 1.000 inches wide.

IONIZATION CURRENT MEASURING CIRCUITRY

The ionization current from each side of the ionization cell was measured by a Cary Model 31 (Applied Physical Corp.) vibrating reed electrometer driving a Multiple Range Brown Model 39 (Minneapolis-Honeywell) recording potentiometer. For the long diffusion runs a method of switching between the chambers with time was provided by a timer and pneumatic switching assembly. In Figure 4 the ionization cell current measuring and automatic switching circuits are shown.

Five 45 volt "B" batteries provided the ionization cell voltage with the outer electrode at 220 volts negative to ground. The input to the cell was through 1/4" I.D. flexible copper hose attached to a spring loaded electrode assembly which fitted the axle attachment to contact the fastening nut on the outer electrode sleeve. The output cable for a chamber was threaded through 3/16" copper tubing which lead to a switch box assembly. The copper tubing served as an electrical shield as well as the means of introducing and keeping a dry CO₂ atmosphere (8psig) in the axle housing. The copper tubing to signal line space was packed off at the switch box. The switch box contained a rotary ceramic switch and the housing for the 10¹¹ ohms Hi-Meg (VictoreenCo.) resistor used. The housing switch was made so that the vibrating reed electrometer head could be inverted to set upon it with contact being made from the output side of the switch to the pickup electrode of the head. The switch connections were made in such a fashion that when one side of the cell was connected to the head input the other side was grounded.

FIGURE 4: CURRENT MEASURING CIRCUIT

The main function of the head unit was to convert the D.C. voltage drop across the 10^{11} ohm resistor into a proportional A.C. voltage which is more readily amplified⁽⁶⁹⁾. After an initial stage amplification in the electrometer head unit the A.C. signal passed along a multi-lead cable to the vibrating reed main amplifier unit which provided the necessary amplification and rectification for driving the strip chart recorder. The recorded signal in volts is a direct measure of the ionization current which may be approximated as the voltage output divided by the high resistance, 10^{11} ohms. At no time was the actual value of an ionization current required.

The vibrating reed electrometer has ten voltage ranges for a total range of 0 to 30 volts. It has a very stable zero which may be readily set. The Brown multiple range recorder can automatically switch scales on a 120 millivolt slide wire to provide a range of 0-1020 millivolts or effectively a full scale chart of 1020 chart units (10 chart widths) wide for each of the ten ranges of the electrometer.

For an ionization cell with rocking (stirring) it was necessary to control three units. These included:

1. the rotary switch which inputs A or B side currents to the electrometer head,
2. the recording potentiometer,
3. the cell rocking motor and brake.

The control unit for this consisted of a specially designed and built timer. The timer powered by a synchronous clock motor operated a commutator over contact points on Lucite discs on a ten minute cycle basis. Various combinations of switching could be obtained. The A or B side current switching was effected by a solenoid valve operated pneumatic cylinder operating on the rotary switch by suitable leverage linkages. The timer controlled the switching by means of the actuating voltage to the solenoid air valve. The

recording potentiometer chart drive was switched on or off by timer control of the chart drive motor. As no readings could be made while the cell was being rocked, the rocking motor had to be controlled. In order to obtain consistent current readings the rocking had to be controlled in such a manner that the cell was in a consistently normal upright position each time. This control was accomplished by a pneumatically operated stop acting on a revolving lever of the hydraulic drive speed reduction unit supplying the rocking power. Usually the cell was rocked for seven minutes and allowed to rest for one minute after which a one minute reading on the A side was made. This was followed by a one minute reading on the B side and the cycle was started anew. No response problems were encountered for this timing procedure because of the very fast response of the electrometer.

THE SCINTILLATION CELL

The concept of scintillation detection and measurement has been applied by Drickamer and coworkers^(36,37,88,89) to high pressure unsteady state Loschmidt type diffusion cells. In this investigation the principle was applied to a quasi-stationary state diffusion cell. The method of detection and measurement depends upon the "counting" of the light flashes induced in a scintillation crystal by radiation from radioactive sources. Thus, in the scintillation cell used here an anthracene crystal was placed in each diffusion chamber. For each side the scintillations were "piped" to a photomultiplier tube which converted them to a counting rate (current) which could be measured in a normal manner. This counting rate represents the concentration of radioactive gas in the cell and the method of analysis is the same as for the ionization cell.

The essential features of the scintillation cell are shown by Figures

5 and 6. Again, this cell consisted basically of two stainless steel flanges each with a cell chamber bolted across a porous plug insert. The flanges were machined from seven inch diameter type 303 stainless steel stock and each side was $2 \frac{3}{16}$ inches wide. The center line diffusion chambers were 1 inch in diameter and $\frac{7}{8}$ " deep. Ten $\frac{1}{2}$ inch 18-8 stainless steel bolts held the sides together. The porous ceramic plug insert was of the same design as that discussed earlier. An anthracene scintillation crystal was at the top of each chamber and faced a Lucite light pipe and window combination that "piped" the scintillations to the photomultiplier tube. This cell also featured in-cell valves for complete isolation of the diffusion chambers. Perhaps the main feature of this cell was the magnetic stirring mechanism used⁽⁴³⁾. Until the method of stirring was devised for the ionization cell, the magnetically stirred scintillation cell was considered to be the best equipment for studying the effect of stirring on the diffusion results.

A magnetic stirrer assembly consisted of the stirrer, shaft bearing insert, and outer drive magnet. The stirrer was made from a $\frac{3}{4}$ " diameter by $\frac{1}{2}$ " long two pole face holding magnet. This magnet was placed on a $\frac{1}{4}$ " dia. shaft with a $\frac{5}{64}$ " dia. hardened drill rod bearing pin and a $\frac{1}{16}$ " dia. x $\frac{3}{4}$ " long rod at the other end. This latter rod revolved about $\frac{1}{16}$ " from the face of the porous plug when the stirrer was turning. A special bearing insert of phosphor bronze was screwed into the back wall of the diffusion chamber to provide the support of the stirrer. The inner magnet was actuated across a one-half inch cell wall thickness by a large two pole face holding magnet mounted on the center line directly outside the cell. The same electric motor-hydraulic variable speed reduction unit used for the ionization cell provided the power to turn the large holding magnets.

FIGURE 2
THE SCINTILLATION CELL

The valve assembly for each half of the cell consisted of a replaceable Be-Cu hardened alloy seat, packing, packing nut and valve stem. The $\frac{1}{2}$ " N.F. threaded Be-Cu alloy (Berryllium Co. of America) was machined with a 59° cone press fit seal area. The seat was hardened by the usual precipitation process recommended for this alloy. The 59° cone sealed against a 60° center-drilled cone when the seat was screwed into the cell body. The $\frac{1}{8}$ " stem guide hole terminated at the valve seat hole ($\frac{1}{16}$ ") a mere $\frac{1}{4}$ " from the diffusion chamber for closure as close to the diffusion chamber as possible. Teflon packing and stainless steel packing spreaders sat on top of the valve seat and were followed by the packing nut with internal stem threads ($\frac{5}{16}$ " - 32 per inch). The valve stem consisted of a $\frac{1}{4}$ " stainless steel threaded upper stem and a $\frac{1}{8}$ " drill rod lower stem with a 15° hardened tip. The high pressure inlet was a Ruska $\frac{1}{8}$ " high pressure tubing fitting with the entrance drilled through the valve seat after it had been screwed into the cell body.

At the top of each chamber an anthracene crystal ($\frac{7}{16}$ " dia. x $\frac{1}{8}$ " thick) was cemented (Lucite cement) in a Lucite light pipe ($\frac{9}{16}$ " dia.). The light pipe and the window ($1\frac{3}{16}$ " diam. x 1" thick) were machined from a single piece of Lucite and given a high polish with jeweler's rouge. The light pipe insert into the cell was somewhat larger than the lapped hole into which it fitted. The Lucite window-light pipe unit was first cooled in liquid nitrogen and then quickly pressed into the cell body light pipe hole where it expanded to give a very tight fit. A $\frac{1}{8}$ " thick Teflon packing gasket about the light pipe underneath the window provided the pressure seal. Each window was fastened down by a one inch stainless steel lid with four $\frac{1}{2}$ " and two $\frac{5}{16}$ " fastening screws about the window cavity. A bracing screw was placed at each corner to provide a proper relief of the stresses on the window. A copper gasket disc under the lid bore against

FIGURE 6: SCINTILLATION CELL PHOTOGRAPH

the window and a Teflon gasket about this made the joint light-tight. A polished Lucite light pipe ($\frac{1}{2}$ " dia. x 3" long) was fitted into the window cover hole and optically sealed to the window surface with Dow-Corning 5 Compound.

COUNT RATE MEASURING CIRCUITRY

The scintillation cell count rate measuring and switching circuitry is shown by Figure 7. A brass sleeve encased each of the light pipes protruding above the top of the cell. To each sleeve a nine inch long brass cylinder (2" O.D. x $\frac{1}{8}$ " thick) was fitted. A photomultiplier (P.M.) tube and preamplifier assembly could be pushed into each tube so that the P.M. tube face butted against the Lucite light pipe. A $\frac{3}{16}$ " brass rod along the center line provided the means of holding the assembly in place. The compact P.M. tube-preamplifier assembly converted the light flashes from the scintillator into electrical pulses of sufficient magnitude to be counted. A DuMont type 6467 photomultiplier tube was used with a positive high voltage resistance network and a cable driving single tube cathode follower circuit. This circuit is very similar to that described by Price⁽⁶⁹⁾, page 188, with minature component selection. The P.M. tube fitted into a brass sleeve socket with an outside O'ring which bore against the brass cylinder walls to insure light tightness in the photomultiplier tube area.

A Baird-Atomic Model 312 Super Stable High Voltage Power Supply provided the necessary high voltage (usually 1167 volts) for driving the photomultiplier tubes. The high voltage to the high reading P.M. tube was first dropped across an external variable high voltage resistor. The function of this resistor was to decrease the high voltage to the higher reading assembly so that both sides of the cell would give approximately the same counting rate for the same concentration of radioactive gas in the chambers.

FIGURE 7: COUNT RATE MEASURING CIRCUIT

The output of the cathode follower for each side was fed through a rotary ceramic switch switchbox to a Baird-Atomic Model 215 Non-Overloading Amplifier which amplified the signals and passed them to the Nuclear-Chicago Model 1620 Analytical Count Rate Meter. The count rate meter integrated the signals with respect to time to give the counting rate in counts per minute on a meter or recording potentiometer. The same multiple range Brown recorder used for the ionization cell was used here. Several run conditions were determined by the settings of the various dials on the instrument panels. On the amplifier these included the gain and pulse height. For the rate meter the time constant and counts per minute meter scale were set. The high voltage setting was important also.

The switching mechanism consisted of the same timer-pneumatic cylinder leverage action on the ceramic rotary switch discussed for ionization cell. Due to the slow response of the rate meter the best switching procedure was to switch in a side and allow a minute or so for the rate meter to establish an equilibrium reading before switching the chart drive on. Because the stirrers were operated continuously the procedure could be followed. The slowest chart speed ($\frac{1}{2}$ " per minute) of the Brown recorder did not permit a continuous chart for most runs.

SERVICE EQUIPMENT

Besides the electronic measuring equipment there was an extensive amount of service equipment needed for a proper utilization of the potentialities of the diffusion cells. The general distribution of the equipment may be obtained from Figure 1. The service equipment included among other things the ventilating hood and the cell mounting framework with the hydraulic speed reduction stirrer drive units, the vacuum and pressure generating and measuring equipment, and the temperature baths and regulation

systems.

A special front opening floor to ceiling hood was constructed for this investigation. The hood was eight feet high, four feet wide and four feet deep. The necessary draft was provided by an exhaust fan which exhausted through a window into the upward stream from a water cooling tower. This arrangement fulfilled the necessary requirements for operation with the radioactive krypton of this investigation. Inside this hood both cells could be conveniently placed side by side on a common welded heavy angle iron framework which was securely fastened to the concrete floor and a brick wall nearby. An angle iron framework also supported the quarter horsepower electric motor-hydraulic speed reduction unit used for the stirring and rocking power. The output speed of this unit could be varied continuously from zero to 200 r.p.m. The same unit was used for the scintillation and ionization cell stirring at different times. A shaft and bevel gear arrangement transmitted the power to the drive magnets for the scintillation cell. An eccentric linkage (not shown by Figure 1) provided the rocking power to the ionization cell.

The cell charging system is shown by Figure 8 for the general case of bath cells in service for the same gas system. High pressure 1/8" stainless steel tubing serviced the cells. This tubing was spiralled for the ionization cell in order to obtain the flexibility needed for rocking. One side (A side) of each cell was connected to the hot (radioactive) gas supply bomb while the other (B side) was connected to the cold gas storage cylinder. A bypass valve was provided. The pressure measuring gage was connected to the cold gas side. Various pressure gages as coded in Appendix G were used. However, the 2000 psi and 10,000 psi Heise gages were used for the majority of the runs. The high pressure cold gas storage cylinder was the high pressure supply to the cells. This cylinder had a capacity of

310 cc and was equipped with a 15,000 psi Crosby gage. The usual practice was to pressurize this cylinder to more than 7,000 psi. with the gas being studied and use this high pressure gas as the main charge to the diffusion cells. Two different pressurizing pumps were used. A specially designed and constructed high compression ratio hand operated screw pump with a Bridgeman unsupported area seal piston (16) was particularly helpful in compressing the rather limited (25 liters at S.T.P.) supply of krypton to the high pressures needed. The other pressurizing device was a Corblin 10,000 psi. air-oil driven diaphragm intensifier. Also, for many of the runs bottle gas pressure was sufficient. Ruska type high pressure valves and fittings were used.

Two oil baths could be placed side by side in the hood. The cells were mounted underneath the mounting frame and the oil baths could be raised to immerse the cells. An angle iron frame and cable winch was used to lift the scintillation cell bath. A large laboratory jack was constructed for the purpose of raising or lowering the ionization cell oil bath. The rectangular box baths were made of 18-8 stainless steel and of approximately 12 gallons capacity. These were inside a larger shell of 3/16" carbon steel plate with normally two inches of insulation. The bath liquid for the 35°C runs was white mineral oil. Denatured ethyl alcohol was used for the -25°C scintillation cell runs. The bath liquids were stirred by fractional horsepower electric stirrers. Nichrome heating coils were used in both baths. A 1/3 h.p. Freon-12 compressor-condenser unit provided cooling capacity for the -25°C runs.

Copper-constantan thermocouples with a Leeds-Northrup 100 millivolt portable potentiometer were used to measure bath and temperatures. A rotary ceramic switch was used to select the thermocouple and the reference junction was immersed in a distilled water ice bath. Each cell had a

FIGURE 8: CELL CHARGING FLOW DIAGRAM

thermocouple positioned approximately midway of it and at one inch from the cell chambers. The calibrations for these thermocouples are given in Appendix G. Temperature regulation for the early runs was made with an ethyl ether expansion driven mercury switch and relay assembly. The drift of this assembly was considerable and the cell temperature regulation was good to only $\pm 0.05^{\circ}\text{C}$. A Resistotrol - platinum resistance regulator was adopted for all the ionization cell runs with Porous Plug B. The cell regulation obtained was on the order of $\pm 0.02^{\circ}\text{C}$. A thermonitor-thermistor control unit provided regulation for the -25°C runs to within 0.1°C .

IV. EXPERIMENTAL PROCEDURES

That part of the experimental program which dealt with the design and construction of the experimental apparatus is discussed in the previous section. Here the methods of operating this equipment in order to obtain the diffusion coefficient of krypton-85 in various gases are discussed. Also, the method of calculating the diffusion coefficient from the run data are examined and discussed.

GAS SAMPLE PREPARATION

Because this investigation was concerned with the diffusion of trace quantities of krypton-85 in pure bulk gases no problems of mixing run sample gases were encountered. The manufacturer's specifications for the gases used are given in Appendix H. In order to prepare the hot gas samples a number of small size (80 cc) stainless steel sample bombs was made. Each bomb had a high pressure valve and fitting on one end. To prepare the hot gas samples a 10 millicurie krypton-85 ampoule was placed in a tight fitting non-magnetic stainless steel cylinder, a piece of $\frac{1}{4}$ " drill rod was inserted over the break off seal, and a $\frac{1}{4}$ " pipe needle valve was screwed into the cylinder mouth. This was placed on a manifold with three of the hot gas sample bombs. The system was evacuated to less than 50 microns of mercury and flushed with cold krypton. The evacuation was carried out again and a couple inches of mercury pressure of cold krypton was introduced into the cylinder containing the ampoule which was then isolated from the system. The drill rod was induced to break the break off seal by magnetic or other means. After a Geiger counter showed that the ampoule was broken the cylinder valve was opened to let the gas flush into the three evacuated sample bombs. These were sealed off and each was filled with a desired bottled gas to bottle pressure.

IONIZATION CELL PROCEDURES

In order to begin an ionization cell diffusion run the temperature bath was first brought to temperature and regulated to hold this temperature. Usually eight hours or more were allowed for temperature equilibrium to be established. Also, four hours or more were allowed for the vibrating reed electrometer warmup. After this initial startup the equipment was left on continuously until it had to be shut down for some reason. The voltage was generally left on continuously. For a new series of runs with a different base gas (bulk gas component) the cell was evacuated by an oil vacuum pump to less than 50 microns of mercury pressure, flushed with 20 psig. of the base gas, and re-evacuated. After this the cell was filled to some pressure above atmospheric and about 100 psig below the desired operating pressure if the pressure was below the available hot gas (radioactive krypton-85 traced gas) pressure. The cold gas source for most runs was the high pressure cold gas storage cylinder. For the case of a pressure below the hot gas sample bomb pressure, a run was initiated by injecting hot gas into the A side of the ionization cell until almost a full scale deflection on the chosen voltage range occurred. More cold gas was introduced into the B side to bring the cell to the pressure desired. For the case of a desired operating pressure well above hot gas storage pressure the injection of hot gas into the A side was made at a low pressure and then cold gas was injected into the B side until the desired pressure was obtained. The process involved considerable exercise of judgment on the part of the operator to obtain a high A side meter deflection at the desired pressure. Where calibrations of current versus density at constant concentration of krypton-85 were carried out calculations could be made to predict the current reading at a given low pressure for approximately full scale deflection at a high pressure. Another procedure for introducing

hot gas into the cell consisted of first injecting hot gas into the A side service line and then force this into the cell with higher pressure cold gas. Generally, the cell pressure was not a definitely predetermined operating condition and considerable bounds of adjustment were available to the operator in order to obtain the best operating conditions. Obviously, because of the greater accuracy involved, a high A side reading compared to the B side reading for a given voltage scale was the goal. The vibrating reed voltage scale used was determined by the stability of the readings for this scale. Depending upon the gas and the pressure each voltage scale produced a reading that fluctuated about a mean. An acceptable spread of these fluctuations was considered to be ten chart units or less.

After the cell was pressurized the A side cell valve was closed by swiftly lowering the oil bath, closing the valve, and raising the bath again. This caused no serious temperature fluctuations. Shortly thereafter, the readings of the ionization currents with time were begun. For a low pressure run the procedure might consist of simply switching back and forth between the A and B sides with a continuous chart recording. For the other runs the procedure would involve the automatic timing of the switching to take an A side and a B side reading consecutively every ten minutes. The general procedure if the cell was rocked meant that for a ten minute cycle the cell was rocked seven minutes, rested for one minute after which the consecutive A and B side readings were made. As explained in the preceding section all of these procedures were controlled by a ten minute cycle timer actuation of A and B side pneumatic switch, chart drive motor and rocking motor. The B side cell valve was closed after it was determined that the pressure was being held. This pressure was recorded as the beginning pressure. Also, during the course of the run at various times the millivolt readings of the cell thermocouple were recorded.

The length of a run was determined by balancing the time required for further readings against their reliability. This was denoted by the difference between the A and B side readings weighted by the spread of the fluctuations present. The usual procedure followed was to discontinue a run when the difference between the A and B side readings approached 200 chart units provided a high startup difference was obtained. After a run was discontinued the pressure was recorded as the end pressure and the gas was vented through the hood to the atmosphere to a lower pressure. It was not necessary to evacuate the cell between runs for the same gas. The usual procedure consisted of venting the gas until low current readings were obtained after which the injection procedure could be repeated for another run.

The charging procedure for the krypton runs was different because of the limited supply at limited pressures. For this series of runs the initial runs were made at low pressures and after each run more cold krypton was introduced into the B side to give a useful initial difference in currents at a higher pressure. Also, for these runs the krypton was injected directly into the cell by the hand operated high compression ratio pump.

The important primary data for an ionization diffusion cell run consisted of the following:

1. Date,
2. Base Gas,
3. Porous Plug,
4. Pressure Gage,
5. Beginning Pressure,
6. End Pressure,
7. Barometric Pressure,
8. Cell Thermocouple Millivolt Readings,

9. Cell Temperature,
10. Voltage Range,
11. Chart Speed,
12. Rocking (stirring) Speed),
13. Time Cycle,
14. Ionization Currents vs Time (Strip Chart).

These items are recorded in a brief form for each run in Tables A-1 and A-2 of Appendix A.

IONIZATION CELL ANALYSIS

Before the ionization currents in chart units could be used to obtain a diffusion coefficient for a run it was necessary to know the relationship between the readings from bath chambers at the same concentration of krypton-85 encountered in the run. Also, it is necessary to know the relationship between the ionization current and the concentration of krypton-85 at the pressure or density of the run. In order to obtain this information various calibration runs as detailed in Appendix D were made.

For the determination of the ratio f of the A side reading to the B side reading at the same krypton-85 concentration hot gas was introduced into the cell and the pressure was increased by cold gas injection in such a manner as to give approximately the same A and B side readings at an elevated pressure. Equilibrium was allowed to be established after which readings of currents (chart units) versus pressure (density) were made as the pressure was reduced by steps. This information allowed f to be determined as a function of pressure or density. This calibration was necessary for each porous plug and each gas. In order to determine if f was a function of current magnitude (concentration of krypton-85) the procedure was repeated for selected gases over the same pressure range but at different

current magnitudes. No dependence on concentration was found. The gases could be correlated on f versus pressure plots to within reasonable accuracy except for the helium runs. An f versus mass density plot (Figure D-6) almost correlated the helium data. The value of f increased about three per cent up to 250 grams/liter after which it became fairly constant. This type of behavior cannot be attributed to pressure induced displacement of the electrode elements because of the helium data. A difference in the relative mass density distortion of the electric fields for the two chambers probably accounts for this effect.

For the purpose of determining the f of a given run these plots of f versus pressure or density are available in Appendix D. Figure D-5 shows f versus pressure for argon, nitrogen, and helium with Plug A in place. Figure D-6 shows f versus mass density for various gases with Plug B in place. Figure D-7 shows f versus pressure for helium with Plug B in place. The helium run data were not used in drawing the curve of Figure D-6. The maximum here is on the order of $\frac{1}{2}$ per cent with the main deviation caused by the nitrogen data. For the other plots the deviations are negligible. For a given diffusion run the proper chart was selected and the value of f read for the run pressure or mass density. For krypton no calibration runs were made but the density plot was considered applicable.

In order to determine the relationship between krypton-85 concentration and the ionization current a series of calibration runs were made in the following manner. The porous plug was removed from the cell and replaced by a plug with a 11/16" hole instead of the porous plug. Hot gas was introduced into the cell at a low pressure. All supply lines were evacuated and filled with cold base gas. Cold gas was then introduced into the cell in a series of steps. After each injection equilibrium was established and the pressure and current for the A side were recorded. In this manner the

variation of ionization current with pressure or density is obtained for a constant krypton-85 concentration. The procedure was repeated for other concentrations.

In Figure D-1 a plot is given of ionization current versus density for typical runs of each of the gases studied. The effect of recombination of ion processes in the ionization chamber for the different gases may be noted. In nitrogen the recombination becomes important at much lower pressures than for argon and helium. It was discovered that the argon results could be fitted to an equation of the type,

$$\frac{p}{I} = a\rho + b. \quad (46)$$

Curves of $\frac{p}{I}$ vs. ρ for the argon runs are shown by Figure D-2 to be straight lines in accordance with this relation. The analysis in Appendix D shows that the ratio of any two ionization currents, I_1 and I_2 , on different concentration lines approach the inverse ratio of the slopes, m_1 and m_2 , at densities approaching zero. A very good assumption may be made that at low densities the ionization is directly proportional to the concentration of a radioactive species over large concentration ranges^(10,61). If this assumption

$$I \propto C \quad (47)$$

is made, the criteria that must be fulfilled for it to hold over the argon density range of interest is that

$$\frac{I_1}{I_2} = \frac{a_2}{a_1}. \quad (48)$$

This criteria is shown by Table D-2 to hold for argon and the conclusion may be made that Equation (47) holds over the density range studied. Two calibration runs apiece at wide concentration differences were made for helium and nitrogen. A relationship of the form of Equation (46) does not

hold (c.f. Figures D-3 and D-4). A verification of the constancy of the ratio of the two currents with density in each case can be made, however. If the assumption of current-concentration proportionality at low densities is made, the constancy of the current ratios justifies the application over the density range. The proportionality between the ionization current and the krypton-85 molar concentration of Equation (47) was assumed to be applicable to all systems at the densities encountered in this investigation.

The mathematical analysis of the quasi-stationary type of diffusion cell used in this investigation has been reviewed previously. Again it must be pointed out that the assumptions were made that a linear gradient in concentration is established across the porous diffusion plug and that there is complete mixing in the two chambers of the cell. For this type of cell the describing equation was found to be

$$\log_e (C_A - C_B) = -K D t + R_1 \quad (41)$$

where

$$K = \frac{A}{L} \left(\frac{1}{V_1} + \frac{1}{V_2} \right), \quad (42)$$

and the other symbols have been identified previously. Now as the ionization cell currents are proportional to krypton-85 concentrations and since the ionization currents are directly proportional to the A and B side chart readings in chart units, this equation may be written as

$$\log_e (A - fB) = -K D t + R_3 \quad (49)$$

where A and B are the A and B side chart readings at the time t and R_3 is a constant of integration.

A plot of $\log_e (A - fB)$ versus time for the ionization cell run I-37BS is given by Figure 9. The excellent straight line that results is a good argument in favor of the assumption that a linear gradient in concentration exists within the porous plug. The slope of this line is equal to the product of the cell constant and the diffusion coefficient for run I-37BS. With a knowledge of the cell constant for Porous Plug B (Appendix F) the diffusion coefficient may be obtained.

As has been indicated previously two types of porous plugs were used in the ionization cell. Porous Plug A consisted of 67 glass capillaries mounted in the steel insert plug. The average cross-sectional area of this plug was determined with very good precision by the two methods of weight of mercury calibration and mercury resistance calibration. With this data and the measurements of the other geometrical constants for Equation (42) the cell constant K_B for the ionization cell with Porous Plug A in place was determined to be $3.3053 \times 10^{-3} \text{ cm}^{-2}$ with at least four figure significance. The calibrations and calculations are recorded in Appendix F. Porous Plug B consisted of the 10 micron retention porous ceramic filter mounted in a steel insert plug. This plug was calibrated against the Glass Capillary Porous Plug A at the lower density range. As recorded in Appendix F the cell constant K_B for the ionization cell with Porous Plug B in place was determined to be $3.337 \times 10^{-2} \text{ cm}^{-2}$. The constants K_A and K_B were the cell constants used for calculating the diffusion coefficients from the data represented by Equation (49).

The extensiveness of this investigation in regards to number of diffusion runs and data points per run made automatic computing techniques attractive. A medium speed LGP-Royal McBee computer was available for analyzing the data by a least mean squares (LMS) routine. The standard extended range floating point interpretative least mean square program for this

computer was used. For a given run the data in the form of A and B readings at given times as shown by Table A-2 (Appendix A) and the value of f for the run were stored in the memory of the computer. A subroutine calculated the factor $(A - fB)$ and placed it with its respective time t in the memory of the LMS program. The LMS program fitted an equation of the form,

$$y = \log_e (A - fB) = mt + b, \quad (50)$$

to the data points by a least mean squares procedure. The output of the program consisted of the following items:

1. the slope m;
2. the intercept b;
3. the factor $y_1 = \log_e (A - fB)$
of the experimental data at the input
times t;
4. the factor y_2 of the fitted Equation (48) at
the input times t;
5. the difference $(y_2 - y_1)$ between the calculated
factor y_2 and the experimental factor y_1 at
the input times t;
6. E = the sum of the squares of $(y_2 - y_1)$ for
the input times t.

Rounded values of these items for run I-37BS are shown in Appendix C for the sample calculations of run I-37BS.

The chief item of interest is, of course, the slope m because

$$m = 60 K D \quad \text{min.}^{-1} \quad (51)$$

for time inputs in minutes. However, items 3, 4, and 5 are important from the standpoint of determining the deviation of the experimental points from

the LMS fit. Thus, obvious input errors may be spotted. The main significance resides in the determination of the curvature of the $\log_e (A - fB)$ versus time plot. If this is not a straight line, the analysis is in error. Curvature may result from the transient effects at the beginning of a run and from the indeterminate nature of the readings towards the end of a run, especially for low concentration differences. In order to mitigate these effects an initial selection of data points was made with suspicious points near the beginning and the end of a run being eliminated. This elimination was based on the constancy of the sum of the two ionization current readings, A and B, with proper respect for the factor f.

If the output of the LMS program indicates excessive curvature, points at the beginning and end of the time spread may be eliminated and a second fit obtained.

The factor E serves as a ready indicator of the precision of the fit as explained in Appendix A. In Table A-3 (Appendix A) the derived results for each run include;

1. the pressure P_a ,
2. the compressibility factor Z,
3. the mole density ρ ,
4. the mass density w ,
5. the factor f,
6. the LMS slope m, and
7. the factor E.

SCINTILLATION CELL PROCEDURES

The procedure for making a diffusion run with the scintillation cell was very similar to that described for the ionization cell. The main difference was in the operation of the electronic equipment and that is the

chief topic of the discussion that follows.

The electronic equipment was allowed to warm up for several hours before a run was started. In general the equipment was left on continuously. The high voltage to the photomultiplier tubes was set at 1167 volts positive. No plateau of counting rate versus high voltage was observed because of the beta emission. The amplification gain of the non-overloading amplifier was normally set at a value of 1600 for the diffusion runs. A pulse height selection of 1.00 volts was ordinarily made. These settings were arrived at for the best operation with a minimum of noise. The rate meter constant was generally set for a 10 sec. time constant. A time constant of 2 sec. did not provide sufficient damping for a useful chart whereas a 50 second time constant gave poor response characteristics. The 100,000 counts per minute count rate scale was used for all the runs. This scale was used in order to give statistically meaningful results. For a ten second time constant and the 100K CPM range the Model 1620 rate meter, requires 45 to 55 seconds to give a reading within the probable error of the true average⁽⁶⁶⁾. This slow response made it necessary to time the switching between the A side and B side of the cell in conjunction with the chart drive of the recorder in such a manner that at least a minute elapsed between the A-B side switch and the reading recorded on the chart. It was determined that the operation of the stirrers improved slightly the quality and consistency of the chart readings. For this reason the stirring mechanism operated continuously during a run. A stirring rate of 22 rpm. was normally used for a run. After the scintillation cell was charged in the same fashion as outlined for the ionization cell, the counting rates for both sides were recorded as a function of time on the strip chart. The important data obtained were the same as those of the ionization cell except for different electronic instrumentation conditions. Tables B-1 and B-2

are the records of the important primary data for the diffusion runs made with the scintillation cell.

SCINTILLATION CELL ANALYSIS

Again, in order to reduce the diffusion run readings to a common basis it was necessary to know the relative readings of the A and B sides of the same krypton-85 concentration of the run. This was determined for many of the runs by allowing the run to proceed to equilibrium and obtaining the ratio f as the ratio of the A side reading to the B side reading at the equilibrium concentration. This ratio was largely determined by the adjustment of the external high voltage variable resistor in the high voltage feed to the high reading photomultiplier. In order to set this resistor hot gas was introduced into the cell with equal introduction of cold gas to some reasonably low pressure, the cell was allowed to come to equilibrium, and the variable resistor was set so that the readings of both sides were very nearly the same. For the scintillation runs five different adjustments were made as indicated in Appendix E. Besides the run equilibrium method of determining f the procedure indicated for the ionization cell was used also. Due to the aging of the photomultiplier tubes the value of f changed with time so that new adjustments had to be made. Adjustment I and V of Appendix E (Figure E-2) have similar pressure dependence characteristics. The other adjustments were not calibrated sufficiently to give a true indication of this behavior for them. Adjustment I corresponding to the argon 35°C runs and Adjustment V corresponding to the nitrogen -25°C runs were used for these runs. For the argon -25°C runs the equilibrium values were used where possible. The best estimates of f for the others were made after consideration of the constancy of the sum of the A and B side readings and interpolation in Figure E-2.

There are many factors such as thermionic emission by the photocathode and ohmic leakage which cause a photomultiplier tube to produce spurious signals which may be amplified and appear as counts. Also, thermal and natural radioactive radiation induced scintillations may appear as counts. All of these factors give rise to a background reading. Background was determined periodically for the scintillation cell by filling the cell with cold gas and recording the A and B side readings. The background did not appear to vary with the pressure of cold gas in the cell. The background estimated for each run appears at the beginning of the counts per minute tabulation in Appendix B (Table B-2)

In much the same manner as indicated for the ionization currents the counting rates for argon at 35°C at various densities were determined for various concentrations of krypton-85 (Table E-1). Here again a relative analysis was indicated because of the unknown concentrations. The reciprocal of the counting rate versus the pressure was plotted in Figure E-1 (Appendix E). It was determined that the ratios of the run count rates determined from the zero pressure intercept ratios were constant within experimental error over the pressure range investigated. If the assumption of counting rate proportionality with krypton-85 concentration at low pressures may be made, the application over the pressure range studied follows from these results. The krypton-85 concentration-counting rate proportionality was used in the analysis of the diffusion runs. However, it must be regarded as one of the assumptions of the method.

The mathematical analysis of the scintillation cell runs was based on Equation (49). Where the A and B side readings are in counts per minute corrected for background. Semi-log paper was used to plot $(A - fB)$ on the ordinate versus t on the abscissa. The slope m_s of this line is related

to the diffusion coefficient through

$$m_s = (2.303)(60) K_c D \text{ min.}^{-1} \quad (52)$$

the value of K_c was determined by meshing the product $\rho K_c D$ of the argon (35°C) scintillation runs with the similar product ($\rho K_e D$) of the argon (35°C) ionization cell runs for the density range to 5 moles/liter.

The value of K_e was determined to be $2.759 \times 10^{-2} \text{ cm}^{-2}$.

V. DIFFUSION RESULTS

The results of this experimental investigation of the diffusion of krypton-85 through various dense gases are shown in the form of tables and graphs. The first exposition consists of three tables (Tables II, III, and IV) which present for each diffusion run the important experimental run conditions and diffusion coefficient of krypton-85 through the gas. These tables of the diffusion results for krypton-85 (Kr*) diffusion in various systems with the range of state variables indicated are as follows:

TABLE II. Ionization Cell-Glass Capillary Porous Plug A;

Kr*-A	at	35.1 °C	to	1.754	moles	per	liter.
Kr*-He	"	35.1°C	"	2.410	"	"	"
Kr*-N ₂	"	35.1°C	"	1.385	"	"	"
Kr*-Kr	"	35.0°C	"	0.632	"	"	"

TABLE III. Ionization Cell-Porous Plug B;

Kr*-A	at	35.0°C	to	14.95	moles	per	liter
Kr*-He	"	35.0°C	"	13.87	"	"	"
Kr*-CO ₂	"	35.0°C	"	3.48	"	"	"
Kr*-N ₂	"	35.0°C	"	12.79	"	"	"
Kr*-C ₂ H ₄	"	25.0°C	"	12.38	"	"	"
Kr*-Kr	"	35.0°C	"	11.96	"	"	"

TABLE III. Scintillation Cell-Porous Plug C;

Kr*-A	at	35.0°C	to	5.48	moles	per	liter
Kr*-A	"	-25.0°C	"	10.68	"	"	"
Kr*-N ₂	"	-24.9°C	"	10.08	"	"	"

The run numbers for the ionization cell runs are in the form of I-XYZ where the I indicates an ionization cell run number X while Y may be an A or B indicating the respective porous plug used and if an S replaces the Z the cell chambers were stirred during the run. All of the ionization cell

runs that were stirred were rocked for seven minutes out of ten at 22 cycles per minute except for the runs listed below with their respective seven minute stirring rates:

Run No. I-94BS - - - 11 cpm.,
 I-95BS - - - 44 "
 I-96BS - - - 44 "
 I-99BS - - - 33 "

The scintillation cell diffusion runs are indicated by an S followed by the run number. Since all of these runs were made with Porous Plug C no definition of the porous plug is indicated. Also, all of these runs were made with a continuous stirring rate of 22 rpm. except for the runs indicated below with their respective continuous stirring rates:

Run No. S-2 at 10 rpm,
 S-3 at 40 rpm.

The diffusion results are also shown in the form of plots of the density-diffusivity product versus density for each gas system. Figures 10 and 11 present the density-diffusivity product versus density data of Table II for the ionization cell runs with the Glass Capillary Porous Plug A. The diffusion coefficients determined with the Glass Capillary Plug A are absolute determinations and for this reason they are shown separately. The values of the density-diffusion coefficient product at low pressures determined by the Chapman-Enskog theory as well as applicable determinations from previous experimental investigations at low pressures as given by Table IV of the next section are conveniently displayed on Figures 10 and 11. Figures 12 and 13 are the density-diffusivity product versus density plots for the results of Table III for the ionization cell with Porous Plug B. The Glass Capillary Porous Plug A results are also shown on these figures. The density-diffusivity determinations made for the diffusion of

krypton-85 in the argon and nitrogen systems are shown plotted against the density by Figures 14 and 15.

It was not believed pertinent to present here the krypton-85 diffusion in krypton results as self-diffusion coefficients by the use of Equation 16 because this multiplying factor is only 1.004 and within the precision of the results.

The compressibility data of the Michels group^(46,53,54,55,56,57,58) was generally used to determine the compressibility factors for the base gases other than krypton. The N.B.S. data⁽³⁰⁾ was used to supplement this data. The data of Beattie, et al.^(4,5) was used to determine compressibility factors and thus densities for the krypton runs.

TABLE II
DIFFUSION RESULTS
IONIZATION CELL-GLASS CAPILLARY POROUS PLUG A

Run No.	Pressure (atm)	Density (gm. moles/liter)	Diffusivity ₃ (cm ² /sec.x10 ³)	$\rho \text{ D} \times 10^3$
ARGON at 35.1°C				
I-3A	2.525	0.09987	5.602	5.595
I-4A	2.593	0.1027	5.540	5.690
I-8A	4.219	0.1672	3.397	5.680
I-2A	5.185	0.2055	2.819	5.793
I-1A	9.240	0.3673	1.563	5.741
I-5A	14.92	0.5946	0.9876	5.872
I-7A	25.09	1.0047	0.5701	5.728
I-6A	43.46	1.754	0.3347	5.871
HELIUM at 35.1°C				
I-14A	3.709	0.1464	16.92	25.77
I-12A	4.471	0.1765	14.08	24.85
I-9A	6.743	0.2657	9.48	25.19
I-10A	20.55	0.8046	3.222	25.92
I-15A	30.74	1.199	2.170	26.02
I-11A	52.06	2.011	1.338	26.91
I-13A	60.15	2.410	1.150	27.72
NITROGEN at 35.1°C				
I-20A	3.137	0.1241	5.011	6.219
I-18A	4.933	0.1951	3.263	6.366
I-17A	7.614	0.3012	2.131	6.419
I-21A	22.10	0.8748	0.7434	6.503
I-19A	24.14	0.9558	0.7014	6.704
I-16A	34.93	1.385	0.4738	6.562
KRYPTON at 35.0°C				
I-25A	3.649	0.1455	2.765	4.023
I-24A	3.807	0.1518	2.622	3.980
I-23A	7.463	0.3001	1.317	3.952
I-22A	15.50	0.6320	0.6487	4.100

TABLE III
DIFFUSION RESULTS
IONIZATION CELL-POROUS CERAMIC PLUG B

Run No.	Pressure (atm)	Density (gm. moles/liter)	Diffusivity (cm ² /sec.x10 ³)	$\rho D \times 10^3$
ARGON at 55.0°C				
I-28B	7.15	0.2837	20.06	5.787
I-91B	11.00	0.4379	13.50	5.914
I-81B	11.00	0.4379	13.19	5.779
I-26B	11.02	0.4384	13.19	5.783
I-93B	20.63	0.8244	7.135	5.882
I-31B	20.65	0.8254	7.102	5.862
I-29B	34.49	1.388	4.279	5.938
I-92B	48.42	1.960	3.030	5.939
I-27B	48.44	1.960	3.049	5.976
I-30B	73.42	2.997	2.028	6.078
I-37BS	73.48	3.041	2.041	6.205
I-32B	133.02	5.490	1.132	6.216
I-94BS	133.12	5.495	1.128	6.198
I-33BS	133.15	5.495	1.121	6.157
I-96BS	133.15	5.495	1.135	6.238
I-99BS	133.21	5.499	1.132	6.224
I-96BS	133.22	5.499	1.138	6.259
I-38BS	133.32	5.502	1.143	6.288
I-44BS	103.65	4.265	1.447	6.172
I-43BS	174.5	7.192	0.8754	6.296
I-100B	206.5	8.455	0.7259	6.137
I-34BS	206.5	8.455	0.7474	6.319
I-41BS	242.8	9.816	0.6434	6.316
I-98B	272.9	10.934	0.5516	6.030
I-39BS	272.9	10.934	0.5801	6.343
I-42BS	302.3	11.876	0.5281	6.212
I-40BS	333.1	12.820	0.4914	6.299
I-35BS	375.7	14.044	0.4451	6.251
I-97B	375.8	14.046	0.4320	6.067
I-36BS	410.1	14.945	0.4216	6.301

TABLE III (cont'd)

Run No.	Pressure (atm)	Density (gm. moles/liter)	Diffusivity ₃ (cm ² /sec.x10 ³)	ρ Dx10 ³
HELIUM at 35.0°C				
I-35B	24.81	0.9701	27.32	2.641
I-53B	60.17	2.316	11.56	2.678
I-45B	91.50	3.474	7.695	2.673
I-49B	111.51	4.198	6.354	2.667
I-47B	130.28	4.866	5.565	2.708
I-51B	186.09	6.794	4.101	2.786
I-54B	211.94	7.656	3.574	2.736
I-48B	240.2	8.579	3.268	2.804
I-56B	279.0	9.812	2.801	2.744
I-50B	312.1	10.84	2.563	2.778
I-55B	353.6	12.09	2.326	2.812
I-52B	415.1	13.87	2.057	2.852
CARBON DIOXIDE at 35.0°C				
I-61B	5.675	0.2330	20.47	4.769
I-57B	13.66	0.5780	8.408	4.860
I-62B	21.55	0.9410	5.046	4.748
I-59B	30.36	1.418	3.485	4.940
I-60B	43.80	2.265	2.251	5.097
I-58B	57.48	3.441	1.535	5.281
I-63BS	57.89	3.484	1.522	5.303
NITROGEN at 35.0°C				
I-64B	17.88	0.7080	8.845	6.262
I-66B	24.55	0.9724	6.591	6.409
I-65B	34.93	1.383	4.714	6.521
I-67B	69.33	2.733	2.438	6.662
I-68BS	135.74	5.217	1.289	6.724
I-70BS	203.8	7.549	0.9192	6.940
I-72BS	273.5	9.610	0.7175	6.895
I-69BS	339.7	11.287	0.6287	7.095
I-71BS	408.4	12.790	0.5487	7.017

TABLE III (cont'd)

Run No.	Pressure (atm)	Density (gm. moles/liter)	Diffusivity ₃ (cm ² /sec.x10 ³)	$\rho D \times 10^3$
ETHYLENE at 25.0°C				
I-77B	13.69	0.6113	7.975	4.875
I-75B	30.25	1.541	3.179	4.899
I-74B	45.80	2.822	1.823	5.145
I-73BS	62.07	4.375	0.9800	5.335
I-78BS	70.07	8.413	0.6401	5.385
I-79BS	79.94	10.306	0.5002	5.155
I-80BS	89.46	11.198	0.4517	5.058
I-76BS	112.12	12.384	0.3815	4.724
KRYPTON at 35.0°C				
I-82B	7.458	0.2979	13.71	5.083
I-83B	15.48	0.6311	6.718	4.240
I-84B	29.53	1.238	3.413	4.224
I-85B	67.41	3.008	1.393	4.189
I-90BS	46.27	4.589	0.9376	4.303
I-88BS	110.08	5.372	0.8147	4.376
I-86BS	134.85	6.822	0.6358	4.338
I-89BS	187.86	9.839	0.4178	4.111
I-87BS	227.9	11.955	0.3446	4.119

TABLE IV
DIFFUSION RESULTS
SCINTILLATION CELL-POROUS CERAMIC PLUG C

Run No.	Pressure (atm)	Density (gm. moles/liter)	Diffusivity ₃ (cm ² /sec.x10 ³)	$\rho D \times 10^3$
ARGON at 35.0°C				
S-7	14.44	0.576	9.94	5.719
S-9	28.59	1.147	5.30	6.078
S-1	41.26	1.665	3.446	5.738
S-2	41.77	1.686	3.556	5.974
S-3	41.97	1.694	3.496	5.923
S-8	57.68	2.313	2.714	6.278
S-4	68.84	2.807	2.151	6.038
S-5	102.8	4.228	1.487	6.285
S-6	132.8	5.483	1.171	6.419
ARGON at -25.0°C				
S-14	13.73	0.687	7.29	5.005
S-10	41.84	2.176	2.364	5.145
S-15	66.53	3.568	1.513	5.399
S-11	92.60	5.113	1.058	5.411
S-12	132.7	7.571	0.735	5.561
S-12	185.2	10.68	0.545	5.819
NITROGEN at -24.9°C				
S-19	7.37	0.364	15.49	5.641
S-16	22.18	1.109	5.10	5.650
S-20	42.22	2.135	2.844	6.071
S-21	103.08	5.286	1.098	5.805
S-17	131.6	6.702	0.944	6.331
S-18	207.7	10.08	0.655	6.603

FIGURE 10: PLUG A IONIZATION CELL DIFFUSION RESULTS for Kr-85 in A, N₂, and Kr

FIGURE 11: PLUG A IONIZATION CELL DIFFUSION
RESULTS for Kr-85 in He.

FIGURE 4. IONIZATION CELL DIFFUSION RESULTS FOR CO_2 IN H_2O , CO_2 IN H_2O , and N_2

FIGURE 13: IONIZATION CELL DIFFUSION RESULTS FOR Kr-85 IN He

FIGURE 14: SCINTILLATION CELL DIFFUSION RESULTS
 for Kr-85 in A at -25°C and 35°C

FIGURE 15: SCINTILLATION CELL DIFFUSION RESULTS
for Kr-85 in N₂ at -25°C

VI. DISCUSSION OF RESULTS

The product of the density and diffusion coefficient of krypton-85 for the various systems consistently increases in the lower density region (3 to 5 moles per liter) after which it remains essentially constant or decreases. The usual order of magnitude of increase is about 10 per cent over the intercept density-product corresponding to low pressure. This density dependence is consistent for diffusion runs with both cells and all the diffusion plugs used.

In this section the results of the previous section are compared with the results predicted by diffusion theory and by previous applicable investigations of these systems. The extrapolated results of this investigation in the low density limit are compared with applicable previous low pressure experimental investigations and with the predictions of the Chapman-Enskog theory. The density variations of the diffusion coefficient as observed for this investigation are compared to predictions by methods based on the Enskog rigid sphere theory. The effect of stirring on the diffusion results is discussed. Also, the accuracy and internal precision of the diffusion runs are evaluated and discussed. Finally the sources of error and major difficulties encountered in this investigation are reviewed and evaluated. Technical improvements are suggested where applications are warranted.

KRYPTON-85 DIFFUSION COMPARISONS AT ONE ATMOSPHERE

The mean curve through the results shown by Figures 10 and 11 for the ionization cell with the Glass Capillary Porous Plug A in place was extrapolated to one atmosphere pressure equivalence in density and the density-diffusivity product was determined for one atmosphere. This procedure was followed for the krypton, helium, argon, and nitrogen cases at 35°C. For

the carbon dioxide and ethylene cases the extrapolation was performed with the composite ionization cell results of Figure 12. For the argon and nitrogen cases at -25°C the extrapolation was performed with the scintillation cell results given by Figures 14 and 15. The diffusivity was evaluated for each case and is shown along with the density-diffusivity product by Table V. Now, Table V also shows the predictions of the Chapman-Enskog theory for each case as well as the applicable previous low pressure results (Section II). The Chapman-Enskog results were calculated with a Lennard-Jones⁽⁶⁻¹²⁾ interaction potential with the usual combination values for the viscosity force constants⁽³¹⁾ given by Equation (14). This assumes that the force constants for krypton-85 are identical to those of krypton. This assumption is valid because the addition of neutrons does not severely affect the interaction potential. Groth and Harteck⁽²⁶⁾ first determined the self-diffusion coefficient for krypton at 293°K . The value shown at 35°C was determined from this result by applying the temperature ratio predicted by the dilute gas theory of Equation (13). Now, Schäfer and Schuhman⁽⁷⁶⁾ indicated a natural logarithm temperature relationship for their results so that a logarithmic interpolation was followed here to arrive at the values shown for these investigators. The results cited for Srivastava and Srivastava⁽⁸⁰⁾ were determined from a graphical representation of their results. These results were all converted to krypton-85 diffusion results by dividing the factor 1.004 given by Equation (16).

Table V clearly shows that the results of this investigation when extrapolated to low densities are in accord with the dilute gas theory predictions and the experimental observations. Among the exceptions must be noted the poor predictions for helium and the polyatomic molecular carbon dioxide and ethylene systems. This deviation is not too disappointing when it is realized that the theory assumes relatively simple molecules (poten-

tial) with no quantum effects. In general the order of magnitude discrepancy observed here has been found quite regularly for similarly complex molecular systems⁽⁷⁸⁾ as well as for systems with helium or hydrogen (quantum effects). The utility of the combination rules for predicting the interaction of simple molecules is justified, however. Because the results at -25°C for argon and nitrogen with the scintillation cell must be regarded as being of lower accuracy than the 35°C ionization cell runs, the larger discrepancy for these runs should not be taken too seriously.

The disagreement with the Schäfer and Schuhman study for argon is not surprising in light of the earlier discussion (Section II) of the disagreement with the results of Srivastava and Srivastava⁽⁸⁰⁾. Here, the krypton-argon results agree with those of the latter investigators. Apparently, the Schäfer and Schuhman results for the argon system, at least, are in error. All of the krypton in krypton results are in very good agreement.

TABLE V
KRYPTON-85 DIFFUSION COMPARISONS
AT ONE ATMOSPHERE

System	T, °C	Experimental ⁽¹⁾		Chapman- Enskog	Other Investigations	
		$\rho D \times 10^3$	D	D	D (2)	D (3)
Kr*-A	35.1	5.68	0.144	0.145	0.1442	0.207
	-25.0	4.96	0.101	0.097	0.0986	0.161
Kr*-Kr	35.0	3.99	0.101	0.103	(4) 0.105	(3) 0.100
Kr*-N ₂	35.1	6.29	0.159	0.161		
	-25.0	5.61	0.114	0.108		
Kr*-He	35.1	24.8	0.627	0.704		
Kr*-CO ₂	35.0	4.72	0.119	0.110		
Kr*-C ₂ H ₄	25.0	4.72	0.115	0.110		

NOTES:

(1) $\rho D \times 10^3$ in units of cm²-mole per sec per liter.

D in units of cm² per sec.

(2) Srivastava and Srivastava⁽⁸⁰⁾

(3) Schäfer and Schuhman⁽⁷⁶⁾

(4) Groth and Harteck⁽²⁶⁾

DENSE GAS COMPARISON-KRYPTON SELF-DIFFUSION

The krypton-85 diffusion coefficients in krypton may be regarded as self-diffusion results upon multiplying by the molecular weight correction factor of 1.004 given by Equation (16). For the purposes of the comparison here this will not be necessary because this study is concerned with the dimensionless density-diffusivity ratio, $\frac{\rho D}{(\rho D)^0}$, rather than the absolute values. A factor F_E is defined as the ratio of the experimental density-diffusivity product at a given density to this product $(\rho D)^0$ as the density approaches zero. Thus,

$$F_E = \frac{\rho D}{(\rho D)^0} \quad (53)$$

This factor was evaluated at even values of the density for the krypton results and is tabulated in Table VI and shown by Figure 16 as F_E versus ρ . These values were compared to the Enskog rigid sphere theory given by Equations (17), (19), and (20).

$$F_1 = \frac{\rho D}{(\rho D)^0} = \frac{1}{Y} \quad (17)$$

and

$$Y = 1 + \frac{5}{8} b_0 \rho + \dots \quad (19)$$

Values of F_1 determined in this manner with Lennard-Jones⁽⁶⁻¹²⁾ collision diameters are also shown in Table VI and Figure 16. Now the suggestion of Enskog, that real gas PVT properties be used, was followed according to the specifications of Equations (22), (24), and (27). These are

$$F_2 = \frac{\rho D}{(\rho D)^0} = \frac{\rho b_0}{Y} \quad (22)$$

$$Y = \left[\frac{1}{\rho R} \left(\frac{\partial P}{\partial T} \right)_\rho - 1 \right] \quad (24)$$

$$b_0 = B + T \frac{dB}{dT} . \quad (27)$$

Here, b_0 is now regarded as an empirical constant determined by Equation (27) in order that F_2 converge to unity as ρ approaches zero. The compressibility data of Beattie, et al.^(4,5) were used to determine the temperature derivatives required for y and b_0 at 35°C. With this information F_2 was calculated and is also shown in Table VI and Figure 16.

It is apparent from Table VI and Figure 16 that the Enskog method based on PVT properties greatly improves the prediction of F over the rigid sphere prediction. The Enskog PVT prediction deviates at most three per cent from experiment for krypton self-diffusion at 35°C over the density range of interest. The limited viscosity data⁽⁴⁰⁾ at 20°C did not permit evaluations by Equation (29).

The Slattery Chart⁽⁷⁸⁾ based on Equation (35) may be used to predict self-diffusion coefficients. With generalized compressibility charts⁽³²⁾ this chart may be used to obtain density-diffusivity products. However, for the comparison here the experimental results were determined as functions of reduced pressure, P_r , and compared in the form of $PD/(PD)^\circ$ to the results predicted by the Slattery chart. These results are given in Table VII. The deviation of the Slattery prediction is consistently of the order of 10 per cent low except for the reduced pressures above four. The Slattery chart is greatly influenced by the compressibility factor over the range of $P_r > 4$. In this range predictions show little density dependence so that it is not surprising that the experimental results are about 10 per cent higher than the Slattery prediction.

TABLE VI
KRYPTON SELF-DIFFUSION COMPARISON
at 35°C

Moles/liter	F_E	F_2	F_1
		Enskog PVT $b_0 = 0.07147$	Rigid Spheres $b_0 = 0.05886$
0	1.000	1.000	1.000
1	1.044	1.028	0.964
2	1.061	1.055	0.928
3	1.091	1.081	0.893
4	1.093	1.102	0.859
5	1.091	1.119	0.818
6	1.084	1.111	0.793
8	1.064	1.103	0.730
10	1.039	1.032	0.671
12	1.015	--	0.616

TABLE VII
KRYPTON SELF-DIFFUSION COMPARISON
WITH THE SLATTERY CHART

Reduced Pressure P_r	$\frac{PD}{(PD)^{\circ}}$ Expt'l	$\frac{PD}{(PD)^{\circ}}$ Slattery
0.5	0.991	0.900
0.8	0.980	0.870
1.0	0.969	0.845
2.0	0.886	0.772
3.0	0.805	0.755
4.0	0.780	0.755

DIFFUSION RESULTS-BINARY SYSTEMS

The methods of predicting binary diffusivities rest ultimately on the Enskog dense rigid sphere theory. In order to present the comparisons in a general fashion, the different methods and procedures for predicting the density-diffusivity ratio F are indicated:

Method 1: Method 1 consists of a prediction of F_1 for a given system by the Thorne Equations (31) and (31). These are

$$F_1 = \frac{PD}{(PD)^0} = \frac{1}{Y_{12}}, \quad (30)$$

where

$$Y_{12} = 1 + 0.15768 \sigma_2^3 \left(8 - \frac{3\epsilon_2}{\sigma_{12}} \right) \rho. \quad (31)$$

Here, Equation (31) has been reduced because the trace (krypton-85) gas number density approaches zero. The conversion to density dependence with collision diameters in Angstroms has been made, also.

Correspondence Methods: Methods 2, 3, and 4 that follow all depend on the definition of a reduced temperature for a binary isotherm of this investigation. The reduction is of the form for low pressure corresponding states theory; namely,

$$T^* = \frac{kT}{\epsilon_{12}} \quad (54)$$

where

$$\epsilon_{12} = (\epsilon_1 \epsilon_2)^{\frac{1}{2}}. \quad (14)$$

Now, the T^* for a given binary isotherm is equated to the reduced temperature equation for the base gas 2 and a pseudo-temperature T_f is determined by

$$T_f = \frac{T^* \epsilon_2}{k} = T \left(\frac{\epsilon_1}{\epsilon_2} \right)^{\frac{1}{2}}. \quad (55)$$

This, pseudo-temperature is the temperature of the base gas corresponding to the reduced binary temperature. Once the pseudo-temperature has been determined the Enskog dense gas theory as modified for use with PVT properties is applied. This procedure is further divided into three different procedures or methods depending upon the method of determining the now empirical constant b_0 . Thus, methods 2 and 3 consist of defining T_f and using the dimensionless Enskog Equations (22) and (24) such that

$$F_2, F_3 = \frac{\rho D}{(\rho D)^0} = \frac{\rho b_0}{\gamma}, \quad (22)$$

and

$$\gamma = \left[\frac{1}{\rho R} \left(\frac{\partial P}{\partial T} \right)_\rho - 1 \right]. \quad (24)$$

The temperature derivatives of the pressure at constant densities are evaluated at the pseudo-temperature, T_f . Thus, with these methods the state properties of the base gas at T_f define the variation of the density-diffusivity product with density.

Method 2: The evaluation of F_2 for Method 2 proceeds as indicated above but with the determination of b_0 by Equation (27):

$$b_0 = B + T \frac{dB}{dT}. \quad (27)$$

Method 3: The determination of F_3 by Method 3 consists of determining b_0 by the convergence condition that

$$\rho b_0 \rightarrow \gamma \quad (25)$$

as ρ approaches zero. In order to use this procedure ρ/γ is plotted versus ρ and the intercept as ρ approaches zero is equated to the reciprocal of b_0 .

Thus,

$$b_0 = \left(\frac{1}{(\rho/\gamma)^0} \right)^0 \quad (56)$$

where $(\rho/\gamma)^0$ is determined as ρ approaches zero. This method requires very good PVT data at the lower densities in order for the derivatives to follow a consistent convergence pattern.

Method 4: Method 4 consists of determining T_f and evaluating the density-diffusivity ratio with a knowledge of viscosity data at this temperature according to Equation (29),

$$F_4 = \frac{\rho D}{(\rho D)^0} = \frac{\mu}{\mu^0} (1 + 0.8\gamma + 0.761\gamma^2)^{-1} \quad (29)$$

where $\frac{\mu}{\mu^0}$ is the ratio of the viscosity at a high density to that as $\rho \rightarrow 0$ (usually one atmosphere).

In order to correspond the results at T_f with the experimental results at T a density reduction is indicated. The core of interaction between molecules of species 1 and 2 may be indicated by a rigid sphere second virial coefficient. Thus, a reduced density may be specified such that

$$d_{12}^* = \left(\frac{2}{3} \pi N \sigma_{12}^3 \right) \rho, \quad (57)$$

in order to compare the experimental results with the predictions of T_f on the same basis where the reduced density is given by

$$d^* = \left(\frac{2}{3} \pi N \sigma_2^3 \right) \rho. \quad (58)$$

Now, in this investigation it was desirable to predict the density dependence of the diffusion coefficient on the basis of the PVT properties of the base gas at the experimental run conditions. This amounts to a self-diffusion prediction and corresponds to Method 2 above. The density-diffusivity product ratio calculated in this manner is indicated as $F_2)_T$ to

indicate the general Method 2 but at the experimental diffusion run temperature, T .

In order to compare the binary experimental data with the different methods outlined here, the experimental density-diffusivity product ratio F_E was determined. This is shown in Table VIII for the systems of interest. The Thorne Equation rigid sphere ratio F_1 is indicated also. This was determined with Lennard-Jones viscosity collision diameters. If sufficient PVT and viscosity data at T_f were available, F_2 , F_3 , and F_4 were determined and shown in Table VIII. The pseudo-temperature T_f of helium is quite low and the available compressibility data⁽³²⁾ has limited applications so that this gas was omitted. Because of the limited range of the CO_2 data it was not shown either. For the argon and nitrogen systems the compressibility compilations by Michels, et al.^(57,58) were used to determine F_3 at the pseudo-temperature. The convergence of ρ/γ to zero density is quite erratic for this data. However, a plot of ρ/γ versus ρ will in general show the form of the density dependence and the setting of b_0 is only a means of specifying the axis position. For ethylene F_2 was determined from Michels⁽⁵⁵⁾ PVT data. Here, b_0 was determined from the temperature dependence of the second density constant in the low density pressure-volume expansion. Also, for nitrogen at $35^\circ C$, F_4 was determined with the viscosity data of Ross and Brown⁽⁷⁵⁾ extrapolated to $T_f = 60^\circ C$. The Comings, et al.⁽¹⁵⁾ viscosity data was used to determine F_4 for ethylene. For argon and nitrogen at $35^\circ C$ the self-diffusion calculation of $F_2)_T$ was carried out using the Michels^(56,58) PVT data.

The comparisons of Table VIII are shown by the F versus ρ plots of Figures 17 through 21. For all of the cases except ethylene the differ-

ence between the density reduction is not significant. However, for ethylene the distinction of d_{12}^* and d_1^* is of significance and accordingly in Figure 21 the values of F_1 and F_E are plotted versus d_{12}^* while F_2 and F_4 are plotted versus d_1^* on a common d^* axis.

An inspection of Table VIII and Figures 17 through 21 reveals that the Thorne rigid sphere approximation F_1 always decreases well below the experimental results. The plots, of course, show the consistent increase with density for the experimental data. For the argon and nitrogen cases the specification of the pseudo-temperature T_p increases the agreement with experiment up to 20 per cent over the self-diffusion calculations of the base gas at the diffusion run temperature T . For the argon at -25°C case the pseudo-temperature calculations are in very good agreement with experiment. Calculations by Method 4 with the viscosity ratio tend much lower than those based on state properties at T_p . The erratic behavior of F_4 of Figure 21 is due to the combination of the rapid increase in viscosity and γ inflection in this density range. The values of F_2 for ethylene are somewhat higher than the experimental values but the trend in the curves of these are similar.

It may be concluded that the Enskog method based on base gas PVT data at the pseudo-temperature T_p is the best method of predicting the density dependence of the krypton-85 diffusivities of this investigation.

TABLE VIII
DENSITY DEPENDENCE COMPARISONS
FOR BINARY SYSTEMS WITH KRYPTON-85

ARGON

ρ	<u>(35°C Isotherm)</u>				<u>(-25°C Isotherm)</u>	
	F_1	F_E	F_3	$F_2)_T$	F_E	F_3
2	0.938	1.052	1.035	0.945	1.038	1.000
4	0.884	1.085	1.033	0.917	1.069	1.015
6	0.835	1.100	1.023	0.888	1.101	1.045
8	0.791	1.113	1.010	0.857	1.131	1.081
10	0.752	1.116	0.986	0.825	1.161	1.116
12	0.716	1.113	0.960	0.792		

NITROGEN

ρ	<u>(35°C Isotherm)</u>					<u>(-25°C Isotherm)</u>	
	F_1	F_E	F_3	F_4	$F_2)_T$	F_E	F_3
2	0.928	1.045	1.014	0.958	0.935	1.030	0.996
4	0.855	1.070	1.022	0.922	0.894	1.064	0.986
6	0.812	1.087	1.021	0.888	0.854	1.096	0.981
8	0.764	1.100	1.009	0.860	0.809	1.129	0.964
10	0.722	1.108	0.975	0.825	0.764	1.161	0.934
12	0.684	1.112	0.917	0.768	0.718		

ETHYLENE

ρ	d^*_{12} $\times 10^2$	F_1	F_E	d^*_1 $\times 10^2$	F_2	F_4
2	15.2	0.909	1.071	19.1	1.050	0.886
4	30.4	0.832	1.125	38.1	1.139	0.855
6	45.6	0.767	1.152	57.4	1.260	0.911
8	60.8	0.712	1.146	76.5	1.316	0.975
10	76.0	0.664	1.104	95.6	1.205	0.936
12	91.2	0.623	1.027	114.7	1.021

FIGURE 16: KRYPTON SELF-DIFFUSION COMPARISONS

FIGURE 17: KRYPTON-ARGON DIFFUSION COMPARISONS
at 35°C

FIGURE 18: KRYPTON-ARGON DIFFUSION COMPARISONS
at -25°C

FIGURE 19: KRYPTON-NITROGEN DIFFUSION COMPARISONS
at 35°C

FIGURE 20: KRYPTON-NITROGEN DIFFUSION COMPARISONS
at -25°C

FIGURE 21: KRYPTON-ETHYLENE DIFFUSION COMPARISONS
at 25°C

ACCURACY AND PRECISION OF RESULTS

The absolute accuracy of the diffusion results is best indicated by the agreement of the low pressure extrapolation results with the Chapman-Enskog theory and previous investigations. These results agree with the dilute gas theory results certainly to within the accuracy claimed for this theory with the usual Lennard-Jones potential. The agreement with previous low pressure investigations is within three per cent which is within the usual experimental accuracy.

In order to ascertain the internal precision of the results, mean lines were drawn through the experimental points for each isotherm on the density diffusivity plots of Figures 10 through 15. Only three runs (I-2A, 5A and 19A) deviate more than one per cent from the average lines through the experimental points for the Glass Capillary Porous Plug A results. The maximum deviation is about 2.5 per cent for the high I-19A run. Deviations of points from the mean isotherm lines of Figures 12 and 13 for Porous Plug B are less than one per cent for the higher density region extending from about three moles per liter to higher densities. The low density region below three moles per liter has a fair amount of scatter in the density-diffusivity product versus density plot. This result is expected when it is realized that here the pressure measurement becomes important. However, even in this region the highest deviations from the mean lines were less than three per cent. The average deviation is consistent with the one per cent deviation noted above.

The scintillation cell results of Figures 14 and 15 show a larger scatter than the ionization cell results. A number of diffusion runs show deviations of up to five per cent from the mean curves. The most serious deviations are unfortunately in the argon 35°C run used in calibrating the Porous Plug C. Runs S-8 and S-9 tended to be higher than the other runs.

The averaging curve was biased in favor of the lower points because the data analysis showed these runs to have better consistency. The argon -25°C isotherm deviations are relatively small. The average deviation of the scintillation cell results is within two per cent.

EFFECT OF CELL CHAMBER STIRRING ON DIFFUSION RESULTS

The effect of stirring the chambers of the ionization cell may be noted by reference to the argon 35°C mean isotherm lines of Figure 12. Here at a density of approximately four moles per liter two lines of density-diffusivity product branch off at higher densities. The lower line represents the mean of several diffusion runs made without stirring the cell chambers while the higher line represents the mean of the points determined with cell chambers being stirred. The highest experimental point deviation is about one per cent except for the low density (3.04 moles/liter) point for Run I-37BS which is about two per cent high. The non-stirring mean line tends to lower values of the density-diffusivity product as the density is increased. At 12 moles per liter this deviation from the stirred results amounts to about 4.5 per cent. Now seven runs were made at about 5.5 moles per liter density with varying stirring rates ranging up to 44 cycles per minute for a seven minute cycle. These runs did not show any variation of diffusivity with stirring rate. Therefore, it may be concluded that stirring the cell chambers begins to affect the diffusion results in the four to five mole per liter range for krypton-85 diffusion in argon. There is no reason to believe that this would not apply for gases of like molecular weight. It should be noted that the helium runs were not stirred because they were of such a short time duration that no convenient stirring and ionization current reading cycle could be used. However, it is believed that stirring would have had little, if any, affect on the results for these

runs. On the other hand, the 22 cpm. for 7 min. rate may have not been sufficient to properly stir the chambers for the krypton-85 diffusion runs. It is not believed that the electrode design impeded the natural or forced mixing to any important extent. The outer electrode had side 5/64" holes about its cylindrical shell to aid in mixing.

An important point is concerned with the effect mixing has on promoting bulk flow through the porous plug. All stirring runs with the ionization cell were made with the Porous Ceramic Filter Plug B (10 micron retention). It is not believed that stirring eddy currents were transmitted any appreciable distance into this porous medium. The overall precision of the results seems to confirm this. Also, no effect was noted for the 5.5 mole per liter argon runs with varying stirring rates. Stirrer convection currents could be very important for a tube bundle porous plug of like area to length ratio.

From the meager stirring effect data of this investigation, no hard and fast rules for stirring prediction criteria can be made. There are many variables that would need to be studied. However, the best comparison criteria appears to be the cell constant for a given gas system. The cell constant, K_B , for the Porous Plug B was found to be 0.03337 cm^{-2} . This may be compared to cell constants of 0.01025 and 0.01414 cm^{-2} for the investigation by Bray⁽¹⁰⁾ and a porous metal plug cell constant of 0.02119 cm^{-2} for the cell used by O'Hern⁽⁶⁴⁾. With the tritiated hydrogen tracer used by Bray, it is doubtful if stirring would have affected the diffusion results to any great extent in view of the effect observed in the heavier krypton-argon system investigated here. However, the O'Hern results for the carbon dioxide self-diffusion situation may be slightly low although possibly only a fraction of the effect observed here. At present the stirring effect observed here can be regarded as an upper-bound because of the

high molecular mass of the krypton-argon interaction. The limited supply of krypton prevented studying this effect in the heavier krypton-krypton system.

The stirring effect was not studied with the scintillation cell and in general a set stirring rate was consistently used.

SOURCES OF ERROR AND MAJOR DIFFICULTIES

O'Hern⁽⁶⁴⁾, Chou⁽¹⁴⁾ and Bray⁽¹⁰⁾ have reviewed many of the sources of errors and difficulties encountered with the ionization type of diffusion cell. Many of these will be reviewed again for purposes of evaluation and comparison to this investigation. Special difficulties with the scintillation cell are also discussed here.

Two important sources of error mentioned by O'Hern⁽⁶⁴⁾ do not appear with the ionization cell of this investigation. These are the effect of stirring and the incomplete isolation of the cell chambers. The previous discussion showed that stirring has a measureable effect as the density of the diffusion run gas increases from four moles per liter. All of the isotherms, except helium, were made with stirring for densities in this range. As indicated, it is believed that the helium results were not affected by the lack of stirring. Because all of the scintillation cell runs were made with stirring, there is no error due to lack of stirring. In order to insure positive close-off of the diffusion cell chambers each cell has in-cell valves. Thus, the problem of tracer gas diffusing into the service lines was non-existent.

The half-life of krypton-85 is 10.3 years⁽²⁴⁾. This time is insignificant when compared to the time for a diffusion run. Thus the measurements were not significantly affected by concentration changes due to radioactive decay.

In order that the diffusion results be truly representative of the diffusion in the gas system studied, "wall effects" must be minimized. These effects may result in a surface transfer of the diffusing species or physical impairment of the diffusion process due to collision with the capillary walls.

It is not believed that surface transfer of krypton-85 between the diffusion cell chambers was important. Any excessive transfer would be indicated by curvature in the logarithm of concentration versus time plots used to analyze the data. No systematic curvature pattern was found. Also, the fact that the pressure dependence of the results for the Glass Capillary Plug A and the Porous Ceramic Plug B used in the ionization cell were similar indicates that no adverse surface effect resulted from the manifold increase in surface area.

If the capillary diameters in the porous plug are small compared to the mean free path of the gas, collisions with the capillary walls will be important. Mathematical analysis^(19,29,67) of self-diffusion in a capillary has shown that the ratio of the diffusion coefficient, D_c , in the capillary to the diffusivity, D , in free space for rigid spherical molecules is given by

$$\frac{D_c}{D} = \left(1 - \frac{3}{4} \frac{\lambda}{d}\right), \quad (59)$$

where λ is the mean free path⁽⁶⁸⁾ of a gas molecule and d is the diameter of the capillary. For krypton self-diffusion the correction factor is on the order of 10^{-4} for the Glass Capillary Plug A for 35°C at 1 atm. conditions. For the porous ceramic plugs this would be on the order of 10^{-3} based on the retention size as the pore diameter. These plugs were used mainly at pressures higher than this and as the factor decreases inversely with the pressure the correction is entirely negligible. Al-

though these are rigid sphere estimates, they serve to indicate an order of magnitude effect and it is believed that this effect is negligible and that the porous plugs served their sole purpose of providing the diffusion path between the cell chambers.

Surface effects may have been important in the ethylene runs with the ionization cell. Here, the background increased greatly with pressure in the region over 100 atm. A thin oily film was found on the chamber surfaces and may have been due to polymerization of the ethylene in the higher pressure storage vessel. Although the background was calibrated and corrections made in the analysis, the deposition of this film in the pores of the porous plug may have influenced the results through surface transfer of krypton-85. After the porous plug was cleaned by benzene washing, Run I-81B with argon showed no after effects of this situation.

The manufacturer's specifications for purity of the gases are given in Appendix H. Except for ethylene it is believed that the gases used were of these specifications. The gases were not dried so that traces of water may have been present. The ethylene, however, was flowed through silica gel and charcoal before being compressed. As noted above the ethylene apparently polymerized upon being compressed. For this case the polymer impurities may have affected the diffusion results.

Because of the very good agreement (0.059 per cent of the mean) of the two calibrations (Appendix F) of the cross-sectional area of the Glass Capillary Plug A, it is believed that this determination is of high accuracy. The determinations of the volumes of the cell chambers by the weight of mercury technique were precise to within a few parts per thousand. Thus, errors in the determination of the Glass Capillary Plug A cell constant K_A probably amounted to two tenths of a per cent or less.

One of the more serious sources of error for the low pressure diffusion runs was the pressure measuring system. The error in reading the Heise 2000 psi gage with 2 psi subdivisions could amount to 1% at the lower pressures. Since the results are presented in the form of the density-diffusivity versus density plots gage reading errors would have an immediate effect particularly if the density-diffusivity product varies. It is believed that this accounts for the larger scatter in the low density experimental points. At the higher densities pressure measurement errors were not as important and are negligible. The determinations of the compressibility factor from the PVT data of the Michels group (Appendix H) were highly reliable and no appreciable error should have resulted.

Sources of error peculiar to the ionization cell would include ionization current measurements and calibration procedures. Fluctuations in the chart readings could cause difficulty in the subsequent analysis. Generally, the voltage range of the vibrating reed electrometer was selected to keep the A and B side fluctuations to a spread of 10 chart units out of a total of 1000. These fluctuations decreased with the current difference decrease as diffusion progressed. The per cent fluctuation based on this difference between the A and B side was usually less than 2 per cent. The averaging process of drawing consistently continuous curves through the readings greatly reduced any discrepancy caused by the current fluctuations. The main problem with the multiple range recorder chart is meshing the readings at the end of a chart with those at the beginning of the next chart. The systematic procedure of drawing the curves minimized this. The introduction of a dry gas about the pickup electrodes in the axle housing (Figure 2) considerably improved the ionization current readings. The fact that background was negligible is a good indication of the performance and reliability of the electronic circuitry. However, for the ethylene runs an increase

in background was noted. When the cell was disassembled a thin oily film possibly due to polymerization coated the electrodes. When this was cleaned off no background was noted for the other gases subsequently investigated.

The best criteria for determining the precision of a given run are the deviations of the experimental readings from the least mean squares fit of the computer LMS program. A measure of these deviations, namely the sum E of the sum of the squares of the deviations is given for the ionization cell diffusion runs in Appendix A (Table A-2). As explained there, an E of order 10^{-5} implies at most a one-half per cent deviation of any of the experimental current differences from the fitted curve.

The f calibration for the ionization cell showed a density dependence in the low density region. In order to check this three argon diffusion runs, I-91B, 92B and 93B were made with the high concentrations of radioactive krypton in the B side chamber. Thus, this f was the inverse of the usual f (A side high) at these conditions and any significant error should be evident. The results showed no deviation from the results of the usual procedure that was not within the normal deviation of the results in this region. These runs may be compared to their A side counterparts I-26B, 27-B and 31B. The determination of the current ratio factor f by the methods of Appendix D are believed to be accurate to within one per cent and the effect on the final results would certainly cause an error of lesser magnitude.

There were more sources of error in the scintillation cell counting rate measurement circuitry than in the ionization cell current measurement circuitry. Generally speaking, the errors were of a more serious nature, also. An important source of error in the final results is the background counting rate. This was always significant and varied with time. The background was assigned to each run from average background determinations

at periodic intervals. These are given for each run in Table B-2 (Appendix B). If the background errors for the two sides of the cell were in the same direction, they tended to cancel out in the analysis. Because this is the more realistic situation, errors due to this cause were minimized.

The fluctuations of the counting rates for the scintillation cell during a run were higher in terms of chart units than those of the ionization cell. Also, because of the slow response these fluctuations were not as easily averaged as those of the ionization currents. When the continuous curves were drawn through the counting rate readings for a diffusion run, the reading during the last half-minute of the two minute indication was considered the most accurate and the curve was averaged through this portion. For these reasons it was harder to mesh properly the readings as the chart scales were switched. Since the scales overlapped it was an easy matter to assign the same reading for a time in this region and draw the curves through these points. The difficulty arose in determining the curvature of the counting rate curves in the mesh region due to the poor resolution resulting from the automatic switching back and forth between chart scales as a consequence of the fluctuations in the readings. For these reasons the averaging procedure with the scintillation cell assumed greater importance than for the ionization cell. This is reflected in the recorded diffusion run readings of Appendix B (Table B-2) where only three figure significance is indicated. With consistent procedures these averaging errors were minimized. However, the graphical analysis of the diffusion runs indicated that the reading errors could cause errors up to five per cent in the final result.

Because the photomultiplier tubes of the scintillation cell changed characteristics with time, it was necessary to readjust the counting rate ratio of the A to B side readings periodically. The pressure dependence

of the f factor set in this way is shown by Appendix E (Figure E-2). Five adjustments were made during the course of the diffusion runs. The first and last were calibrated for pressure variation of f . Many of the diffusion runs were allowed to proceed to equilibrium and the f determined in this manner. The determination of f was not entirely satisfactory. Errors caused by estimating this factor could certainly be significant and cause errors up to three per cent in the final results.

VII. CONCLUSIONS AND SUMMARY

The primary objectives of the research recorded here were to determine the Fick's law diffusion coefficients on an absolute basis for krypton-85 diffusion through various dense gases for which no data were available, and to compare these results with predictions based on the kinetic theory of gases. For the type of diffusion cell employed in this investigation it was desired to study the effect that stirring the cell chambers had on the diffusion results.

A quasi-stationary ionization type diffusion cell was designed and constructed which differed in certain important respects from those of previous investigators. In order to eliminate diffusion into the service lines, this cell was constructed with in-cell valves for isolating the cell chambers during a diffusion run. In order to study the effect that mixing the cell chambers had on the diffusion results this cell was designed and mounted so that a rocking motion would actuate pendulum stirrers in the cell chambers. The electrode assembly of this cell consisted of inner and outer electrodes. This allowed better utilization of the fine electronic current measurement instrumentation afforded by the vibrating reed electrometer used in conjunction with a multiple range recorder.

Also, a scintillation detection diffusion cell of the quasi-stationary state type was designed and constructed with in-cell valves and magnetic stirring devices. The counting rate measurement circuitry consisted of photomultiplier-amplifier combinations with ratemeter drive of a recording potentiometer.

A glass capillary tube bundle porous plug for use with the ionization cell was constructed. The average cross-sectional area of this plug was determined with high precision by weight of mercury and resistance of mercury calibration techniques. The cell constant for this plug in the ioniza-

tion cell was determined solely from accurately measured geometrical constants. Thus, absolute determinations of the diffusion coefficients could be made for the gas systems at the lower density range with this plug. Two porous ceramic plugs were constructed and calibrated with results of the capillary plug.

The procedure for a diffusion run consisted of introducing radioactive krypton-85 into one side of the cell charged with the base gas and recording with time the increase on one side and the decrease on the other side of the krypton-85 concentration. This procedure is preferred over procedures which rely on the specification of initial and final concentrations and, thus, are subject to transient effects. The time chart recording permits the determination of the diffusivity from many experimental observations during the time for which the very simple quasi-stationary state mathematical analysis is applicable.

In this way the diffusion coefficients for krypton-85 (Kr^*) diffusion in various gases for various experimental conditions of temperature and density were determined as follows:

1. Ionization Cell System;

- a. Kr^*-A at $35^\circ C$ to 15 moles per liter,
- b. Kr^*-N_2 at " to 14 " " " ,
- c. Kr^*-He at " to 14 " " " ,
- d. Kr^*-CO_2 at " to 4 " " " ,
- e. $Kr^*-C_2H_4$ at $25^\circ C$ to 13 " " " ,
- f. Kr^*-Kr at $35^\circ C$ to 12 " " " ,

2. Scintillation Cell System;

- a. Kr^*-A at $35^\circ C$ to 5 moles per liter,
- b. Kr^*-A at $-25^\circ C$ to 10 " " " ,
- c. Kr^*-N_2 at $-25^\circ C$ to 10 " " " .

The diffusion results along with the temperature and density are tabulated (Tables II, III, and IV) and are graphically represented as the density-diffusivity product versus the density by Figures 10 through 15. Mean curves were drawn through the experimental points. The low pressure extrapolation of these results agreed very well with the results of previous investigations of krypton self-diffusion to within three per cent which is within the experimented error claimed for these determinations. The krypton-argon extrapolation agreed within two per cent of a determination made previously but was in marked disagreement with another determination which is believed to be in error. All of the low pressure extrapolations agreed with the Chapman-Enskog non-uniform dilute gas theory to within the accuracy (normally a few per cent) claimed⁽⁷⁸⁾ for this theory when used with Lennard-Jones(6-12) viscosity interaction force parameters.

The dense gas diffusion results are compared to the Enskog dense gas theory in its various modifications. Recently developed theories based on the non-equilibrium distribution function have not progressed to the point where useful predictions may be made. The Enskog dense rigid sphere theory did not predict the diffusion results with any meaningful accuracy. However, the modification of this theory for use with compressibility properties predicted to within three per cent the density dependence of the krypton self-diffusion coefficient. The predictions by the Slattery corresponding states self-diffusion chart were consistently low by about ten per cent below the experimental results over the valid reduced pressure range of this chart.

Because the binary systems of this study were of trace quantities of krypton-85 diffusing through another essentially pure gas, two methods are outlined for predicting the density dependence of the diffusivity by the Enskog theory modified for use with base gas PVT properties at a pseudo-

temperature. The pseudo-temperature is defined as the temperature of the base gas which when reduced by its characteristic Lennard-Jones(6-12) potential temperature gives a reduced temperature that corresponds to the reduced temperature of the diffusion run. This latter reduction is made with the combined Lennard-Jones interaction potential temperature, (ϵ_{12}/k) . The density reduction indicates the reduction of the experimental diffusion run density by the rigid sphere second virial coefficient based on the core of interaction between the unlike molecules. This compares equally on the scale determined by the reduced density for the base gas alone at the pseudo-temperature.

A third method of prediction involves utilizing the density dependence of the base gas viscosity along with PVT properties at the pseudo-temperature.

These methods are compared for the binary system isotherms of this investigation where application is practical. In general, the Enskog PVT methods predict the experimental results more accurately than the method based in part on viscosity. Both of these methods showed considerable improvement over the rigid sphere approximation. Density dependence predictions based on the Enskog method with the PVT properties of the base gas at the diffusion run temperatures tended to be lower than determinations made at pseudo-temperatures.

It is noted that for both diffusion cells the density-diffusivity product increases with density in the lower density region below about five moles per liter for all the isotherms. This consistency between the results of the two cells appears to verify the assumptions of proportionality between the krypton-85 concentration and the counting rates of each detection method. This is further emphasized by the fact that the counting rates for each method vary differently with density for constant krypton-85 con-

centration.

The precision of the ionization cell results is better than that for the scintillation cell. The average deviation of the ionization cell results from the mean isotherm curves is well within one per cent with only a couple points above three per cent. Several points for the scintillation cell results deviate about five per cent from the mean isotherm lines, although the average deviation is less than two per cent. The errors associated with the scintillation detection measurement circuitry are much more serious than those of the ionization cell circuitry. The main objection is the time instability of the photomultiplier tubes which necessitates frequent calibrations for the f ratio of the reading for one chamber to that of the other chamber for the same concentration of krypton-85. The absence of background plus the fact that the precision of the ionization current measurements permits electronic computer analysis of the data makes the ionization cell even more attractive.

It is shown that for the krypton-argon system at 35°C the effect on the diffusion results of stirring the ionization cell chambers begins in the 4 to 5 moles per liter region and becomes more pronounced as the density increases. At 12 moles per liter the results with stirring are about 4.5 per cent higher than the non-stirred results. It is believed that this represents an upper bound for gases because of the heavy molecular weight krypton-argon interaction. Because the high density experimental runs were made with diffusion chamber stirring this does not appear as a source of error.

SUGGESTIONS FOR FUTURE RESEARCH

Other than the general suggestion of further experimental studies of diffusion in dense gases this author would like to suggest specific areas

for application of the equipment now available as a result of this investigation. It is suggested that the ionization cell be used for further determinations of krypton-85 diffusion coefficients in dense gas systems with argon, carbon dioxide and nitrogen at higher temperatures such that the pseudo-temperatures are within the range of applicability of the very good PVT data of the Michels group (Appendix H) and also the viscosity data of this same group^(52,59,60). This would permit a better comparison of the prediction methods. This data would also be of value for determining the temperature dependence of the dense gas diffusivities which this author has hesitated to evaluate with the limited temperature range of the data available here.

For purposes of comparing with the results of this investigation it would be of value to know the density dependence of argon diffusivities in krypton at 35°C. These could be determined with argon -37 as the tracer. It is believed that the ionization cell of this investigation would give somewhat more consistent and reliable results than the experimental apparatus employed by Mifflin⁽⁶¹⁾ for argon self-diffusion measurements. The now hot krypton salvaged from this investigation could be used to make up krypton-argon mixtures for further studies.

Recently, a number of theoretical derivations^(4,72,79) based on the non-equilibrium pair distribution function have been made for transport phenomenon description in dense fluids. Generally, these theories have been developed for viscosity and thermal conductivity in terms of diffusion coefficients. Many of the assumptions of the theories qualify them to simple dense fluids. The best fluids for evaluating these assumptions are the liquid rare gas elements. It is suggested that the scintillation cell be used at low temperatures to investigate diffusion processes of krypton-85 or other rare gas tracers in very dense argon.

The determination of a diffusion coefficient by the methods of this investigation requires a considerable amount of physical endeavor. The recent developments of nuclear magnetic resonance techniques by the McCall group⁽⁵⁰⁾ for the study of self-diffusion in liquids warrant investigation of applicability to dense gas systems. This is a much faster determination method and is not limited by the availability of radioactive tracers.

APPENDIX A

TABULATION OF EXPERIMENTAL RUN
DATA FOR IONIZATION CELL RUNS

1. Table A-1; Primary Experimental Run
Data Except for Ionization
Current Data
2. Table A-2; Ionization Current Data
3. Table A-3; Derived Experimental Run
Data Except for Diffusivities

In this appendix the experimental data is given for the experimental diffusion runs carried out with the ionization cell. In order to obtain a compact assembly the data has been arranged in three tables. In Table A-1 the averaged basic data for each run are given with the exception of the ionization currents which have been presented in the best form by Table A-2. In Table A-3 the derived run data except for the actual diffusion coefficients are shown.

An explanation of the various headings in the tables follows:

Date - - the date that the run was started.

Run No. - - the notation for indicating the run number is of the form I-XYZ where I indicates an Ionization Cell run X while Y may be either A or B indicating the porous plug used and if an S replaces Z then the cell was stirred.

Base Gas - - the gas in which the Kr-85 is diffusing.

Pressure, Gage - - the pressure gage used as coded in Appendix G.

Pressure, Avg. - - the average of the absolute pressures at the beginning and end of a run.

Avg. T. C. - - the average run cell thermocouple millivolts.

Avg. Temp. - - the average cell temperature.

Chart Record - - A ten minute cycle reading scheme is indicated by a 10. Now C-1 and C- $\frac{1}{2}$ indicate continuous chart at one inch and one-half inch per minute, respectively.

Voltage Range - - The particular vibrating reed voltage range used is indicated by the number of volts for full scale deflection corresponding to 1000 chart units.

Z - - the compressibility factor of the run gas at run conditions.

f - - the equilibrium current ratio of the A side reading to the B side reading.

LMS Slope - - the slope of $\ln (A - fB)$ vs. t obtained by the least mean squares computer program.

E - - the sum of the squares of the differences between the LMS fit and the experimental data.

t - - the diffusion time in minutes.

A - - the number of chart units which is a measure of the ionization current from the A side of the ionization cell.

B - - the number of chart units which is a measure of the ionization current from the B side of the ionization cell.

S - - average spread (chart units) of the random fluctuations for a reading.

Thermocouple IT-1 (Appendix G) was used for the runs up through I-20A and IT-2 was used thereafter.

The standard stirring (rocking) procedure was 7 min. out of every 10 at 22 cycles per min. However, for five runs the speed of rocking was different as follows:

IB - 38S - - - 11 cpm,

IB - 94S - - - 11 " ,

IB - 95S - - - 44 " ,

IB - 96S - - - 44 " ,

IB - 99S - - - 33 " ,

Since in general only negligible background was observed and the recorder was adjusted to zero for a run, there were no corrections to the chart unit readings, A or B. However, background was important for several of the ethylene runs.

The ionization current data in chart units versus time (minutes) was processed on a Royal McBee LGP-30 medium speed computer. Scaled readings of t , A, and B of Table A-2 plus the value of f for the run were placed

in computer memory. A subroutine computed $A-fB$ and placed this with t in the proper memory section of the regular Extended Range Floating Point Least Mean Squares Program available for this computer. This program enabled the computer to least mean square fit the data in the form

$$\log_e (A-fB) = -mt + b. \quad (A-1)$$

At the given times (t 's) values of $\ln (A-fB)$ both for the experimental data points and the fitted function as well as the difference between them were printed out. Also, the slope m , the intercept b , and the sum of the squares of the differences E , as noted above, were printed. The slope m is, of course, related to KD and is the primary information obtained from the program. The print out format enables the operator to quickly spot any discrepancies or errors. The value of E serves as a useful guide to the reliability of the fit. An E of the order of 10^{-5} implies that no difference in the natural log of a data point and the fitted equation exceeded much over 10^{-3} as there were usually 10-14 points summed. This means that the maximum deviation of a data point from the fitted equation is less than $\frac{1}{2}\%$ in most cases.

In general the ionization current readings, A and B , were divided by 100 to scale them to a range of 0-10 for input into the computer. The times, t , were also scaled so that the independent variable range was close to but greater than unity.

TABLE A-1

PRIMARY EXPERIMENTAL RUN DATA EXCEPT FOR
IONIZATION CURRENT DATA

Date	Run No.	Base Gas	Pressure Gage Avg.	Avg. T.C.	Avg. Temp.	Chart Record	Voltage Range	
(1960 1961)			(psia)	(mv)	(°C)		(volts)	
11-15	I-1A	A	B	135.8	1.400	35.0	C- $\frac{1}{2}$	1
11-17	I-2A	"	"	76.2	1.402	35.1	10	1
11-20	I-3A	"	M	37.10	1.400	35.0	C-1	1
11-21	I-4A	"	M	38.11	1.403	35.1	C- $\frac{1}{2}$	0.3
11-21	I-5A	"	B	219.3	1.404	35.1	10	3
12-30	I-6A	"	C	638.7	1.406	35.2	10	10
12-31	I-7A	"	C	368.7	1.404	35.1	10	10
12-31	I-8A	"	A	62.0	1.401	35.1	C- $\frac{1}{2}$	1
1-1	I-9A	He	A	99.1	1.400	35.0	C-1	0.3
1-3	I-10A	"	C	302.0	1.405	35.2	C- $\frac{1}{2}$	1
1-3	I-11A	"	C	754.0	1.400	35.0	10	3
1-4	I-12A	"	A	65.7	1.400	35.0	C-2	0.1
1-5	I-13A	"	C	883.9	1.401	35.1	10	1
1-5	I-14A	"	A	54.5	1.402	35.1	C-2	0.1
1-6	I-15A	"	C	451.8	1.400	35.0	10	1
1-8	I-16A	N ₂	C	513.3	1.400	35.0	10	3
1-9	I-17A	" ²	A	111.9	1.401	35.1	10	1
1-10	I-18A	"	A	72.5	1.401	35.1	C- $\frac{1}{2}$	0.3
1-10	I-19A	"	C	354.8	1.401	35.1	10	3
1-11	I-20A	"	A	46.1	1.401	35.1	C-1	0.3
4-1	I-21A	"	C	324.7	1.402	35.1	10	3
4-1	I-22A	Kr	"	227.8	1.399	35.0	10	30
4-2	I-23A	"	"	109.7	1.399	35.0	C- $\frac{1}{2}$	10
4-2	I-24A	"	H	55.94	1.400	35.0	C- $\frac{1}{2}$	3
4-3	I-25A	"	H	53.63	1.401	35.0	C- $\frac{1}{2}$	3
1-29	I-26B	A	C	161.9	1.400	35.0	C-1	3
1-29	I-27B	"	C	711.9	1.400	35.0	C- $\frac{1}{2}$	10
1-29	I-28B	"	A	105.0	1.397	35.0	C-1	3
1-30	I-29B	"	C	506.9	1.399	35.0	C- $\frac{1}{2}$	10
1-30	I-30B	"	"	1079.0	1.404	35.1	10	10
1-30	I-31B	"	"	303.4	1.400	35.0	C-1	3
1-31	I-32B	"	"	1955	1.400	35.0	10	10
2-6	I-33BS	"	"	1957	1.400	35.0	10	10
2-6	I-34BS	"	D	3035	1.400	35.0	10	10
2-7	I-35BS	"	"	5522	1.400	35.0	10	10
2-8	I-36BS	"	"	6027	1.402	35.0	10	10
2-10	I-37BS	"	C	1079.8	1.400	35.0	10	10
2-11	I-38BS	"	C	1959.3	1.402	35.0	10	10
2-11	I-39BS	"	D	4010	1.400	35.0	10	10
2-12	I-40BS	"	D	4895	1.400	35.0	10	10

TABLE A-1 (cont'd.)

Date	Run No.	Base Gas	<u>Pressure</u>		Avg. T.C.	Avg. Temp.	Chart Record	Voltage Range
			Gage	Avg.				
				(psia)	(mv)	(°C)		(volts)
2-12	I-41BS	A	D	3568	1.400	35.0	10	10
2-13	I-42BS	"	"	4450	1.400	"	10	10
2-14	I-43BS	"	"	2565	1.400	"	10	10
2-15	I-44BS	"	C	1523	1.400	"	10	10
2-16	I-45B	He	"	1345	1.400	"	C-2	3
2-17	I-46B	"	"	364.6	1.400	"	C-2	1
2-17	I-47B	"	"	1915	1.400	"	C-1	3
2-18	I-48B	"	D	3530	1.400	"	C- $\frac{1}{2}$	3
2-18	I-49B	"	C	1639	1.400	"	C-1	3
2-19	I-50B	"	D	4587	1.400	"	C- $\frac{1}{2}$	3
2-19	I-51B	"	"	2735	1.400	"	C-1	10
2-19	I-52B	"	"	6100	1.400	"	C- $\frac{1}{2}$	3
2-19	I-53B	"	C	884.2	1.400	"	C-1	10
2-20	I-54B	"	D	3115	1.400	"	C- $\frac{1}{2}$	10
2-20	I-55B	"	D	5197	1.400	"	C- $\frac{1}{2}$	3
2-20	I-56B	"	"	4100	1.399	"	C- $\frac{1}{2}$	3
2-21	I-57B	CO ₂	C	200.7	1.401	"	C-1	3
2-21	I-58B	"	"	844.7	1.399	"	C- $\frac{1}{2}$	3
2-21	I-59B	"	"	446.2	1.404	35.1	C- $\frac{1}{2}$	3
2-22	I-60B	"	"	643.7	1.398	35.0	C- $\frac{1}{2}$	3
2-22	I-61B	"	A	83.4	1.402	"	C-2	1
2-23	I-62B	"	C	316.7	1.398	"	C- $\frac{1}{2}$	3
2-23	I-63B	"	"	850.8	1.400	"	10	3
2-24	I-64BS	N ₂	"	262.8	1.400	"	C-1	3
2-24	I-65B	"	"	513.3	1.400	"	C-1	3
2-25	I-66B	"	"	360.8	1.399	"	C-1	3
2-25	I-67B	"	"	1019	1.399	"	C- $\frac{1}{2}$	10
2-26	I-68BS	"	"	1995	1.401	"	10	10
2-26	I-69BS	"	D	4992	1.400	"	10	10
2-27	I-70BS	"	"	2995	1.400	"	10	10
2-27	I-71BS	"	"	6002	1.400	"	10	10
2-28	I-72BS	"	"	4020	1.400	"	10	10
3-3	I-73BS	C ₂ H ₄	C	912.2	0.994	25.1	10	3
3-3	I-74B	"	"	673.1	0.989	25.0	C- $\frac{1}{2}$	3
3-4	I-75B	"	"	444.6	0.989	25.0	C- $\frac{1}{2}$	3

TABLE A-1 (cont'd.)

Date	Run No.	Base Gas	<u>Pressure</u>		Avg. T.C.	Avg. Temp.	Chart Record	Voltage Range
			Gage	Avg.				
				(psia)	(mv)	(°C)		(volts)
3-4	I-76BS	C_2H_4	C	1647.7	0.989	35.0	10	3
3-6	I-77B		"	201.2	0.989	25.0	C-1	3
3-7	I-78BS		"	1029.7	0.990	25.0	10	3
3-8	I-79BS		"	1174.8	0.990	25.0	10	3
3-11	I-80BS	"	"	1314.7	0.990	25.0	10	3
3-13	I-81B	A	"	161.7	1.398	35.0	C-1	3
3-16	I-82B	Kr	"	109.6	1.399	35.0	C-2	10
3-16	I-83B	"	"	227.5	1.400	35.0	C-1	10
3-17	I-84B	"	"	434.0	1.400	35.0	C- $\frac{1}{2}$	10
3-18	I-85B	"	"	990.6	1.400	35.0	C- $\frac{1}{2}$	10
3-19	I-86BS	"	"	1981.7	1.399	35.0	10	10
3-20	I-87BS	"	D	3350	1.399	35.0	10	10
3-20	I-88BS	"	C	1617.8	1.400	35.0	10	30
3-20	I-89BS	"	D	2761	1.400	35.0	10	30
3-21	I-90BS	"	C	1414.7	1.400	35.0	10	30
3-29	I-91B	A	"	161.7	1.399	35.0	C-1	3
3-29	I-92B	"	"	711.6	1.399	35.0	C- $\frac{1}{2}$	10
3-30	I-93B	"	"	303.1	1.400	35.0	C-1	10
3-23	I-94BS	"	"	1956.3	1.401	35.0	10	10
3-23	I-95BS	"	"	1956.8	1.400	35.0	10	10
3-24	I-96BS	"	"	1957.8	1.399	35.0	10	10
3-25	I-97B	"	D	5523	1.399	35.0	10	10
3-28	I-98B	"	D	4010	1.399	35.0	10	10
3-30	I-99BS	"	C	1957.6	1.400	35.0	10	10
3-31	I-100B	"	D	3035	1.400	35.0	10	10

TABLE A-2
IONIZATION CURRENT DATA

t	A	B	t	A	B	t	A	B
<u>Run</u> <u>No. I-1A</u>			<u>Run</u> <u>No. I-2A</u>			<u>Run</u> <u>No. I-3A</u>		
10	938.0	144.8	20	848.8	261.8	0	569.7	188.7
20	926.1	157.9	40	817.6	247.8	10	549.0	211.0
30	914.7	169.9	60	789.0	328.3	20	529.9	231.0
80	855.3	225.0	80	762.5	354.3	30	512.6	249.3
120	815.3	264.3	100	739.2	379.0	40	497.3	264.8
160	781.3	299.3	120	719.6	402.0	50	484.3	279.3
200	751.9	330.3	140	700.9	421.8	60	472.4	292.1
240	725.6	357.4	160	684.5	439.8	70	461.3	303.8
280	701.8	382.1	200	656.2	469.7	80	452.2	314.3
320	681.2	403.0	240	633.7	493.8	90	443.9	324.0
360	663.0	421.9	S	5.0	5.0	100	436.2	332.2
400	646.7	439.4				110	429.9	339.6
440	632.0	453.5				120	423.9	346.0
S	8.0	6.0				130	419.0	352.6
						S	5.0	4.0

<u>Run</u> <u>No. I-4A</u>			<u>Run</u> <u>No. I-5A</u>			<u>Run</u> <u>No. I-6A</u>		
4	527.8	83.9	40	920.5	205.0	100	781.9	34.8
8	518.2	93.6	80	892.5	234.0	150	769.0	47.3
12	507.3	103.4	120	865.3	259.8	200	756.1	59.3
16	498.9	113.0	160	841.3	284.0	300	731.8	82.3
20	490.9	122.0	200	818.6	306.0	400	709.9	103.0
30	471.4	143.4	240	797.0	326.3	500	689.2	123.5
40	453.4	162.2	280	777.3	345.0	600	669.7	142.0
50	431.0	179.4	320	759.0	362.4	700	651.2	159.3
60	422.8	194.6	360	741.6	378.5	800	634.9	175.5
70	410.0	208.3	400	726.0	393.2	900	618.8	190.7
80	399.0	220.0	440	711.0	407.5	1000	604.1	204.9
90	389.0	231.7	480	697.6	419.3	1100	590.2	218.9
S	6.0	6.0	520	685.6	431.2	1200	577.6	231.3
			560	674.0	441.7	S	4.0	2.0
			S	5.0	4.0			

TABLE A-2 (Cont'd.)

t	A	B	t	A	B	t	A	B
<u>Run No. I-7A</u>			<u>Run No. I-8A</u>			<u>Run No. I-9A</u>		
50	723.2	124.8	10	770.0	148.4	15	781.0	318.2
100	705.1	142.3	30	730.3	187.5	20	761.1	343.0
150	688.3	158.3	40	711.0	206.3	25	742.3	366.1
200	673.0	173.7	50	693.7	225.9	30	724.6	386.7
250	658.1	188.1	60	678.7	242.4	35	708.3	405.8
300	644.0	202.0	70	664.00	258.3	40	694.0	422.0
350	631.6	215.4	80	651.0	274.1	45	681.0	437.2
400	620.3	228.0	90	638.0	288.0	50	670.0	453.0
450	607.5	238.5	100	624.7	300.7	55	658.8	465.0
500	597.0	250.3	110	612.9	312.1	60	648.7	477.1
550	586.7	261.0	120	602.1	324.7	65	640.0	488.1
600	577.0	270.2	140	583.2	345.0	Eq.	568.0	616.5
650	567.8	279.3	S	5.0	5.0	S	6.0	6.0
S	4.0	3.0						

<u>Run No. I-10A</u>			<u>Run No. I-11A</u>			<u>Run No. I-12A</u>		
10	878.4	93.3	30	921.0	207.8	4	676.8	247.0
20	852.3	118.0	40	911.1	217.4	8	653.0	274.5
30	827.5	141.5	50	899.7	227.5	12	633.0	300.0
40	804.9	163.6	80	869.0	251.6	16	614.3	320.8
50	784.0	184.8	100	851.6	268.2	20	598.6	340.0
60	764.6	204.1	120	834.7	283.7	24	586.0	358.6
70	745.6	223.0	140	818.7	298.5	28	573.0	375.0
80	727.5	240.2	160	802.3	313.4	32	561.0	389.5
90	711.2	257.0	180	788.8	326.3	36	551.2	400.8
100	696.7	272.6	200	775.4	338.9	40	543.0	411.0
120	669.4	301.0	240	751.1	362.3	44	536.0	422.0
140	645.1	325.8	280	728.7	383.4	48	528.8	431.3
160	624.0	348.1	320	708.0	403.0	52	522.5	440.0
180	605.7	367.3	360	690.2	420.0	S	6.0	6.0
S	5.0	5.0	S	3.0	3.0			

<u>Run No. I-13A</u>			<u>Run No. I-14A</u>			<u>Run No. I-15A</u>		
20	928.7	291.2	4	680.4	272.8	70	884.6	267.1
40	912.9	306.2	6	665.8	288.7	80	871.0	281.0
60	896.2	321.1	8	653.7	303.0	100	844.1	307.5
80	881.6	334.6	10	641.7	316.1	120	819.3	331.5
100	868.3	347.9	12	630.1	329.1	140	796.7	354.0
140	843.6	372.3	14	620.0	341.3	160	777.5	373.6
180	821.4	394.6	16	611.2	352.17	180	759.0	391.4
220	799.1	415.3	18	601.0	364.7	200	742.2	409.4
260	780.4	433.3	20	593.4	374.6	220	725.3	424.7
300	762.0	450.2	22	586.2	383.5	240	711.0	438.8
340	746.6	465.1	24	579.3	392.0	260	697.3	452.2
380	732.5	480.0	26	572.5	399.5	280	685.2	464.2

TABLE A-2 (Cont'd.)

t	A	B
420	718.0	492.3
460	705.0	504.5
500	693.5	513.9
540	682.9	523.5

t	A	B
28	566.5	406.7
30	560.3	414.8

t	A	B
320	664.0	485.0
360	646.2	502.7

Run No. I-16A

40	980.2	99.8
120	948.6	133.2
200	917.2	164.0
280	888.0	192.8
360	863.5	219.3
440	838.4	245.0
520	816.0	266.9
560	805.0	278.0
600	794.5	288.6
680	775.3	308.3
760	758.0	326.5
840	739.5	343.0
920	723.6	359.0
1000	709.2	374.7
S	3.0	3.0

Run No. I-17A

60	857.0	345.0
80	833.6	368.4
100	812.3	390.2
120	794.5	409.5
140	778.4	428.0
160	763.2	444.7
180	748.6	459.7
200	735.2	474.0
220	723.0	487.0
240	711.8	499.0
260	701.8	510.0
300	684.2	529.8
340	669.8	546.0
380	657.0	560.0
S	4.0	

Run No. I-18A

10	930.1	254.2
20	907.0	278.7
30	886.7	299.3
40	868.0	318.8
50	850.0	338.0
60	832.0	356.2
70	814.6	373.6
80	800.0	389.0
90	786.3	403.3
100	773.5	417.0
110	760.4	430.5
120	749.4	442.7
130	739.0	453.5
140	729.4	464.0
150	719.5	474.5
160	710.3	484.2
S	8.0	8.0

Run No. I-19A

100	885.5	274.5
150	864.6	296.3
200	844.7	316.6
250	825.8	336.3
300	807.7	354.7
350	791.9	371.5
400	777.8	387.2
450	762.5	402.1
500	749.5	416.0
550	736.7	428.5
600	725.0	440.2
650	714.0	450.3
700	703.3	462.2
750	694.5	472.0
800	686.0	480.7
850	677.6	488.5
S	7.0	7.0

Run No. I-20A

30	818.1	447.0
35	807.5	457.8
40	797.3	467.5
45	789.1	476.7
50	780.0	485.0
55	772.1	494.0
60	764.4	503.4
65	757.6	511.9
70	750.0	518.6
75	743.3	525.7
80	738.4	532.0
85	732.5	538.7
S	10.0	7.0

Run No. I-21A

80	892.8	159.3
120	871.5	182.0
160	850.6	203.7
200	831.0	223.1
240	813.0	242.0
280	796.1	260.0
360	764.2	292.6
400	750.2	308.0
440	736.1	320.8
480	722.8	333.9
520	710.7	346.1
560	699.7	357.8
600	689.0	368.8
640	679.3	379.2
S	4.0	3.0

TABLE A-2 (Cont'd.)

t	A	B	t	A	B	t	A	A
<u>Run</u> <u>No.</u> <u>I-22A</u>			<u>Run</u> <u>No.</u> <u>I-23A</u>			<u>Run</u> <u>No.</u> <u>I-24A</u>		
40	969.2	315.8	50	940.7	370.0	10	976.7	483.9
80	950.3	333.0	80	917.8	393.9	20	963.1	498.3
120	933.7	349.2	100	903.9	408.6	30	950.6	512.7
160	918.0	365.0	120	890.6	423.0	40	939.0	525.8
200	902.5	379.8	140	877.9	436.9	50	927.4	538.6
240	887.7	393.4	160	865.8	449.8	60	915.7	550.3
280	874.0	406.8	180	854.3	462.3	70	905.4	561.6
320	861.1	419.0	200	843.7	474.0	80	896.1	572.1
400	837.0	442.7	220	833.2	485.1	90	887.0	582.3
480	816.2	464.2	240	823.0	495.3	100	878.7	592.0
560	795.4	482.3	260	813.0	505.0	120	862.3	609.8
640	792.6	498.6	280	804.8	514.5	140	848.4	626.0
720	760.0	513.1	300	796.2	523.0	180	823.3	653.7
800	744.8	526.7	320	787.8	531.8	200	812.7	665.8
S	3.0	2.0	S	3.0	2.0	S	4.0	3.0
<u>Run</u> <u>No.</u> <u>I-25A</u>								
10	992.7	452.7						
20	977.2	469.1						
30	962.9	484.5						
40	947.3	499.7						
50	934.8	513.0						
60	922.2	526.1						
70	910.5	538.5						
80	899.5	550.3						
90	889.1	561.8						
100	879.2	572.1						
120	861.0	591.2						
140	844.5	609.0						
160	829.7	624.6						
180	816.7	638.7						
S	4.0	3.0						

TABLE A-2 (Cont'd.)

t	A	B	t	A	B	t	A	B
320	649.8	271.5	320	659.4	283.3	360	794.9	367.3
360	631.6	288.2	360	642.6	300.4	400	781.0	380.5
400	614.9	303.8	400	627.1	316.2	440	769.3	393.2
440	600.4	317.4	440	612.4	330.5	480	757.0	405.7
480	586.9	329.8	480	599.0	344.0	520	746.0	415.3
520	574.2	341.6	520	587.0	355.5	560	735.8	425.5
560	563.3	352.2	560	576.2	366.2	600	726.6	435.8
S	5.0	3.0	S	5.0	3.0	640	718.5	445.3
						S	6.0	5.0

Run No. I-35BS

150	883.3	297.1
200	871.2	311.1
250	858.8	324.0
300	846.9	336.8
350	835.2	349.0
400	824.7	360.5
450	814.1	371.7
500	804.7	382.5
600	788.3	402.4
700	771.6	421.2
800	755.6	437.4
900	740.9	452.5
1000	727.7	466.0
1100	716.1	478.1
S	5.0	3.0

Run No. I-36BS

200	904.3	325.0
250	891.8	337.6
300	880.3	350.1
350	868.9	361.5
400	857.3	372.3
450	847.1	382.5
500	836.8	392.4
600	818.0	410.9
700	799.8	429.0
800	784.4	445.0
900	769.6	460.4
1000	755.7	473.8
1100	743.3	485.8
1200	732.8	497.3
1300	722.7	508.3
S	6.0	4.0

Run No. I-37BS

40	847.6	93.0
60	817.0	124.0
80	788.0	152.0
100	762.1	178.5
120	739.2	202.4
140	716.8	224.8
160	696.3	244.7
180	677.8	263.2
200	660.7	280.0
240	630.4	311.8
260	616.0	324.7
280	603.9	337.0
300	592.6	348.8
S	4.0	3.0

Run No. I-38BS

100	887.8	281.3
150	848.4	321.3
200	818.0	351.1
250	791.8	377.8
300	767.9	401.3
350	746.3	421.9
400	726.6	440.0
450	708.5	456.2
500	693.1	470.3
550	678.8	482.8
600	665.3	493.2
S	5.0	4.0

Run No. I-39BS

100	972.8	285.2
150	952.7	305.8
200	934.0	324.4
250	915.8	342.7
300	899.5	360.0
350	883.5	376.3
400	869.0	391.2
450	854.5	405.0
500	841.5	418.3
550	828.8	431.3
660	817.3	443.2
650	804.7	454.4
700	794.3	465.0
750	784.7	474.6
S	7.0	5.0

Run No. I-40BS

100	969.3	214.0
150	950.8	232.8
200	933.2	250.3
300	899.6	282.8
350	884.7	298.0
400	869.7	314.0
450	856.0	328.3
500	843.2	341.4
550	830.6	353.8
600	818.5	366.1
700	796.1	388.8
800	777.5	409.0
900	758.9	427.5
1000	742.3	444.6
S	6.0	4.0

TABLE A-2 (Cont'd.)

t	A	B	t	A	B	t	A	B
<u>Run No. I-41BS</u>			<u>Run No. I-42BS</u>			<u>Run No. I-43BS</u>		
160	936.3	282.4	160	927.1	236.6	160	812.3	159.7
200	919.7	299.6	200	912.5	251.4	200	789.3	182.0
240	903.0	315.3	240	898.8	265.8	240	768.0	203.5
280	887.4	330.7	280	885.2	279.5	280	748.4	222.6
320	872.7	345.2	320	872.2	292.5	320	729.7	241.4
360	858.3	359.3	360	859.8	304.6	360	712.1	258.3
400	845.2	371.8	400	847.3	317.8	400	695.7	273.9
440	832.3	384.1	480	825.8	340.1	440	680.7	288.6
480	820.6	396.3	560	804.7	360.6	480	657.0	302.1
520	809.0	407.6	640	786.0	379.8	520	653.3	315.3
560	798.1	418.1	720	769.6	397.7	560	641.6	327.3
600	789.0	428.0	800	753.1	413.4	600	630.5	339.0
640	779.5	437.4	880	738.8	428.0	680	610.0	359.1
680	770.0	446.6	960	725.1	441.5	S	5.0	4.0
720	760.6	455.9	1040	712.0	454.5			
S	6.0	4.0	S	5.0	4.0			
<u>Run No. I-44BS</u>			<u>Run No. I-45B</u>					
80	900.2	246.3	12	869.9	147.9			
100	880.6	265.4	16	846.3	169.5			
120	862.9	283.5	20	825.3	190.0			
160	829.1	316.9	24	803.2	208.9			
200	798.9	346.3	28	784.3	227.7			
240	773.0	372.0	32	767.0	245.1			
280	749.9	395.2	36	749.0	261.6			
360	709.3	434.7	40	734.2	276.7			
400	692.8	451.3	44	719.1	291.1			
440	678.5	465.7	48	704.5	304.6			
480	664.9	478.8	52	691.4	317.0			
S	6.0	5.0	56	679.3	329.7			
			60	668.7	340.7			
			64	657.8	351.0			
			S	3.0	3.0			
<u>Run No. I-46B</u>			<u>Run No. I-47B</u>			<u>Run No. I-48B</u>		
3	830.7	259.7	15	940.4	201.8	30	952.1	419.6
4	815.0	275.4	20	920.0	222.4	40	933.8	437.4
5	798.7	290.2	30	879.3	260.4	50	916.7	454.2
6	784.0	304.4	40	844.0	294.0	60	889.0	470.0
8	757.3	331.4	45	827.8	309.1	70	883.0	484.5
10	733.2	355.5	50	812.3	324.6	80	869.6	498.0
12	711.9	377.0	55	798.3	338.6	90	855.3	511.1
14	692.5	396.5	60	784.3	351.3	100	842.6	522.8
16	675.6	412.9	65	771.4	363.7	110	830.6	533.2
18	660.7	429.1	70	759.0	375.3	120	819.0	543.0

TABLE A-2 (Cont'd.)

t	A	B	t	A	B	t	A	B
20	647.2	443.9	75	746.8	386.3	130	809.0	552.0
22	634.7	455.8	80	736.1	396.6	140	799.1	560.9
24	624.2	467.1	90	715.8	415.9	S	5.0	4.0
26	614.8	476.8	100	697.1	432.7			
S	3.0	3.0	S	4.0	3.0			
<u>Run No. I-49B</u>			<u>Run No. I-50B</u>			<u>Run No. I-51B</u>		
25	796.2	186.7	40	928.7	293.9	20	845.5	139.5
30	776.3	206.0	50	911.5	310.4	25	829.9	153.7
35	756.8	224.4	60	895.0	326.3	30	815.5	167.5
40	739.2	241.6	70	879.4	341.2	35	801.0	180.6
45	721.7	257.4	80	865.0	355.4	40	787.2	193.6
50	706.5	272.5	90	851.7	369.3	50	761.5	217.0
55	691.5	286.7	100	837.9	382.0	60	737.7	239.2
60	678.0	299.6	120	812.8	406.9	70	715.7	259.0
70	653.0	323.3	140	791.5	427.5	80	696.2	277.7
80	631.0	344.8	160	771.4	446.6	90	678.6	294.5
90	611.8	363.3	180	752.7	463.7	100	661.1	309.9
S	4.0	3.0	200	736.6	477.1	110	645.4	325.0
			240	708.6	504.5	120	631.7	337.9
			S	5.0	4.0	130	618.6	350.5
						S	3.0	1.0
<u>Run No. I-52B</u>			<u>Run No. I-53B</u>			<u>Run No. I-54B</u>		
40	940.5	281.4	10	855.2	269.4	30	899.5	241.7
50	925.4	295.0	12	840.1	283.1	40	875.3	265.4
60	912.1	308.2	14	826.0	296.1	50	852.9	288.0
80	886.4	333.8	16	812.8	308.8	60	831.9	308.9
100	863.7	356.7	18	800.0	320.8	70	811.8	328.0
120	841.3	377.6	20	787.9	332.2	80	793.6	345.6
140	820.9	397.1	22	776.9	342.9	90	776.8	362.2
160	803.0	415.1	24	765.7	353.1	100	761.1	377.7
180	786.1	432.12	28	745.7	372.1	110	746.0	391.6
200	769.9	446.5	32	726.5	390.2	120	733.0	404.5
220	755.3	460.1	36	709.6	406.3	130	720.0	416.8
240	742.0	472.7	40	695.0	420.8	140	708.5	428.2
260	729.1	483.9	S	2.0	1.0	S	3.0	2.0
S	5.0	4.0						
<u>Run No. I-55B</u>			<u>Run No. I-56B</u>			<u>Run No. I-57B</u>		
40	934.8	248.6	20	926.4	91.3	15	850.7	209.6
50	917.0	265.0	30	901.7	114.3	20	822.7	235.9
60	901.6	280.9	40	879.6	137.4	25	796.4	260.8
80	872.2	310.0	50	858.1	158.8	30	773.5	283.3
100	844.9	336.8	60	837.3	178.0	35	752.2	304.8
120	821.0	360.6	70	819.1	197.3	40	731.4	323.3

TABLE A-2 (Cont'd.)

t	A	B	t	A	B	t	A	B
160	776.8	401.8	80	801.3	215.0	45	712.7	341.4
180	758.1	419.5	90	784.3	231.8	50	696.8	357.6
200	742.5	435.7	100	768.3	247.9	55	681.5	372.4
220	726.3	450.1	120	739.0	276.8	60	667.7	386.6
240	711.9	463.8	140	711.9	303.0	65	654.5	399.0
260	699.8	476.1	160	689.1	326.0	70	642.5	411.0
280	687.3	486.9	180	668.6	346.4	S	3.0	2.0
S	5.0	3.0	200	650.1	366.1			
			S	4.0	3.0			

Run No. I-58B

80	852.2	141.7
100	829.2	163.7
120	807.5	184.0
140	787.9	204.0
160	770.2	220.8
340	648.3	340.6
360	636.7	351.0
380	627.0	360.0
400	618.3	368.4
420	608.9	376.8
S	4.0	2.0

Run No. I-59B

30	883.6	114.6
40	854.6	141.4
60	804.9	189.7
70	782.7	210.8
80	762.0	230.9
100	724.3	266.7
120	692.6	297.8
140	664.8	325.2
160	640.0	349.0
180	619.0	369.0
S	4.0	3.0

Run No. I-60B

40	812.6	84.5
50	795.9	100.3
60	780.0	116.4
80	749.7	145.9
100	722.3	173.0
120	697.1	197.7
140	674.3	219.8
160	652.8	240.0
180	634.9	259.0
200	616.1	275.6
220	600.5	291.0
240	585.8	305.7
260	573.0	318.4
280	560.2	330.1
S	3.0	2.0

Run No. I-61B

4	797.0	171.4
6	772.0	196.8
8	747.0	221.0
10	724.7	243.0
12	704.0	262.9
14	686.0	281.4
16	669.0	298.6
18	652.3	314.3
20	637.3	328.8
22	623.4	342.3
24	611.0	354.5
26	598.1	365.5

Run No. I-62B

20	888.0	110.0
24	871.3	125.3
32	841.0	154.7
40	813.3	182.3
48	787.8	209.3
56	763.9	233.8
64	741.6	255.5
72	721.1	275.0
80	702.0	293.7
90	680.7	314.2
100	661.1	333.0
110	643.5	
120	627.7	365.1
130	613.0	379.0
S	4.0	3.0

Run No. I-63B

60	768.8	143.8
80	750.2	162.9
120	716.0	198.4
160	683.8	228.6
200	655.4	256.0
240	632.0	280.1
280	610.3	302.0
320	591.8	321.3
360	575.0	338.1
400	559.6	352.5
S	4.0	2.0

TABLE A-2 (Cont'd.)

t	A	B	t	A	B	t	A	B
<u>Run No. I-64B</u>			<u>Run No. I-65B</u>			<u>Run No. I-66B</u>		
12	736.0	195.0	24	846.4	136.7	12	924.2	106.2
16	717.8	214.0	28	832.0	150.4	16	902.7	127.8
20	698.6	232.2	32	817.7	163.0	20	881.3	148.0
24	681.8	248.8	36	803.8	174.7	24	861.0	167.7
28	665.6	264.4	40	791.1	186.3	28	841.7	186.3
32	650.5	279.0	50	761.8	214.0	32	823.9	203.8
36	636.2	292.7	60	734.6	239.0	36	806.7	220.0
40	623.0	305.0	70	710.0	261.0	40	790.6	236.0
48	599.1	327.5	80	686.7	282.7	50	753.6	271.8
56	578.2	347.3	90	666.4	301.7	60	721.2	303.6
S	4.0	3.0	100	648.3	318.6	70	692.4	330.4
			110	630.9	333.3	80	667.7	355.0
			120	615.0	347.6	S	5.0	3.0
			S	5.0	4.0			
<u>Run No. I-67B</u>			<u>Run No. I-68BS</u>			<u>Run No. I-69BS</u>		
30	723.6	53.5	60	812.0	76.2	120	818.8	84.9
40	706.1	69.9	80	792.8	96.0	160	800.0	103.0
50	690.6	85.7	100	774.6	114.1	200	782.9	121.4
60	675.0	100.3	120	757.9	132.0	240	767.3	138.6
70	660.3	114.9	140	742.1	148.2	280	752.0	155.0
80	647.0	128.3	160	727.0	163.6	360	723.2	184.9
90	634.2	141.1	200	697.1	192.7	400	709.6	198.6
100	621.1	153.0	240	672.1	217.9	480	684.6	224.1
120	598.1	175.3	280	648.3	241.1	560	662.1	247.4
140	576.7	195.3	320	626.9	262.2	640	641.4	268.2
160	557.1	213.3	360	606.9	280.3	720	622.1	286.9
180	539.3	229.8	400	589.6	296.9	800	605.3	303.4
200	523.6	244.7	440	574.5	312.2	880	589.4	319.0
220	509.0	258.3	480	560.1	325.9	960	576.0	332.6
S	3.0	2.0	S	3.0	2.0	S	2.0	1.0
<u>Run No. I-70BS</u>			<u>Run No. I-71BS</u>			<u>Run No. I-72BS</u>		
80	878.6	179.0	120	818.3	97.2	80	958.9	80.6
120	851.6	204.5	160	802.1	113.0	120	934.9	105.3
160	827.7	228.6	200	787.3	128.5	160	910.6	130.0
200	804.7	250.9	280	759.8	157.6	200	888.8	152.9
240	784.0	271.3	360	734.3	184.2	240	867.8	174.3
280	765.0	290.6	440	710.9	208.7	280	847.9	194.0
320	747.5	308.4	520	689.8	230.9	320	829.2	213.0
360	731.9	325.2	600	670.7	251.3	360	811.2	230.9
400	717.8	341.0	680	652.0	269.7	400	794.7	247.8
480	689.7	367.9	760	634.8	286.3	480	764.9	278.8
560	662.2	391.3	840	618.3	301.6	600	723.6	318.6
640	646.1	412.0	920	603.8	315.6	680	700.0	341.1
S	2.0	1.0	S	2.0	2.0	S	2.0	2.0

TABLE A-2 (Cont'd.)

t	A	B	t	A	B	t	A	B
<u>Run No. I-73BS</u>			<u>Run No. I-74B</u>			<u>Run No. I-75B</u>		
100	870.3	205.6	30	942.5	206.8	30	911.0	242.5
120	858.8	220.3	40	928.3	220.9	40	888.3	264.8
160	835.7	247.6	60	902.2	247.3	50	868.0	285.5
200	815.0	273.0	80	877.6	271.5	60	848.5	305.1
240	794.6	296.3	100	854.6	294.4	70	830.0	322.7
280	775.8	317.6	120	833.5	315.2	80	812.3	339.1
320	758.6	337.0	140	813.7	334.7	90	796.3	354.9
360	742.3	355.0	160	795.8	352.5	100	781.3	369.6
400	727.7	372.0	180	778.8	368.9	120	754.0	395.7
440	713.7	386.9	200	762.7	384.5	140	730.4	418.8
480	701.0	401.0	220	747.7	398.8	160	709.7	439.0
520	689.3	415.1	240	734.4	411.5	180	690.3	456.8
S	2.0	1.0	260	721.6	423.6	S	3.0	3.0
			280	709.4	434.6			
			S	3.0	2.0			
<u>Run No. I-76BS</u>			<u>Run No. I-77B</u>			<u>Run No. I-78BS</u>		
50	991.9	79.6	10	877.7	222.9	100	862.1	76.0
100	974.6	97.3	15	850.9	248.5	150	838.9	101.6
150	957.8	114.3	20	826.2	273.3	200	815.4	125.3
200	943.0	131.0	25	802.8	297.0	250	793.3	147.8
250	929.4	146.9	30	781.0	317.4	300	773.5	168.9
300	915.4	162.2	35	761.7	336.4	350	754.0	188.4
350	900.6	176.9	40	743.9	354.4	400	737.0	206.3
400	887.3	190.5	45	727.1	370.7	450	722.0	225.0
450	874.1	203.8	50	711.5	385.2	500	705.2	241.5
500	861.8	217.3	55	697.1	399.7	600	676.3	270.8
600	837.8	241.6	60	684.1	412.0	700	650.3	296.4
700	815.9	263.9	70	661.0	434.7	800	627.4	318.8
800	795.9	284.3	80	641.4	453.5	S	3.0	2.0
900	777.1	303.7	90	625.2	469.9			
S	2.0	1.0	S	4.0	3.0			
BK	19.0	4.8						
<u>Run No. I-79BS</u>			<u>Run No. I-80BS</u>			<u>Run No. I-81B</u>		
150	935.8	79.8	100	946.7	51.8	6	823.7	108.7
200	915.7	101.7	150	926.2	71.3	8	804.9	127.5
300	876.7	141.9	200	907.8	90.7	12	770.2	163.8
400	840.6	178.0	300	871.8	127.3	16	739.3	196.4
500	808.6	210.8	350	855.0	143.9	20	710.9	225.8
550	793.6	226.0	400	838.3	160.0	24	686.1	252.4
600	779.6	240.8	500	808.1	190.5	28	663.0	276.3
650	766.0	254.2	600	780.3	218.0	32	641.7	298.8
700	752.9	267.3	700	756.0	243.0	36	622.7	317.6
750	740.5	279.5	800	732.6	266.0	40	606.7	335.1

TABLE A-2 (Cont'd.)

t	A	B	t	A	B	t	A	B
800	728.4	290.8	900	711.1	286.6	48	579.0	365.1
900	706.0	312.4	1000	691.9	305.5	56	556.2	389.8
950	695.6	322.2	1100	674.6	322.9	S	3.0	2.0
1000	686.0	331.4	1200	659.0	338.6			
S	2.0	1.0	BK	2.9	1.3			
BK	1.0	0.5						

Run No. I-82B

2	947.7	195.3
4	926.0	216.6
6	905.3	236.7
8	886.9	256.0
10	869.1	274.3
12	852.6	292.0
16	820.1	323.1
20	793.6	351.2
24	767.9	376.4
28	746.4	399.0
32	726.1	419.0
36	708.0	437.1
40	691.8	453.3
44	678.0	467.4

Run No. I-83B

5	883.1	331.9
10	963.6	350.8
15	845.8	369.0
20	829.2	386.1
25	814.1	402.0
30	799.4	417.0
35	785.5	431.1
40	772.8	443.9
50	749.1	467.2
60	729.8	487.4
70	712.5	505.2
80	696.3	520.6
S	4.0	3.0

Run No. I-84B

20	884.6	237.4
30	863.0	262.3
40	842.6	283.2
50	823.5	303.0
60	805.6	321.9
70	788.4	339.2
80	772.7	355.4
90	758.0	370.2
100	744.3	384.1
120	719.0	409.0
140	697.3	430.8
160	678.5	449.7
180	662.1	465.3
200	648.1	479.9
S	5.0	3.0

Run No. I-85B

10	832.6	219.0
20	824.3	228.0
30	815.7	236.3
40	806.6	244.6
60	791.1	261.0
80	776.7	276.8
100	763.5	291.1
120	750.0	304.2
140	737.8	317.7
160	726.3	329.8
200	704.8	352.7
240	684.4	372.2
280	667.4	389.5
320	650.8	404.7
S	5.0	4.0

Run No. I-86BS

100	851.5	260.5
150	833.1	279.9
200	817.0	298.3
250	800.4	316.1
300	785.3	331.9
350	771.0	346.7
400	757.1	360.3
500	732.2	385.9
550	720.3	397.0
600	709.5	407.7
650	699.3	417.6
700	689.9	426.7
750	681.2	435.0
800	672.9	442.8
S	5.0	4.0

Run No. I-87BS

100	784.7	298.4
150	775.0	306.2
200	766.6	314.7
250	758.4	322.8
300	750.3	330.1
400	735.1	345.1
500	721.1	358.9
600	708.0	371.1
700	695.7	382.1
800	684.5	392.8
900	674.5	403.3
1000	663.7	412.2
1100	653.9	421.0
1200	644.8	429.0
S	5.0	3.0

TABLE A-2 (Cont'd.)

t	A	B	t	A	B	t	A	B
<u>Run No. I-88BS</u>			<u>Run No. I-89BS</u>			<u>Run No. I-90BS</u>		
20	871.9	119.0	80	832.1	295.1	80	925.0	290.3
40	859.3	131.7	120	823.0	305.0	120	902.4	314.5
80	836.0	156.3	200	805.7	323.0	160	881.0	336.2
120	814.3	179.0	320	782.7	347.8	200	860.3	356.7
160	794.1	200.6	400	767.8	363.1	240	840.7	375.9
200	775.7	220.7	480	753.9	377.2	280	821.8	393.7
240	758.1	239.5	560	741.2	390.4	320	805.0	409.1
280	741.6	256.9	640	729.3	402.7	360	789.7	423.8
320	725.2	273.0	720	718.0	413.7	400	775.0	437.3
400	696.0	301.6	800	707.0	424.4	440	761.2	450.0
480	670.6	326.3	880	696.7	433.0	480	749.0	461.8
560	647.5	347.9	960	687.0	440.8	520	737.2	472.6
640	628.0	366.8	1040	677.0	448.8	600	716.1	491.8
680	618.6	375.2	1200	661.6	463.8	680	698.7	508.1
S	3.0	2.0	S	3.0	2.0	S	5.0	4.0
<u>Run No. I-91B</u>			<u>Run No. I-92B</u>			<u>Run No. I-93B</u>		
4	202.0	911.1	30	894.6	154.3	16	870.0	193.6
6	220.8	892.7	40	874.1	175.2	24	836.1	228.5
8	237.0	876.1	50	854.3	195.5	32	805.9	259.7
12	267.4	846.5	60	836.2	214.5	36	791.8	274.0
16	295.3	818.8	70	818.9	231.8	40	778.6	287.5
20	320.2	794.5	80	803.2	248.3	44	766.3	299.9
24	342.8	772.4	100	774.2	279.3	48	754.2	312.0
28	363.3	752.7	120	747.7	306.5	52	743.2	323.2
32	381.4	735.3	140	724.9	329.5	60	722.9	344.2
36	398.1	719.6	160	704.8	351.2	68	704.1	362.9
40	412.8	705.9	180	686.8	370.0	76	688.4	379.9
44	426.2	693.0	200	670.8	386.2	84	673.7	394.8
48	438.0	681.5	220	656.6	400.8	92	660.8	408.0
52	449.4	671.8	240	643.7	413.6	100	648.7	419.3
S	4.0	3.0	S	3.0	2.0	S	3.0	2.0
<u>Run No. I-94BS</u>			<u>Run No. I-95BS</u>			<u>Run No. I-96BS</u>		
80	918.3	113.3	80	922.2	191.3	80	913.3	241.3
120	882.8	148.4	120	888.5	223.8	120	882.1	272.0
160	850.7	180.7	160	858.0	253.7	160	854.2	300.0
200	820.2	210.0	200	830.6	281.2	200	828.3	323.6
240	792.0	237.0	240	805.7	305.9	240	804.4	346.0
280	767.0	261.0	280	782.3	328.3	280	783.0	367.0
320	744.0	282.7	320	761.4	348.8	320	763.9	386.1
360	723.0	303.7	360	742.7	367.4	360	745.7	403.8
400	703.6	321.6	400	724.7	384.0	400	729.5	418.2
440	686.3	338.8	440	708.0	398.7	440	714.3	432.6
480	670.4	354.3	480	692.0	412.4	480	701.2	444.9
520	656.1	368.2	520	678.0	424.8	520	689.0	457.7
S	5.0	3.0	S	5.0	3.0	S	5.0	3.0

TABLE A-2 (Cont'd.)

t	A	B	t	A	B	t	A	B
<u>Run No. I-97B</u>			<u>Run No. I-98B</u>			<u>Run No. I-99BS</u>		
100	959.8	69.8	160	904.0	96.0	80	829.1	120.2
150	940.7	88.8	200	881.6	119.1	120	889.4	156.2
200	922.0	107.3	240	864.7	137.3	160	857.0	189.0
300	887.7	143.6	280	848.4	154.8	200	827.0	219.6
400	855.2	175.0	320	833.2	170.4	240	798.8	246.6
500	826.3	204.4	360	818.7	185.9	280	774.0	271.2
600	800.2	230.7	400	804.3	200.3	320	751.2	293.6
700	775.2	255.6	480	779.0	226.9	360	730.0	314.0
800	752.7	277.8	560	754.9	250.7	400	710.5	332.8
900	731.7	297.8	640	732.7	272.4	440	693.1	350.0
1000	712.9	316.2	720	711.6	292.0	480	677.6	365.8
1100	695.5	333.0	800	692.1	310.0	520	663.4	380.1
1200	679.2	348.3	880	675.6	327.0	560	649.9	393.3
			960	660.3	341.4	600	637.8	405.7
<u>Run No. I-100B</u>								
40	884.6	136.8						
80	861.3	158.7						
120	840.6	178.9						
160	820.7	197.6						
200	803.1	215.9						
240	786.3	233.3						
280	770.9	249.7						
320	756.0	265.3						
360	741.2	279.8						
400	727.3	293.2						
440	714.8	305.6						
480	703.2	318.6						
560	680.1	340.0						
640	659.5	359.3						

TABLE A-3
DERIVED EXPERIMENTAL RUN DATA
EXCEPT FOR DIFFUSIVITIES

Run No.	Pres- sure (atm) (abs)	Z	Mole Density (m/l)	Mass Density (g/l)	f	LMS Slope x 10 ³ (min ⁻¹)	E x 10 ⁻⁵
I-1A	9.240	0.9950	0.3673	14.67	0.9260	3.0989	2.2
I-2A	5.185	0.9975	0.2055	8.21	0.9243	5.5895	1.7
I-3A	2.525	0.9986	0.0999	4.00	0.9232	11.111	8.0
I-4A	2.593	0.9986	0.1027	4.10	0.9232	10.988	2.6
I-5A	14.920	0.9920	0.5946	23.75	0.9280	1.9586	1.4
I-6A	43.46	0.9792	1.754	70.07	0.9369	0.6637	0.8
I-7A	25.09	0.9873	1.005	40.13	0.9316	1.1306	1.6
I-8A	4.219	0.9977	0.1672	6.68	0.9239	6.7372	6.5
I-9A	6.743	1.0032	0.2657	1.075	0.9198	18.791	2.0
I-10A	20.55	1.0095	0.8046	3.222	0.9198	6.3888	0.7
I-11A	52.06	1.0238	2.011	8.052	0.9198	2.6541	-
I-12A	4.471	1.0021	0.1765	0.707	0.9198	27.922	11.9
I-13A	60.15	1.0274	2.410	9.649	0.9198	2.2797	5.9
I-14A	3.709	1.0017	0.1464	0.586	0.9198	33.556	-
I-15A	30.74	1.0141	1.199	4.800	0.9198	4.3034	-
I-16A	34.93	0.9986	1.385	38.76	0.9345	0.9400	-
I-17A	7.614	0.9993	0.3012	8.44	0.9253	4.2254	-
I-18A	4.933	0.9994	0.1951	5.47	0.9242	6.4715	-
I-19A	24.14	0.9985	0.9558	26.78	0.9312	1.3910	-
I-20A	3.137	0.9997	0.1241	3.55	0.9235	9.9376	10.0
I-21A	22.10	0.9986	0.8748	24.51	0.9305	1.4744	0.9
I-22A	15.50	0.9700	0.6320	52.89	0.9332	1.2865	0.9
I-23A	7.463	0.9837	0.3001	25.11	0.9260	2.6121	0.7
I-24A	3.807	0.9917	0.1518	12.71	0.9253	5.1990	1.9
I-25A	3.649	0.9920	0.1455	12.18	0.9252	5.4836	1.7
I-26B	11.017	0.9940	0.4384	17.51	0.9314	26.413	2.2
I-27B	48.44	0.9773	1.906	78.30	0.9412	6.1042	2.0
I-28B	7.145	0.9961	0.2837	11.43	0.9304	40.016	9.1
I-29B	34.50	0.9829	1.388	55.51	0.9350	8.5676	3.1
I-30B	73.42	0.9687	2.997	119.7	0.9469	4.0613	4.1
I-31B	20.65	0.9894	0.8254	32.97	0.9340	1.4220	1.3
I-32B	133.02	0.9582	5.490	219.3	0.9574	2.2669	1.5
I-33BS	133.15	0.9582	5.495	219.5	0.9574	2.2435	5.2
I-34BS	206.50	0.9659	8.455	337.7	0.9618	1.4964	4.4
I-35BS	375.74	1.0581	14.044	561.0	0.9610	0.8911	2.3
I-36BS	410.10	1.0852	15.945	597.0	0.9610	0.8442	2.9
I-37BS	73.48	0.9687	3.041	121.5	0.9471	4.0857	1.2
I-38BS	133.32	0.9582	5.502	219.8	0.9575	2.2882	0.4
I-39BS	272.85	0.9869	10.934	436.8	0.9610	1.1616	1.3
I-40BS	333.07	1.0275	12.820	512.1	0.9610	0.9838	1.8

TABLE A-3 (cont'd)

Run No.	Pres- sure (atm) (abs)	Z	Mole Density (m/l)	Mass Density (g/l)	f	LMS Slope $\times 10^3$ (min ⁻¹)	E $\times 10^{-5}$
I-41BS	242.77	0.9781	9.816	392.1	0.9611	1.2282	2.8
I-42BS	302.79	1.0083	11.876	474.4	0.9610	1.0575	2.1
I-43BS	174.52	0.9597	7.192	287.3	0.9612	1.7527	0.5
I-44BS	103.65	0.9611	4.265	170.4	0.9527	2.8972	1.6
I-45B	91.50	1.0415	3.474	13.91	0.9370	15.407	2.6
I-46B	24.81	1.0114	0.9701	3.88	0.9359	54.506	6.0
I-47B	130.28	1.0588	4.866	19.48	0.9376	11.143	0.6
I-48B	240.18	1.1072	8.579	34.35	0.9395	6.5441	5.5
I-49B	111.51	1.0506	4.198	16.81	0.9373	12.722	1.8
I-50B	312.11	1.1388	10.839	43.40	0.9409	5.1310	6.3
I-51B	186.09	1.0833	6.794	27.20	0.9386	8.2115	1.9
I-52B	415.06	1.1833	13.872	55.54	0.9430	4.1174	0.6
I-53B	60.17	1.0274	2.316	9.26	0.9365	2.3144	3.6
I-54B	211.94	1.0948	7.656	30.65	0.9390	7.1553	2.1
I-55B	353.61	1.1566	12.091	38.41	0.9417	4.6571	3.9
I-56B	278.97	1.1244	9.812	39.29	0.9402	5.6086	2.0
I-57B	13.66	0.9347	0.5780	25.47	0.9318	16.834	0.9
I-58B	57.48	0.6607	3.441	151.6	0.9506	3.0727	9.1
I-59B	30.36	0.8467	1.418	62.46	0.9388	6.9766	1.8
I-60B	43.80	0.7648	2.265	99.79	0.9440	4.5062	1.1
I-61B	5.675	0.9735	0.2306	10.25	0.9305	40.983	2.6
I-62B	21.55	0.9057	0.9410	41.46	0.9355	10.103	2.3
I-63B	57.89	0.6571	3.484	153.5	0.9508	3.0474	0.8
I-64B	17.88	0.9987	0.7080	19.84	0.9318	17.709	1.7
I-65B	34.93	0.9986	1.383	38.76	0.9350	9.4389	1.3
I-66B	24.55	0.9985	0.9724	27.24	0.9331	13.197	0.2
I-67B	69.33	1.0034	2.733	76.55	0.9409	4.8817	7.0
I-68BS	135.74	1.0289	5.217	146.2	0.9500	2.5806	6.0
I-69BS	339.51	1.1902	11.287	316.2	0.9617	1.2587	1.2
I-70BS	203.78	1.0675	7.549	211.5	0.9568	1.8406	2.9
I-71BS	408.39	1.2628	12.790	358.3	0.9615	1.0985	2.3
I-72BS	273.53	1.1257	9.610	269.2	0.9605	1.4366	0.6
I-73BS	62.07	0.4509	5.444	133.2	0.9472	1.9622	0.7
I-74B	45.80	0.6635	2.822	79.16	0.9413	3.6505	2.5
I-75B	30.25	0.8023	1.541	43.23	0.9358	5.3649	4.7

TABLE A-3 (cont'd)

Run No.	Pres sure (atm) (abs)	Z	Mole Density (m/l)	Mass Density (g/l)	f	LMS Slope $\times 10^3$ (min ⁻¹)	E $\times 10^{-5}$
I-76BS	112.12	0.3701	12.384	347.4	0.9616	0.7638	0.6
I-77B	13.69	0.9154	0.611	17.15	0.9314	15.968	8.6
I-78BS	70.07	0.3403	8.413	236.0	0.9588	1.2815	2.1
I-79BS	79.94	0.3170	10.306	252.1	0.9612	1.0016	0.3
I-80BS	89.46	0.3266	11.198	314.1	0.9616	0.9045	1.2
I-81B	11.00	0.9940	0.438	17.49	0.9314	26.405	3.1
I-82B	7.458	0.9837	0.300	24.93	0.9327	27.444	3.1
I-83B	15.48	0.9700	0.631	52.83	0.9373	13.451	4.8
I-84B	29.53	0.9437	1.238	103.6	0.9448	68.336	1.0
I-85B	67.41	0.8863	3.008	251.8	0.9597	2.7881	1.0
I-86BS	134.85	0.7818	6.822	571.0	0.9610	1.2731	2.2
I-87BS	227.93	0.7540	11.955	1000.6	0.9610	0.6899	2.8
I-88BS	110.08	0.8105	5.372	449.6	0.9610	1.6311	1.6
I-89BS	187.86	0.7551	9.839	823.5	0.9610	0.8365	3.3
I-90BS	96.27	0.8297	4.589	384.1	0.9612	1.8772	3.0
I-91B	11.00	0.9940	0.4381	17.50	1.0740	27.030	1.9
I-92B	48.42	0.9773	1.960	78.29	1.0625	6.0672	0.9
I-93B	20.63	0.9894	0.8244	32.93	1.0707	14.286	1.6
I-94BS	133.12	0.9582	5.495	219.5	0.9574	2.2584	0.9
I-95BS	133.15	0.9582	5.495	219.5	0.9574	2.2729	1.2
I-96BS	133.22	0.9582	5.499	219.7	0.9574	2.2788	1.4
I-97B	375.80	1.0581	14.046	561.1	0.9610	8.6489	3.8
I-98B	272.84	0.9869	10.943	473.1	0.9610	1.1043	2.3
I-99BS	133.21	0.9582	5.499	219.5	0.9574	2.2662	2.6
I-100B	206.49	0.9659	8.455	337.7	0.9618	1.4533	1.1

APPENDIX B

TABULATION OF EXPERIMENTAL RUN
DATA FOR SCINTILLATION CELL RUNS

1. Table B-1; Primary Experimental Run
Data Except for Scintillation
Count Rates
2. Table B-2; Scintillation Count Rates
3. Table B-3; Derived Experimental Run
Data Except for Diffusivities

In this appendix the experimental data is given for the experimental diffusion runs carried out with the scintillation cell. This data is presented in three tables. In Table B-1 the averaged basic data for each run are given with the exception of the Count Rates which are in Table B-2. In Table B-3 the derived run data except for the diffusion coefficients are shown.

An explanation of the various headings in the tables follows:

Date - - the date that the run was started.

Run No. - - the notation indicating the run number is of the form

S-X where S indicates a Scintillation Cell run X.

Base Gas - -the gas in which the Kr-85 is diffusing.

Pressure, Gage - - the pressure gage used as coded in Appendix G.

Pressure, Av. - - the average of the absolute pressures at the beginning and end of a run.

Avg. T. C. - - the average run cell thermocouple millivolts.

Chart Record - - A ten minute cycle reading scheme is indicated by a 10. Now C-1 and C- $\frac{1}{2}$ indicates continuous chart at one inch and one-half inch per minute, respectively.

f Adj. - - the adjustment of the external high voltage resistor which determines f coded in Appendix E.

Z - - the compressibility factor of the run gas at the run conditions.

f - - the equilibrium count rate ratio of the A side reading to the B side reading.

Slope - - the slope of $\ln(A-fB)$ vs. t determined by graphical means.

t - - the diffusion time in minutes.

A - - the number of chart units which is a measure of the counting rate from the A side of the scintillation cell.

B - - the number of chart units which is a measure of the counting rate from the B side of the scintillation cell.

BK - - background reading.

Eq. - - equilibrium reading.

S - - average spread (chart units) of the random fluctuations for a reading.

There are several experimental conditions which were essentially constant for the runs and are not indicated in the tables. These are as follows:

High Voltage Setting - - - 1167 volts for all runs.

Time Constant - - - 10 sec. for all runs.

Rate Meter Scale - - - 100,000 counts per minute for all runs.

Amplifier Gain - - - 1600 for all runs.

Pulse Height Level - - - 1.00 volts except for Run S-16 at 1.60 volts and Run S-17 at 1.30 volts.

Stirring Rate - - - 22 rpm except for Run S-2 at 10 rpm and Run S-3 at 40 rpm.

Thermocouple S-1 was used for all the runs.

TABLE B-1

PRIMARY EXPERIMENTAL RUN DATA EXCEPT
FOR SCINTILLATION COUNT RATES

Date	Run No.	Base Gas	<u>Pressure</u>		Avg. T.C.	Avg. Temp.	Chart Record	f Adj.
			Gage	Avg.				
				(psia)	(mv)	(°C)		
(1960)								
10-19	S-1	A	C	606.4	1.400	35.0	10	Eq.
10-21	S-2	"	"	613.8	1.400	35.0	"	I
10-21	S-3	"	"	616.8	1.399	35.0	"	"
10-22	S-4	"	"	1011.7	1.400	35.0	"	"
10-23	S-5	"	"	1510.2	1.393	34.9	"	"
10-23	S-6	"	"	1952.2	1.399	35.0	"	"
10-24	S-7	"	"	212.2	1.401	35.0	"	"
10-25	S-8	"	"	837.7	1.405	35.1	"	"
10-26	S-9	"	"	420.2	1.402	35.0	"	"
10-27	S-10	"	"	614.9	-0.930	-24.9	"	II
11-10	S-11	"	"	1360.8	-0.934	-25.0	"	III
11-13	S-12	"	"	1950.8	-0.933	-25.0	"	"
11-15	S-13	"	E	2722	-0.933	-25.0	"	"
11-18	S-14	"	C	201.7	-0.932	-25.0	C- $\frac{1}{2}$	IV
11-20	S-15	"	"	977.7	-0.933	-25.0	10	-
11-21	S-16	N ₂	"	325.9	-0.933	-25.0	C- $\frac{1}{2}$	V
12-16	S-17	"	"	1934.4	-0.930	-24.9	10	Eq.
12-17	S-18	"	E	3043	-0.930	-25.0	10	V
12-18	S-19	"	A	108.3	-0.936	-25.1	C-1	Eq.
12-21	S-20	"	C	620.4	-0.929	-24.9	10	V
12-23	S-21	"	C	1514.9	-0.929	-24.9	10	V

TABLE B-2
SCINTILLATION COUNT RATES

t	A	B	t	A	B	t	A	B
<u>Run No. S-1</u>			<u>Run No. 2</u>			<u>Run No. 3</u>		
BK	37	24	BK	37	24	BK	37	24
0	792	148	20	807	204	0	834	55
20	731	177	40	780	241	20	785	95
40	696	207	60	756	272	40	749	133
60	670	233	80	731	303	65	712	170
80	646	259	100	707	323	75	694	191
100	622	288	120	690	349	115	644	242
120	602	308	140	674	369	135	620	266
140	587	321	160	657	387	155	602	289
160	576	336	180	643	404	175	588	308
180	562	350	200	629	418	195	574	324
200	550	362	220	616	429	215	560	336
220	540	375	240	605	439	235	547	349
240	532	387	260	598	449	255	535	362
260	523	396	280	590	458	275	524	373
280	515	404	300	584	467	295	516	382
300	507	412	340	573	481	315	509	390
Eq.	467	469				335	505	396
<u>Run No. 4</u>			<u>Run No. 5</u>			<u>Run No. 6</u>		
BK	37	28	BK	37	28	BK	37	30
0	786	37	120	649	203	0	601	132
20	746	46	140	637	215	20	589	140
40	713	64	180	623	236	40	579	148
60	689	86	200	614	247	60	571	155
80	670	106	220	604	256	80	563	163
100	653	127	240	598	266	120	548	178
120	637	147	260	591	274	160	532	192
140	621	164	280	584	281	200	515	207
160	605	181	300	575	287	240	508	221
200	575	209	320	566	293	280	499	233
240	551	237	340	556	301	320	491	242
280	531	259	360	548	309	360	482	252
320	512	278	400	539	321	400	473	261
360	500	295	440	532	333	480	455	280
400	488	311	480	521	342	560	441	295
440	477	323	500	516	347			
			540	506	356			
			600	497	368			
			Eq.	452	435			

TABLE B-2 (Cont'd.)

t	A	B	t	A	B	t	A	B
<u>Run No. 7</u>			<u>Run No. 8</u>			<u>Run No. 9</u>		
BK	37	30	BK	37	30	BK	37	30
0	821	80	0	676	94	0	761	46
4	792	109	10	662	105	10	733	73
8	771	129	20	650	118	20	707	101
12	752	149	40	625	141	30	679	128
16	733	170	60	603	163	40	659	152
20	714	190	80	584	183	50	640	174
28	678	227	100	568	202	60	623	194
36	639	258	120	553	217	80	584	232
44	625	284	140	539	232	100	554	261
52	603	307	160	527	247	120	530	284
60	585	326	180	515	261	140	513	302
68	569	343	200	503	274	160	495	321
76	555	358	240	487	294	180	482	336
84	541	371	280	470	310	200	471	349
			320	454	325	220	460	358
			Eq.	390	400	Eq.	413	413
<u>Run No. 10</u>			<u>Run No. 11</u>			<u>Run No. 12</u>		
BK	42	44	BK	42	48	BK	45	44
0	875	140	0	662	183	0	662	72
20	850	176	40	645	198	40	644	80
40	826	210	80	628	212	120	612	102
80	779	270	120	612	225	200	590	126
100	759	297	160	600	238	240	579	137
120	740	321	200	590	249	380	569	146
140	724	342	240	580	261	320	558	155
160	710	363	280	568	272	400	538	173
180	694	382	320	558	281	480	523	191
200	681	399	360	548	291	560	508	204
220	669	414	400	540	300	640	496	220
240	657	429	480	522	316	720	485	234
260	646	444	560	507	330	800	476	246
280	636	459	640	498	340	880	467	255
320	617	484	720	488	349			
360	602	504	800	480	357			
400	590	519	880	472	367			
440	580	531						
480	570	541						

TABLE B-2 (Cont'd.)

t	A	B	t	A	B	t	A	B
<u>Run No. 13</u>			<u>Run No. 14</u>			<u>Run No. 15</u>		
BK	45	44	BK	45	44	BK	45	44
0	876	206	0	687	124	0	732	129
40	862	215	4	672	135	10	722	137
80	848	223	8	656	146	20	712	145
120	837	233	12	641	157	40	694	159
160	827	243	16	628	169	80	671	186
200	817	252	20	615	179	120	648	211
240	809	263	24	605	190	160	628	230
280	798	272	32	587	210	200	609	250
320	789	281	40	571	225	240	592	269
400	771	299	48	556	240	280	575	284
480	756	317	56	542	255	320	562	298
560	743	335	64	529	270	360	551	311
750	715	382	80	508	295	440	532	334
930	686	408	96	492	315	480	521	343
990	678	415	104	484	321	520	510	353
1110	665	430	120	469	334	560	503	361
<u>Run No. 16</u>			<u>Run No. 17</u>			<u>Run No. 18</u>		
BK	23	27	BK	40	42	BK	60	65
0	706	46	0	784	311	0	629	65
10	675	68	20	772	320	40	613	72
20	650	90	40	761	328	80	598	82
30	627	112	80	741	341	120	585	91
40	606	132	120	727	352	160	574	101
50	585	151	160	715	364	200	564	111
60	564	168	200	698	375	280	547	129
70	544	184	240	688	386	360	531	147
80	526	198	280	681	397	440	515	166
90	512	208	320	672	407	520	498	180
100	500	223	360	665	416	560	490	186
110	488	238	400	659	425	640	476	200
120	481	249	440	653	432	720	464	212
130	473	260	560	628	446	800	454	223
140	465	269	640	614	455	880	445	233
160	448	284	680	609	460	960	435	243
200	422	308	Eq.	526	537	1040	428	252
						1120	421	260
						1200	415	267

TABLE B-2 (Cont'd.)

t	A	B	t	A	B	t	A	B
<u>Run</u> <u>No. 19</u>			<u>Run</u> <u>No. 20</u>			<u>Run</u> <u>No. 21</u>		
BK	51	56	BK	51	56	BK	51	56
0	779	159	0	675	114	0	998	71
4	753	191	10	660	126	20	973	84
8	728	218	20	647	139	40	951	97
12	703	242	30	634	151	60	930	110
16	682	264	40	622	163	80	911	123
20	663	286	60	602	188	100	898	137
24	645	305	80	585	207	160	857	174
28	630	319	100	568	224	200	832	198
32	616	333	120	554	241	240	809	219
36	603	346	140	541	256	280	790	239
40	591	358	160	529	271	320	770	257
48	574	381	180	516	283	360	751	274
56	557	399	200	504	297	400	732	294
64	542	407	240	482	310	440	714	304
72	529	420	280	467	322	480	701	324
Eq.	493	475				520	689	337
						560	677	349
						600	663	358

TABLE B-3

DERIVED EXPERIMENTAL RUN DATA
EXCEPT FOR DIFFUSIVITIES

Run No.	Pressure atm	Z	Mole Density (m/l)	f	Slope $\times 10^3$ (min ⁻¹)
S-1	41.26	0.9802	1.665	0.966	5.705
S-2	41.77	0.9800	1.686	0.971	5.866
S-3	41.97	0.9800	1.694	0.969	5.788
S-4	68.84	0.9700	2.807	0.957	3.561
S-5	102.76	0.9614	4.228	0.950	2.461
S-6	132.84	0.9582	5.483	0.949	1.938
S-7	14.44	0.9923	0.5755	0.988	16.45
S-8	57.68	0.9743	2.313	0.960	4.493
S-9	28.59	0.9856	1.147	0.980	8.772
S-10	41.84	0.9443	2.176	0.825	3.914
S-11	92.60	0.8893	5.113	1.020	1.752
S-12	132.74	0.8610	7.571	1.020	1.216
S-13	185.2	0.8519	10.58	1.010	0.9020
S-14	13.73	0.9810	0.6871	1.010	12.06
S-15	66.53	0.9157	3.568	1.000	2.505
S-16	22.18	0.9819	1.109	0.981	8.440
S-17	131.63	0.9649	6.702	0.982	1.563
S-18	207.1	1.0089	10.08	0.990	1.084
S-19	7.37	0.9933	0.3642	0.991	25.64
S-20	42.22	0.9716	2.135	1.000	4.708
S-21	103.08	0.9581	5.286	0.989	1.818

APPENDIX C

SAMPLE CALCULATIONS FOR A DIFFUSION RUN

Run No. I-37BS

Part 1; Data:

Date; Feb. 2, 1961.

Base Gas; Argon.

Porous Plug; Ceramic Plug B.

Pressure Gage; Gage C (2000 psi. Heise).

Beginning Pressure; 1065.0 psig.

End Pressure; 1065.0 psig.

Barometric Pressure; 14.82 psi.

Average Cell Thermocouple:

IT-2 with 13 readings for an average 1.400 mv.

Method of Charging Cell:

1. Cold argon to 500 psi.
2. Injection of hot argon in A side.
3. Injection of cold argon in B side to 1065.0 psig.

Voltage Range; 10 volts full scale deflection.

Chart Record; 10 min. cycles

Rocking Speed; 7 min. out of 10 at 22 cpm.

Time Cycle; 7 min. rocking, 1 min. rest,
1 min. A side and 1 min. B side.

Ionization Currents; Refer to run I-37BS of Appendix A
(Table A-2)

Part 2; Calculations:

Average Gage Pressure; 1065.0 psig.
Gage Correction; None
Absolute Pressure; 1079.8 psia.
" " 73.48 atm.
Average Temperature; 35.0°C (308.2 °K) (Appendix G)
Compressibility Factor

$$Z = P/pRT; \quad 0.9687 \text{ (Appendix G)}$$

Mole Density,

$$\rho = P/ZRT; \quad 3.041 \text{ gram-moles/liter}$$

Mass Density, $w = \rho M$ (3.041) (39.944) = 121.45 g/
f; 0.9471 (Appendix D, Figure D-6).

Concentration of Kr-85 is proportional to Ionization Current
(Appendix D)

Ionization currents from each side are always in the same proportionality to Chart Readings, A or B

Background: Negligible.
Recorder Zero; Zero chart units.

The defining equation is then

$$y = \log_e (A - fB) = -mt + b \quad (C-1)$$

The least mean square computer fit of the time and ionization current data according to this equation is given by Table C-1.

TABLE C-1

LEAST MEAN SQUARE COMPUTER FIT

For Run I-37BS

Intercept $b = 2.1901$ Slope $m = 4.0857 \times 10^{-3} \text{ min}^{-1}$

t min.	y_1 Expt'l	y_2 Calc.	$y_2 - y_1$ $\times 10^4$
40	2.0275	2.0267	- 8.42
60	1.9453	1.9450	- 3.21
80	1.8626	1.8633	6.53
100	1.7801	1.7815	14.34
120	1.7020	1.6998	3.88
140	1.6172	1.6181	9.10
160	1.5359	1.5364	5.00
180	1.4552	1.4547	- 5.02
200	1.3750	1.3730	-20.53
220	1.2922	1.2912	-10.01
240	1.2092	1.2095	2.86
260	1.1265	1.1278	13.37
280	1.0464	1.0461	- 2.62
300	0.9641	0.9644	2.50

$$E = \text{Sum of the squares of } (y_2 - y_1) = 1.199 \times 10^{-5}$$

A plot of y_1 versus t for Run I-37BS with the least mean square fit drawn through the points is given in the text.

Calculations (cont'd):

$$\text{Slope; } m = 60 \text{ KD} = 4.0857 \times 10^{-3} \text{ min}^{-1}$$

$$\text{Cell Constants; } K_B = 3.337 \times 10^{-2} \text{ cm}^{-2} \text{ (Appendix F)}$$

$$\text{Diffusion Coefficient; } D = \frac{m}{60K_B}$$

$$D = \frac{4.0857 \times 10^{-3}}{(60)(3.337 \times 10^{-2})}$$

$$D = 2.041 \times 10^{-3} \text{ cm}^2/\text{sec.}$$

$$\text{Density-Diffusivity Product; } D = 6.205 \times 10^{-3} \frac{\text{cm}^2}{\text{sec}} \frac{\text{mole}}{\text{liter}}$$

NOTE: The calculation of a scintillation cell run would be similar.

A background correction would have to be made. Also, instead of a computer fit a graphical determination of the slope, m , must be made.

APPENDIX D

IONIZATION CELL CURRENT CALIBRATION DATA

Part 1; The Effects of Density on the
Krypton-85 Concentration-Current
Relationships

Part 2; Ionization Cell Chamber Ratio f
Calibration

Part 3; Ionization Cell Background Data

Part 1; The Effect of Density on the Krypton-85 Concentration-Current Relationships:

In this section the method is given for calibrating the ionization cell for the relationship between the concentration of krypton-85 and the ionization current. The procedure consisted of placing a plug with a large hole in the cell. For a calibration run hot gas was introduced into the cell at low pressures. After the initial injection of hot gas the approach lines were evacuated and filled with non-active base gas. Subsequently, readings of the ionization current versus the pressures were recorded as cold gas was introduced. Sufficient time was allowed after each introduction of cold gas for the cell to come to equilibrium. The primary data obtained is the isothermal variation of the ionization current with pressure (density) at constant volume concentration (moles/liter) of krypton-85 in the cell. The runs were made for various concentrations of krypton-85. However, this method is relative in that the concentrations of krypton-85 are unknown.

In an ionization chamber there are three important factors which determine the amount and rate of charge collections at the electrodes⁽⁶⁹⁾. These are the charge (electron and ion) flow due to the impressed electric field, the recombination of ions to form neutral molecules, and the diffusion of charges out of the active volume of the ion chamber due to the gradient in the ion density. The importance of each of these factors is determined largely by the electric field strength and pressure or density of the ion chamber gas. Due to the complexity of the problem an experimental procedure must be relied upon to determine the current-concentration relationship.

The current-concentration relationship was studied for Kr-85 in argon, helium, and nitrogen. The data is shown by Table D-1. Here I_A is the

TABLE D-1

CONSTANT Kr-85 CONCENTRATION CURRENT VERSUS DENSITY

IA volts	Density (m/l)	IA volts	Density (m/l)	IA volts	Density (m/l)
<u>Run No. 1</u>		<u>Run No. 2</u>		<u>Run No. 3</u>	
0.276	0.1747	2.590	0.2721	0.03960	0.154
0.458	0.4527	3.790	0.4485	0.05085	0.205
1.677	5.357	5.905	0.8465	0.06345	0.280
1.908	12.28	8.015	1.409	0.07980	0.366
		9.530	1.973	0.09250	0.449
		11.800	3.372	0.1270	0.705
		12.930	4.511	0.1970	1.413
		13.850	5.561	0.2340	1.974
		14.030	6.432	0.2950	3.365
				0.3230	4.501
				0.3395	5.544
<u>Run No. 4</u>		<u>Run No. 5</u>		<u>Run No. 5 (cont'd.)</u>	
0.1282	0.1724	0.1010	0.08163	0.8595	1.410
0.1820	0.2644	0.1073	0.08701	1.026	1.971
0.2730	0.4504	0.1226	0.1018	1.295	3.379
0.4235	0.8433	0.1411	0.1213	1.419	4.506
0.5835	1.415	0.1704	0.1518	1.509	5.552
0.6795	1.974	0.2130	0.1975	1.554	6.420
0.7950	2.796	0.2540	0.2474	1.625	7.932
0.8565	3.368	0.2775	0.2738	1.650	8.490
0.9465	4.514	0.4010	0.4488	1.660	9.414
1.004	5.552	0.6290	0.8486	1.680	10.86
1.041	6.436			1.720	12.01
1.095	8.931				
1.128	11.85			12.300	6.140
				12.636	7.091
0.352.5	5.432			13.155	9.73
0.3696	6.673			13.245	12.00
0.3870	8.920				
0.3936	10.613				

TABLE D-1 (Cont'd.)

IA volts	Density (m/l)	IA volts	Density (m/l)
<u>Run No. 6</u>		<u>Run No. 7</u>	
0.01208	0.09301	1.543	0.8439
0.02283	0.2062	2.237	1.400
0.03438	0.3553	2.841	1.909
0.06804	0.9075	3.702	2.686
0.1044	1.634	4.462	3.735
0.1672	3.210	5.230	4.963
0.2152	5.015	6.080	7.366
0.2466	7.530	6.310	10.052
0.2538	9.513		
0.2532	10.43		
0.2520	10.78		

<u>Run No. 8</u>		<u>Run No. 9</u>	
0.1585	0.2660	1.031	0.1622
0.4260	1.369	1.647	0.2848
0.4959	2.877	2.823	0.5836
0.4884	3.405	3.638	0.8626
0.4389	5.101	4.240	1.167
0.3352	7.545	5.032	1.940
0.2400	9.954	5.220	2.737
0.2240	10.44	5.197	2.991
		5.153	3.253
		4.852	4.260
		4.500	5.220
		3.462	7.582
		2.680	9.650
		2.467	10.09

ionization current recorded as volts based on the 10 volt scale of the vibrating reed electrometer. Figure D-1 is a plot of the ionization current, I_A , versus density for a representative run for each of the gases. The current increases rapidly with density at the lower densities. As the density is increased the current becomes constant after which it begins to decrease. For argon and helium the region of the current decrease with density is not evident. However, for the nitrogen run shown the current falls off rapidly with densities above three moles per liter. The reason for this behavior is that at the higher densities recombination of ions becomes important and tends to reduce the current. Nitrogen⁽⁶⁹⁾ is more susceptible to recombination than the rare gases argon and helium.

For argon as shown by Figure D-2 the ionization current I_A can be related to the density ρ by an equation of the form,

$$\frac{\rho}{I_A} = y = a\rho + b, \quad (D-1)$$

where as the density approaches zero y approaches an intercept b and a is the slope of the straight line. Now if I is directly proportional to the volume concentration, C_1 of krypton-85 at vanishing density then for two different concentrations the current ratios are given by an inverse ratio of the intercepts as

$$\frac{I_2}{I_1} = \frac{C_2}{C_1} = \frac{b_1}{b_2}. \quad (D-2)$$

However, for this ratio to hold at another high density where

$$\frac{C_2}{C_1} = \frac{b_1}{b_2} = \left(\frac{1 - a_1 I_1}{1 - a_2 I_2} \right) \frac{I_2}{I_1},$$

the condition is imposed that

$$1 - a_2 I_2 = 1 - a_1 I_1, \quad (D-3)$$

FIGURE D-1: CURRENT-DENSITY PLOTS

FIGURE D-2: RECIPROCAL CURRENT-DENSITY PLOT
for ARGON

FIGURE D-3: RECIPROCAL CURRENT-DENSITY
PLOT for HELIUM

FIGURE D-4: RECIPROCAL CURRENT-DENSITY PLOT
for NITROGEN

so that

$$\frac{I_2}{I_1} = \frac{a_1}{a_2} \quad (D-4)$$

Thus, this Equation (D-4) is the criteria that must be fulfilled in order for the current ratio to be a direct measure at the krypton-85 concentration ratio. If this condition holds, then the ionization current is directly proportional to the krypton-85 concentration or

$$I \propto C \quad (D-5)$$

over the entire density range.

In order to verify this criteria for argon the slope, a , for each run was determined and compared to y at 6 moles/liter. The results are given in Table D-2.

TABLE D-2
COMPARISON OF SLOPES AND CURRENTS
AT 6 MOLES/LITER

Run No.	a^*	I^*
1	1.00	1.00
2	11.60	11.50
3	1.25	1.26
4	1.72	1.73
5	5.05	5.10

Here, a^* and I^* are respectively the slope, a , and current, I , reduced on the basis of Run No. 1

It is quite apparent by Table D-2 that for argon over the density range studied the conditions of Equation (D-4) hold and that equation (D-5) may be employed in the interpretation of the data.

It has been shown by other investigators^(10,64) that the concentration of tritium and carbon-14 dioxide are proportional to the ionization current at low densities and for currents of greater magnitude than encountered here.

The variation of $\frac{P}{I_a}$ with ρ is shown by Figures D-3 and D-4 for the

helium and nitrogen runs. Since a relation of the form of Equation (D-1 is unobtainable the analysis must proceed in a different manner. If the assumption⁽¹⁰⁾ is made that for a sufficiently low density the ionization current is proportional to the krypton-85 concentration, then the constancy of I_2/I_1 with density indicates the applicability over the density range.

For the helium and nitrogen runs the current ratios, I_2/I_1 , (I_2 larger) were computed for various densities from Figures D-3 and D-4. At densities of 2, 6, and 10 mole/liter the helium ratios are 4.00, 4.08, and 4.05, respectively, and the nitrogen ratios are 9.7, 9.8, and 9.8, respectively. It is believed that the constancy of the ratios is within experimental error.

The krypton-85 concentration-current relationships were not investigated for other base gases. However, it is believed that the conclusion that Equation (D-5) holds for the magnitude of currents and densities encountered is valid for all cases.

Part 2; The Ionization Cell Chamber Ratio, f_1 Calibration

Due mainly to geometrical differences the ionization chambers of the ionization cell did not give the same reading for the same concentration of Kr-85 in each. Therefore, it was necessary to calibrate the chambers with respect to each other at the same Kr-85 concentration.

The procedure followed was to inject hot gas into the cell and then inject cold gas in both chambers to a high pressure. The injection was carried out so that both sides read about the same. When the ratio of the currents became constant equilibrium was established. After this the pressure was reduced in steps. The current (chart units) from each side was recorded at each pressure. From these the Ionization Cell Chamber Ratio, $f = A/B$, or the ratio of the A side current to the B side current was ob-

tained for each pressure. These data are given for various gases by Table D-3 for the Glass Capillary Plug A in place and by Table D-4 for the Porous Ceramic PlugB in place.

The following definitions are important:

- V_R - - - voltage range
- A - - - A side reading (chart units)
- B - - - " " " " "
- f - - - Ratio of A to B
- T - - - Temperature, °C
- P - - - Gage Pressure, psid
- P_a - - - Absolute Pressure, atm.
- w - - - Mass density, grams/liter (g/)

In order to use the tabulated information for determining the f of a given diffusion run large scale plots of f versus pressure or mass density were made.

In Figure D-5 a plot of f versus the absolute pressure for the Glass Capillary Plug A case is given. The nitrogen and argon runs coincided; however the helium f's were consistently lower and did not show any variation with pressure. Because of this condition a curve is shown for the argon and nitrogen runs and a separate curve for the helium runs.

The same type of difference between the helium f's and these of the other gases showed up in the Porous Ceramic Plug B case. In an effort to reduce this to a single correlation the f's were plotted versus mass density to give Figure D-6. Although total coincidence of the helium runs with the others is not obtained it is apparent that f depends upon the mass density at the lower densities. This type of behavior has not been observed heretofore. The cell employed in this investigation differs from others^(10,58) in that it has the concentric outer electrode in the cell chamber, and thus

TABLE D-3GLASS CAPILLARY PLUG f CALIBRATION

VR (volts)	A	B	f	T (°C)	P (psig)	Pa (atm)
<u>Run No. 1 (Argon; Jan. 12, 1961)</u>						
30	344.7	368.0	0.9367	35.1	611.0	42.58
30	310.5	331.0	0.9381	"	571.0	39.86
10	758.0	811.0	0.9346	"	502.0	35.17
10	530.2	569.0	0.9318	"	402.0	28.36
10	318.8	343.2	0.9289	"	294.0	21.01
3	381.2	411.0	0.9275	"	159.0	11.83
0.3	245.5	265.7	0.9240	35.0	59.0	5.022
<u>Run No. 2 (Helium; Jan. 2, 1961)</u>						
1	766.5	832.0	0.9213	35.1	804.0	55.72
1	446.0	485.0	0.9196	"	574.0	40.07
1	331.0	360.0	0.9194	"	479.0	33.60
0.3	142.0	154.4	0.9197	"	139.0	10.47
<u>Run No. 3 (Nitrogen; Jan. 7, 1961)</u>						
10	302.5	321.8	0.9400	35.1	786.0	53.81
3	852.0	908.0	0.9383	"	684.0	47.55
3	568.8	608.8	0.9343	"	506.0	35.44
3	290.6	312.7	0.9293	"	322.0	22.92
1	138.4	149.5	0.9258	"	102.0	7.948
0.3	137.5	148.8	0.9241	"	42.0	3.865

TABLE D-4POROUS PLUG B f CALIBRATION

VR (volts)	A	B	f	P (psig)	Pa (atm)	(g/l)
<u>Run No. 1 (Argon; 35.0°C; Feb. 3, 4, & 5, 1961)</u>						
30	550.0	572.3	0.9612	4629	316.0	491.1
30	534.9	555.1	0.9626	4410	301.1	472.1
30	534.0	556.4	0.9597	4415	301.4	472.8
30	498.2	518.3	0.9612	4031	275.3	434.6
30	454.2	472.0	0.9623	3608	246.5	392.1
30	410.5	426.9	0.9616	3232	220.9	359.8
30	359.4	374.4	0.9599	2817	192.7	315.9
30	302.7	316.1	0.9576	2396	164.0	270.3
10	728.0	761.6	0.9559	1969	135.0	222.6
10	566.4	594.4	0.9529	1608	110.4	181.7
10	381.4	402.9	0.9466	1193	75.4	123.5
10	299.3	316.4	0.9460	1008.0	69.6	113.7
10	213.9	226.9	0.9427	804.0	55.7	90.34
3	424.0	451.3	0.9395	576.0	40.47	65.24
3	239.1	255.4	0.9362	402.0	28.36	45.47
1	347.5	372.6	0.9326	259.0	18.63	29.73
<u>Run No. 2 (Helium; 35.0°C; Feb. 18, 1961)</u>						
3	574.7	607.7	0.9446	6020	410.6	55.10
3	562.7	596.4	0.9435	5795	395.3	53.34
3	546.4	578.5	0.9445	5500	375.3	51.01
3	510.7	542.5	0.9414	5000	341.2	46.95
3	473.4	503.5	0.9402	4510	307.9	42.88
3	429.0	457.2	0.9383	4000	273.2	38.56
3	380.1	404.5	0.9397	3500	239.2	34.22
3	322.2	343.1	0.9391	2995	204.8	29.70
3	260.8	278.0	0.9381	2500	171.1	25.17
1	579.8	618.2	0.9379	1985	136.1	20.31
1	383.7	409.7	0.9365	1490	102.4	15.50

TABLE D-4 (Cont'd.)

VR (volts)	A	B	f	P (psig)	Pa (atm)	(g/l)
<u>Run No. 3 (Helium; 35.0°C; Feb. 20, 1961)</u>						
10	496.1	528.7	0.9383	1932	132.5	19.81
10	484.5	516.1	0.9388	1900	130.3	19.49
10	465.7	496.6	0.9378	1848	126.8	18.99
10	430.9	459.4	0.9380	1750	119.4	17.95
3	908.2	968.2	0.9375	1292	88.92	13.54
3	605.2	645.3	0.9379	1004	69.32	10.64
3	414.9	442.8	0.9370	798.0	55.30	7.545
3	261.5	279.6	0.9353	605.0	42.17	6.626
1	781.6	835.6	0.9355	605.0	42.17	6.626
1	393.3	420.9	0.9344	401.0	28.29	4.423
<u>Run No. 4 (Carbon dioxide; 35.0°C; Feb. 22, 1961)</u>						
10	284.4	297.4	0.9563	818.0	56.66	104.5
3	878.1	922.5	0.9519	763.0	52.92	97.25
3	767.4	810.4	0.9469	676.0	47.00	85.80
3	674.2	616.1	0.9430	104.0	42.10	76.49
3	546.2	582.3	0.9380	503.0	35.23	63.55
3	415.3	444.3	0.9347	398.5	28.12	50.36
3	296.0	318.0	0.9308	302.5	21.58	38.41
1	521.5	561.2	0.9293	200.0	14.61	25.82
1	212.9	219.3	0.9284	100.5	7.84	13.77
<u>Run No. 5 (Nitrogen; 35.0°C; Feb. 28, 1961)</u>						
10	553.3	575.0	0.9614	6000	409.3	359.7
10	562.4	583.5	0.9638	5900	402.5	356.6
10	592.7	613.8	0.9656	5495	374.9	340.0
10	636.0	657.5	0.9673	4940	337.2	314.8
10	671.0	693.5	0.9676	4460	304.5	292.3
10	711.3	734.9	0.9679	3800	259.6	258.5
10	729.5	756.7	0.9640	2960	202.4	210.5
<u>Run No. 6 (Ethylene; 25.0°C; Mar. 9, 1961)</u>						
3	681.1	711.4	0.9574	1267.0	87.23	309.4
3	686.8	717.3	0.9564	1258.0	86.62	306.8
3	771.4	803.2	0.9604	1154.0	79.54	287.9

TABLE D-4 (Cont'd.)

VR (volts)	A	B	F	P (psig)	Pa (atm)	(g/l)
3	972.2	1012.5	0.9602	1018.0	70.28	237.0
10	378.2	396.8	0.9531	854.0	59.12	162.4
10	331.4	349.6	0.9480	645.0	44.90	115.9
3	832.5	883.6	0.9422	496.0	34.76	85.89
3	523.3	557.9	0.9380	348.0	24.69	58.12
3	320.4	342.2	0.9363	246.0	47.75	40.37

Run No. 7 (Argon; 35.0°C; Mar. 14, 1961)

30	363.6	384.4	0.9459	984.0	67.96	110.6
30	354.8	375.0	0.9461	967.0	66.81	108.7
30	320.2	339.3	0.9437	902.0	62.38	101.4
10	809.5	858.4	0.9430	800.0	55.44	89.83
10	662.4	703.4	0.9418	700.0	48.64	78.61
10	523.8	556.9	0.9406	600.0	41.83	67.43
10	377.2	402.2	0.9378	487.0	34.15	54.89
10	265.0	283.0	0.9364	391.0	27.61	44.24
3	573.6	613.0	0.9357	300.0	21.42	34.20
3	207.9	223.2	0.9315	162.0	12.03	19.13
1	624.0	669.5	0.9320	162.0	12.03	19.13

Run No. 8 (Argon; 35.0°C; Mar. 14-15, 1961)

10	930.0	969.7	0.9591	6130	418.1	604.0
10	916.8	955.4	0.9596	5975	407.6	594.4
30	305.0	317.8	0.9597	5975	407.6	594.4
10	819.6	927.8	0.9610	5700	388.9	575.4
10	848.2	882.4	0.9613	5300	361.7	545.3
10	813.2	845.6	0.9617	5000	341.3	52.19
10	751.3	781.3	0.9616	4490	306.5	479.2
10	676.5	704.1	0.9608	3930	268.4	428.4
10	604.9	630.5	0.9594	3500	239.2	382.5
10	520.0	542.8	0.9580	3000	205.2	335.7
10	326.3	341.2	0.9563	2000	137.1	226.1
10	269.9	282.7	0.9547	1715	117.7	193.8
3	568.1	599.3	0.9479	1200	82.68	127.0

FIGURE D-5: f versus PRESSURE for PLUG A

FIGURE 2-6: IONIZATION CELL f VERSUS MASS DENSITY FOR PLUG B

FIGURE D-7: f versus PRESSURE for PLUG B
with HELIUM

the cell body is not the outer electrode. The explanation must lie in the distortion of the electric field with density changes. Such distortion would be more important with this type of cell.

In Figure D-7 the helium f 's are plotted versus absolute pressure (atm.) for the Porous Ceramic Plug B case.

In order to determine the value of f for a given diffusion run either Figure D-5, D-6, or D-7 is employed depending upon the experimental run conditions.

Because of its high cost no calibrations were made with krypton and Figure D-6 was generally used to determine f . For those runs with the Glass Capillary Plug A the argon curve of Figure D-5 was used with a molecular weight ratio correction for correspondence in density.

Part 3; Ionization Cell Background Data:

In general the background observed for the different base gases in the ionization cell was negligible. This was checked periodically usually at the beginning of a series employing a new base gas. However, for the ethylene system this was not the case. A definite increase in background with pressure was noted for this gas. A background determination run for only ethylene in the cell at 25°C gave the pressures and currents (chart units) for a 3 volt scale as listed below.

TABLE D-5

BACKGROUND FOR ETHYLENE RUNS

Pressure (psia)	A	B
117	0	0
318	0	0
550	0	0
812	0	0
1096	0	0
1337	3.2	1.4
1426	5.6	2.5
1649	19.0	4.8
1735	34.1	6.0

APPENDIX E

SCINTILLATION CELL COUNT RATE
CALIBRATION DATA

Part 1; Counting Rate versus Pressure

Part 2; Scintillation Cell Chamber Ratio

f Calibration

APPENDIX E

SCINTILLATION CELL COUNT RATE
CALIBRATION DATA

The backgrounds for the two chambers of the scintillation cell were determined periodically. Within the error introduced by the statistical fluctuations no dependence on pressure was noted. The backgrounds for each run are given in Table B-2. It should be noted that background increased with the time the photomultiplier tubes were in use.

Part 1; Counting Rate versus Pressure:

A blank plug was placed in the scintillation cell to isolate the A side chamber. Into this chamber hot argon was introduced, the lines were flushed, and in steps cold argon was introduced. The counting rate versus pressure was obtained. The best representation was found to be reciprocal count rate versus absolute pressure. In Table E-1 the reciprocal background corrected count rate ($1/A^*$) at the absolute pressure (psia) is given. Here, Run No. 2 is at an amplification gain of 1088 with a ratio reading of 3.77 to the usual 1167 volts at a gain of 1600. Figure E-1 is a plot of $1/A^*$ vs. absolute pressure. When the extrapolation to zero pressure is carried out the intercepts are in the ratios of:

$$\text{Run No. 1} = 1.00$$

$$\text{Run No. 3} = 1.87$$

$$\text{Run No. 2} = 3.04$$

These ratios hold within the certainty of their reading over the pressure range.

TABLE E-1
COUNTING RATE VERSUS PRESSURE

Pressure	$1/A^*$ $\times 10^3$	Pressure	$1/A^*$ $\times 10^3$
(psia)	(1/cpm)	(psia)	(1/cpm)
Run No. 1:		Run No. 3:	
82	1.060	57	1.941
171	1.121	142	2.082
317	1.261	275	2.310
487	1.412	494	2.72
625	1.530	714	3.13
831	1.721	904	3.49
967	1.868	1147	4.01
1149	2.061	1412	4.55
1331	2.253	1657	5.13
1552	2.532	2008	5.75
1721	2.73	2798	7.64
1996	3.06		
2451	3.62		
3033	4.31		
Run No. 2:			
503	1.115		
665	1.240		
871	1.393		
1147	1.69		
1456	2.00		
1712	2.28		
1997	2.58		
2505	3.10		
3020	3.60

FIGURE E-1: RECIPROCAL COUNT RATE vs. PRESSURE

Part 2; Scintillation Cell Ratio f Calibration:

For many of the scintillation cell runs sufficient time was allowed to establish equilibrium in order to obtain a value for f . These are indicated by the diffusion run number in Table E-2. Separate calibration runs are numbered separately. The calibration procedure was the same as for the Ionization Cell.

The adjustments designated in Table E-2 refer to the adjustment of the external high voltage resistor to bring the readings into coincidence. An initial adjustment (I) was sufficient for the argon runs at 35°C. More frequent adjustments were necessary after this. Run S-10 was made with a very poor adjustment so that another was made.

A plot of f versus absolute pressure is given by Figure E-2. It is noted that correspondence in form is obtained for the Adjustments I and V.

All readings are at a pulse height of 1.00 volts except where indicated. Here, A^* and B^* are the counting rates corrected for background.

TABLE E-2
SCINTILLATION CELL CHAMBER RATIO f CALIBRATION

Run No.	Pressure (psia)	A*	B*	f
Adjustment I: (Argon, 35°C)				
S-1	607	430	445	0.966
S-2	615	497	512	0.971
S-5	1510	415	437	0.950
S-8	837	353	370	0.954
1	421	376	380	0.984
2	1453	374	393	0.952
2	943	486	505	0.962
2	129	800	809	0.989
Adjustment II: (Argon, -25°C)				
S-10	547	466	565	0.825
Adjustment III: (Argon, -25°C)				
3	547	583	572	1.017
3	65	467	456	1.024
Adjustment IV: (Argon, -25°C)				
4	62	433	429	1.009
S-14	201	363	360	1.008
Adjustment V: (Nitrogen, -25°C)				
5	1934	745	753	0.989
5	1431	668	675	0.990
5	969	557	561	0.993
5	512	380	372	1.022
5	302	258	251	1.028
6	917	376	379	0.992
6	612	301	299	1.007
6	415	232	228	1.018
6	213	140	136	1.030
(Pulse Height = 1.60 volts)				
5	512	153	156	0.981
5	302	104	106	0.981

FIGURE E-2: f versus PRESSURE for SCINTILLATION CELL

APPENDIX F

CELL CONSTANT DATA

In this appendix the calibrations necessary to determine the cell constants are indicated and specified.

Part 1; Calibration of Ionization Cell Chamber Volumes:

The volumes of the ionization cell chambers were determined before the diffusion and also after about two months use during which pressures to 4500 psi were encountered. The volume of the cell chambers proper were determined by mercury weight calibration. This calibration and the corrections due to stirrers, etc. are shown by Table F-1.

TABLE F-1

IONIZATION CELL CHAMBER VOLUME CALIBRATION

<u>Before Making Runs</u>	A side	B side
Mercury Weights (23°C)	124.471 gms	131.464 gms
" "	124.320	131.395
" "		131.349
" " (Avg)	124.395	131.402
Volume	9.188 cc.	9.706 cc.
<u>After Making Runs</u>		
Mercury Weights (23°C)	124.101 gms	131.076 gms
" "	124.153	131.231
" " (Avg)	124.127	131.154
Volume	9.168 cc.	9.687 cc.
Mean Volume before Correction	9.178 cc.	9.697 cc.
<u>Stirrer Dimensions</u>		
Stirrer Pinions	0.188" x 0.039" dia.	0.188" x 0.039" dia.
Wt. of Stirrer	0.8805 gms.	0.8339 gms.
Wt. of Glass Roller	0.1189 "	0.1202 "

TABLE F-1 (cont'd)

	A side	B side
<u>Correction to Chamber Volumes</u>		
Stirrer Pinion Correction	-0.004 cc.	-0.004 cc
Stirrer Correction	-0.107 "	-0.105 "
Glass Roller Correction	-.059 "	-0.054 "
Total Corrections	-0.170 "	-0.163 "
<u>Corrected Ionization Cell Chamber Volumes</u>		
	9.008 cc.	9.534 cc.

Part 2; Calibration of Scintillation Cell Chamber Volumes:

The scintillation cell chamber volumes were calibrated by weight of mercury with stirrers in place. This calibration is given by Table F-2.

TABLE F-2

SCINTILLATION CELL CHAMBER VOLUME CALIBRATION

	A side	B side
Mercury Weight (27.5°C)	104.646 gms	103.911 gms
" "	104.509	103.892
" " (Avg.)	104.58	103.90
<u>Average Volume</u>	7.731 cc.	7.680 cc.

Part 3; Glass Capillary Plug A Data:

The glass capillary plug which is designated as Plug A consists of a bundle of 67 glass capillaries bonded together by an epoxy resin. The 67 capillaries were formed from the pieces of seven 12 inch Corning Glass Pyrex redrawn capillaries.

The average diameter of each long capillary was determined by weight of mercury volume measurements and cathetometer length measurements. This calibration is given by Table F-3.

The average diameter of each short piece was determined by measuring the resistance of a mercury through each capillary with a Mueller resistance

bridge. This calibration is given by Table F-4. Here, R is the resistance in ohms, L is the measured length in inches, and A is the corrected area in ($\text{cm}^2 \times 10^4$).

For the measurements chemically pure mercury was used. A correction⁽⁷⁹⁾ to the resistance measurements to account for the flow of electricity at the end of the tube may be expressed as an additional length equal to 0.82 times the diameter of the bore at the end. A first approximation to the diameter was made for each tube and the corrected cross-sectional area, A , was calculated by

$$A = \frac{\rho L_c}{R} \quad (\text{F-1})$$

where $L_c = L + 0.82d$. Now L is the measured length and d is the tube diameter, R is the measured resistance in ohms and ρ is the mercury resistivity (c.f. Swindells⁽⁷⁹⁾).

Length of Capillary Plug = 0.9618 inches.

TABLE F-3

WEIGHT OF MERCURY CALIBRATION OF LONG CAPILLARIES

Capillary No.	Pieces	Mercury Weights (gms)	Temperature (°C)	Average Weight (gms)	Length (cm)	Average Cross-Sectional Area (cm ²) x 10 ⁴
I	9	0.2225 0.2227 0.2225	24.0 24.0 24.0	0.2226	30.513	5.390
II	10	0.2572 0.2572 0.2572	24.0 24.0 24.0	0.2572	30.500	6.230
III	10	0.2360 0.2361 0.2361	23.0 23.0 23.0	0.2361	30.489	5.705
IV	10	0.2310 0.2311 0.2307	23.5 23.5 23.5	0.2309	30.509	5.591
V	10	0.1894 0.1892 0.1892	23.1 23.1 23.1	0.1893	30.502	4.584
VI	9	0.2579 0.2575 0.2577	23.3 23.3 23.3	0.2577	30.502	6.241
VII	9	0.2123 0.2125 0.2125	23.1 23.1 23.1	0.2124	29.126	5.387
Total Contribution to Plug					374.25	

TABLE F-4

MERCURY RESISTANCE CALIBRATION OF SHORT CAPILLARIES

R	L	A	R	L	A	R	L	A
Capillary No. I (9 pieces, 23.0°C)			Capillary No. II (10 pieces, 23.1°C)			Capillary No. III (10 pieces, 23.2°C)		
0.5458	1.167	5.238	0.4471	1.120	6.165	0.4722	1.099	5.726
0.5274	1.167	5.439	0.4397	1.103	6.175	0.4980	1.111	5.489
0.5230	1.170	5.501	0.4567	1.132	6.098	0.5080	1.118	5.415
0.4883	1.159	5.839	0.4218	1.109	6.471	0.4849	1.104	5.602
0.5347	1.126	5.176	0.4494	1.118	6.123	0.4672	1.130	5.952
0.4796	1.126	5.777	0.4471	1.136	6.251	0.4979	1.121	5.583
0.5380	1.141	5.214	0.4287	1.106	6.349	0.4913	1.114	5.579
0.5296	1.130	5.246	0.4343	1.124	6.369	0.4920	1.117	5.585
0.5480	1.164	5.222	0.4470	1.113	6.128	0.4620	1.141	6.077
			0.4562	1.129	6.090	0.4670	1.122	5.911
Capillary No. IV (10 pieces, 23.1°C)			Capillary No. V (10 pieces, 23.3°C)			Capillary No. VI (9 pieces, 23.3°C)		
0.4654	1.069	5.652	0.5866	1.134	4.752	0.4543	1.132	6.132
0.5096	1.109	5.352	0.6210	1.127	4.463	0.4336	1.127	6.398
0.5087	1.119	5.409	0.6242	1.130	4.449	0.4312	1.113	6.353
0.5014	1.125	5.520	0.6132	1.124	4.507	0.4657	1.120	5.924
0.4776	1.114	5.739	0.6379	1.123	4.326	0.4629	1.114	5.922
0.5110	1.117	5.375	0.5288	1.092	5.079	0.4332	1.116	6.343
0.4927	1.120	5.592	0.5782	1.135	4.826	0.4272	1.115	6.424
0.4692	1.118	5.862	0.6738	1.146	4.180	0.4694	1.124	5.892
0.4548	1.117	6.044	0.5962	1.096	4.521	0.4235	1.120	6.512
0.5184	1.125	5.337	0.6053	1.115	4.529			
Capillary No. VII (9 pieces, 23.3°C)								
0.4925	1.102	5.506						
0.5094	1.132	5.465						
0.5163	1.118	5.327						
0.5013	1.097	5.382						
0.5090	1.118	5.403						
0.5208	1.115	5.266						
0.5228	1.115	5.246						
0.5018	1.113	5.457						
0.4946	1.118	5.562						

Total Cross-Sectional Area = $3.7382 \times 10^{-2} \text{ cm}^2$.

Units:

R - - - (ohms.)

L - - - (inches)

A - - - ($\text{cm}^2 \times 10^4$).

Part 4; Ionization Cell-Glass Capillary Plug A cell Constant K_A :

From Table F-3 and F-4 the average cross-sectional areas are 3.7426 and $3.7382 \times 10^{-2} \text{ cm}^2$, respectively. It is noted that the two methods of calibration are in excellent agreement. Thus,

Mean Average Cross-

$$\text{Sectional Area, } A, = 3.7404 \times 10^{-2} \text{ cm}^2.$$

The deviation of the method average from the mean is 0.059%.

Now, K_A may be calculated by

$$K_A = \frac{A}{L} \left(\frac{1}{V_A} + \frac{1}{V_B} \right), \quad (\text{F-2})$$

where

$$A = 3.7404 \times 10^{-2} \text{ cm}^2$$

$$L = 0.9618 \times 2.540 = 2.4430 \text{ cm.}$$

$$V_A = \text{volume of A side} = 9.008 \text{ cc.}$$

$$V_B = \quad \quad \quad \text{B side} = 0.535 \quad "$$

This gives

$$\underline{K_A = 3.3053 \times 10^{-3} \text{ cm}^{-2}}.$$

It is believed that at least four figures are significant.

Part 5; Ceramic Porous Plug Cell Constants K_B and K_C :

Cell Constant K_B . (Ionization Cell)

The cell constant K_B for the 10μ particle retention (25μ mean pore size) Ceramic Porous Plug B was determined by meshing the density-cell constant-diffusivity product, $\rho K_B D$, obtained from the least mean square slope of the low pressure runs with this product, $\rho K_A D$, from the Glass Capillary Plug A runs.

The best mesh ratios of K_B to K_A are as follows:

Argon - - - - 10.167

Nitrogen - - - 9.956

Helium - - - - 10.094

Average - - - - 10.096

The argon was counted twice in the averaging. Thus

$$\underline{K_B = 3.337 \times 10^{-2} \text{ cm}^{-2}}$$

Cell Constant K_C (Scintillation Cell)

The cell constant for the 25 μ particle retention (52 μ mean pore size) Ceramic Porous Plug C was determined by meshing $\rho K_C D$ with $\rho K_B D$ for argon at 35°C. Thus, the value of the scintillation cell constant follows as

$$\underline{K_C = 2.759 \times 10^{-2} \text{ cm}^{-2} .}$$

APPENDIX G

PRESSURE GAGE AND THERMOCOUPLE CALIBRATIONS

Part 1; Pressure Gage Calibration:

The pressure measuring devices used in this investigation are designated by a capital letter and are as follows:

- A - - - Marsh 100 psi. test gage
- B - - - Ashcroft 600 psi. test gage
- C - - - Heise 2000 psi. gage (#H27188)
- D - - - Heise 10,000 psi. gage (#H24913)
- E - - - Ashcroft 5,000 psi. gage
- M - - - 50 in. Mercury Manometer
- H - - - 100 in. Mercury Column

The Heise Bourdon Tube gages were calibrated by the manufacturer and required no correction. These were used to calibrate gages A, B and E. The calibration is given by Table G-1.

Part 2; Thermocouple Calibrations:

Copper-Constantan Thermocouples were used. Calibration was made in a stirred Dewar water bath with Thermotrol proportional control of a 50 watt heater. Calibrations were made against totally immersed ASTM precision (Tagliabue) thermometers calibrated to the nearest 0.01°C. The following designations are important:

- T-1 - - - - ASTM Thermometer #671438
- T-2 - - - - " " #663736
- IT-1 - - - Ionization Cell thermocouple No. 1
- IT-2 - - - " " " No. 2
- ST-1 - - - Scintillation Cell thermocouple No. 1

I. Calibration at 25°C

T-2 (°C)	IT-2 (mv.)
24.9	0.985
25.0	0.989
25.1	0.993
25.2	0.997
25.5	1.009
26.0	1.029
25.0	0.989
24.8	0.980
24.5	0.968
24.0	0.948

II. Calibration at 35°C

T-1 (°C)	IT-1 (mv.)	IT-2 (mv.)	ST-1 (mv.)
34.0	1.350	1.351	1.351
34.5	1.374	1.375	1.375
34.7	1.384	1.386	1.386
34.9	1.393	1.395	1.395
35.0	1.398	1.399	1.399
35.1	1.402	1.404	1.404
35.3	1.411	1.414	1.414
35.5	1.420	1.423	1.423
36.0	1.440	1.442	1.442

All millivolt readings were made on the Leeds-Northrup No. 1560638 (0-1000 mv.) potentiometer with switch gear and electrical leads in place.

The ST-1 thermocouple was not calibrated at -25°C and standard millivolt-temperature tables were used to determine the temperature.

TABLE G-1

PRESSURE GAGE CALIBRATIONS

I. Calibration B versus C:

B (psi)	C (psi)
26.0	26.0
69.0	69.0
122.0	122.0
152.0	152.0
204.0	204.0
248.0	248.0
300.0	300.0
348.0	348.0
402.0	402.0
453.0	453.0
498.0	498.0
551.0	550.0
578.0	578.0

II. Calibration A versus C:

A (psi)	C (psi)
11.0	10.0
20.9	20.0
50.9	50.0
70.9	70.0
98.9	98.0
98.9	98.0

III. Calibration E versus D:

E (psi)	E (psi)
<u>Pressure Up</u>	
210	210
505	510
995	1003
1188	1205
1500	1503
1740	1752
1992	2003
2198	2207
2400	2415
2600	2612
3000	3014
3192	3205
3400	3413
3806	3818
4182	4198
4615	4630
4805	4815

E (psi)	D (psi)
<u>Pressure Down</u>	
4714	4700
4515	4500
4128	4112
3916	3900
3613	3600
3525	3513
3317	3307
3110	3098
2923	2910
2732	2720
2512	2500
2208	2198
2000	1994
1712	1702
1515	1508
1113	1108
595	592

APPENDIX H

BASE GAS PROPERTIES

In this section the important physical properties, analysis, and molecular parameters for the gases used in this investigation are specified and indicated.

Part 1; Gas Analysis:

The specifications of the company supplying the gas are used. In Table H-1 the supplier and estimated purity are shown.

TABLE H-1

GAS ANALYSIS

Gas	Supplier	Estimated Purity
A	Houston Oxygen Co.	> 99.95%
He	" " "	> 99.95
N ₂	" " "	> 99.9
C ₂ H ₄	Du Pont Co.	> 99.9
CO ₂	Matheson Co.	> 99.9
Kr	" "	> 99.9

The carbon dioxide and krypton were of Research Grade quality from Matheson. The nitrogen was oil-pumped but traces of water may have been in the gas. The argon and helium were independently analyzed by mass spectrometer and found in agreement with the above.

Part 2; Critical Constants:

Table H-2 presents the critical pressure, P_c and the critical temperature, T_c as obtained from Hirschfelder, et al.⁽³¹⁾, Beattie, et al.⁽⁴⁾ and the Handbook of Chemical Physics⁽²⁷⁾.

TABLE H-2
CRITICAL CONSTANTS

Gas	T_c ($^{\circ}\text{K}$)	P_c (atm)
A	15.10	48.0
CO_2	304.2	73.0
C_2H_4	282.9	50.9
He	5.3	2.26
Kr	209.4	54.18
N_2	126.1	33.5

Part 3; Lennard-Jones⁽⁶⁻¹²⁾ Molecular Force Parameters

Table H-3 which follows was derived mainly from Table I-A of Hirschfelder, et al.⁽³¹⁾ with supplements from N.B.S. Circular 564⁽³⁰⁾. The Lennard-Jones force constants ϵ and σ are respectively the depth of the potential well and the separation for zero potential. These constants are those determined from viscosity measurements and differ slightly from those determined from second virial coefficient measurements except for krypton.

TABLE H-3
LENNARD-JONES MOLECULAR CONSTANTS

Gas	ϵ/K ($^{\circ}\text{K}$)	($\text{\AA}$)
A	124	3.418
CO_2	200	3.952
C_2H_4	205	4.232
He	10.22	2.576
Kr	190	3.61
N_2	91.46	3.681

At the present time there is some discussion concerning the values for krypton. The values obtained by transport property measurements differ considerably from second virial parameters. Mason⁽⁴⁷⁾ recently redetermined the force constants for krypton with the latest available experimental data. His determinations are even farther removed from the second virial effort but in reasonable accord with the values given above. He found also that it was not possible to select unambiguously a set of modified Buckingham (exp. -6) parameters.

Kestin and Leidenfrost⁽³⁹⁾ have determined Lennard-Jones⁽⁶⁻¹²⁾ parameters for helium from their viscosity data which are in marked disagreement with those given above. They found that the modified Buckingham (exp. -6) potential gives a better interpretation of their data.

The usual combination rules; namely, $\epsilon_{12} = (\epsilon_1 \epsilon_2)^{\frac{1}{2}}$ and $\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2)$, were followed in determining the force parameters for interaction between krypton and base gas molecules.

For the Kr-A system $\frac{\epsilon_{12}}{K}$ and σ_{12} are calculated to be 153.5 °K and 3.514 Å, respectively. Now, Srivastava and Srivastava⁽⁸⁰⁾ determined these to be 155.0 °K and 3.526 Å, respectively, from experimental diffusion results. Also, they found the values 162.0°K and 3.495 Å by a method employing both experimental diffusion and thermal conductivity results.

Part 4; References for PVT Data:

For all the runs it was necessary to know the compressibility factor, Z, and for the interpretation of the results pressure-temperature derivatives were needed so that reliable pressure-volume-temperature data was needed. For all the base gases the published data of the Michels group was considered the most reliable. The only source of this data for krypton over the range studied is that of Beattie, et al.⁽⁴⁾. In Table H-4 the

references employed in the evaluation of state properties are listed.

TABLE H-4

Investigator	Reference Number	Gas	Temperature Range (°C)	Density Range (m/)
1. Michels, Wijker and Wijker	56	A	0 to 150	34
2. Michels, Levelt and DeGraaf	57	A	-25 to -155	29
3. NBS Circular 564	30	A	--	--
4. " " "	30	N ₂	--	--
5. Michels, Lunbeck and Wolkers	58	N ₂	-125 to + 150	34
6. Lunbeck, Michels and Wolkers	46	N ₂	" "	34
7. Michels and Wouters	54	He	0 to 150	9
8. Michels and Geldermans	55	C ₂ H ₄	0 to 150	23
9. Michels and Michels	53	CO ₂	0 to 150	10
10. Beattie, Brierley and Barriault	4,5	Kr	0 to 300	10

NOMENCLATURE

A	Area, cm^2
A	Side or chamber of a diffusion cell and/or chart reading
b_o	Rigid sphere second virial coefficient, liters/mole
B	Real gas second virial coefficient
B	Side or chamber (opposite to A) of a diffusion cell and/or chart reading
C	Real gas third virial coefficient
C	Concentration, moles per liter
C_A, C_B	Concentration in A and B side diffusion chambers, respectively
C_1, C_2	Concentration of species 1 and 2, respectively
D	Diffusion coefficient, cm^2/sec
D^*	Reduced self-diffusion coefficient
D_c	Diffusivity in a capillary
$D_{12})_1$	Chapman-Enskog first approximation to binary diffusion coefficient
$D_{11})_1$	Chapman-Enskog first approximation to the self-diffusion coefficient
D_{12}	Binary diffusion coefficient
$D_{12})_r$	Reduced binary diffusion coefficient
d	Diameter of capillary, cm
d^*	Reduced density, ρb_o , for base gas at T_f
d^*_{12}	Reduced density, $(2/3 \pi N \sigma_{12}^3)$, for 1-2 interaction
E	Sum of squares of difference between experimental points and LMS fit
E	Activation energy
f	Ratio of A side current or count rate to B side when both chambers have the same krypton-85 concentration
f	Distribution function

F	Ratio of density-diffusivity product at a given density to the one atmosphere value at the same temperature
F_E	F derived from mean line through experimental density-diffusivity product vs. density plots
F_1	F determined by rigid sphere theory
F_2	F determined by Enskog PVT methods at T_f for b_0 set by B
F_3	F determined by Enskog PVT methods at T_f for b_0 as $(\rho/\eta) \rightarrow 0$.
F_4	F determined by Enskog PVT with viscosities at T_f
$F_2)_T$	F determined by Enskog PVT method at the diffusion temperature T with b_0 set by B
g, gm	Grams
I	Ionization Current
I_A, I_B	Ionization currents from A and B sides, respectively
J	Diffusion flux, moles per sec. per cm^2
k	Boltzmann's Constant
K	Cell Constant
K_A	Cell Constant for Porous Glass Capillary Plug A
K_B	" " " " Ceramic Plug B
K_C	" " " " " Plug C
ℓ	Liter
L	Length of capillary, cm
L	Effective length of porous plug
L	Phenomenological coefficient
M	Molecular weight
M	Gram Mole
M_1, M_2	Molecular weight of species 1 and 2, respectively
n	Number of molecules per unit volume

n_1, n_2	Numbers of species 1 and 2 per unit volume
P, P_a	Absolute pressure, atm
P_r	Reduced pressure, P/P_c
P_c	Critical pressure, atm
$\underline{r}$	Radius vector
R	Gas Constant
R	Resistance, ohms
R	Integration constant
t	Time, sec
T	Absolute temperature, °K
T_f	Pseudo-temperature for base gas, $T \left(\frac{\epsilon_1}{\epsilon_2} \right)$
T^*	Reduced temperature, $K T/\epsilon$
T_r	Reduced temperature, T/T_c
T^*_{12}	Reduced temperature, KT/ϵ_{12}
T_c	Critical temperature
U	Internal energy, cal. per mole
$\underline{v}$	Velocity vector
V_A, V_B	Volumes of A and B side chambers, respectively
w	Mass density, grams per cm^3
x	Distance parallel to diffusion flux
y	Dimensionless number given by $\left[\frac{1}{\epsilon R} \left(\frac{\partial P}{\partial T} \right)_\epsilon - 1 \right]$
y	$\text{Log}_e (A - fB)$
Y	Enskog correction factor for self-diffusion
Y_{12}	Enskog-Thorne correction factor for binary diffusion
Z	Compressibility factor
$\propto$	Proportionality sign
Δ	Indicates factor for second approximation to Chapman-Enskog diffusivity

- ∇ Three dimensional space gradient operator
 ϵ_1, ϵ_2 Lennard-Jones forces for species 1 and 2, respectively
 ϵ_{12} Mixed intermolecular force constant,
 λ Mean free path of a molecule, cm
 μ Viscosity
 μ Chemical potential
 ρ Mole density, gram moles per liter
 ρ^* Reduced density, $\rho \sigma^3$
 σ_1, σ_2 Lennard-Jones⁽⁶⁻¹²⁾ collision diameters for molecules 1 and 2, respectively
 $\phi(r)$ Spherically symmetric potential
 $\Omega_{11}^{(1,1)*}$ Lennard-Jones collision integral for 1-1 interaction
 $\Omega_{12}^{(1,1)*}$ Lennard-Jones collision integral for 1-2 interaction
 Superscript
 o Denotes dilute gas theory prediction

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