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A STUDY OF DENSE GAS SELF DIFFUSION
IN THE METHANE-CARBON TETRAFLUORIDE SYSTEM
BY PULSED NMR

by

Fouad Khoury

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NOMENCLATURE

Upper Case Letters

A  echo amplitude
B  second virial coefficient
C  third virial coefficient
D  diffusion coefficient
D_i  self diffusion coefficient of component i
D_i^0  self diffusion coefficient of pure component i
D_i  diffusion coefficient of component i at infinite dilution
D_12  mutual diffusion coefficient
E  activation energy
G  magnetic field gradient
G  Gibbs' free energy
\vec{H}_1  oscillating magnetic field
\vec{H}_z  static magnetic field
I  electric current in gradient coils
K  constant
M  molecular weight
S  entropy
T  absolute temperature
T^*  reduced temperature ( = kT/\epsilon )
NOMENCLATURE (continued)

**Upper Case Letters** (Continued)

T₂  spin-spin relaxation time
V  volume

**Lower Case Letters**

a  activity

b  concentration

f  fugacity

k  Boltzmann's constant

p  pressure

r  distance travelled by a molecule

t  time between pulses

x  mole fraction

z  vertical axis

**Greek Letters**

α  intermolecular force constant

\(\dot{\alpha}\)  angular momentum

α₁₂  factor defined by Equation (14)

γ  gyromagnetic ratio

ε  intermolecular force constant, the potential well depth

μ  chemical potential
NOMENCLATURE (continued)

Greek Letters (continued)

$\vec{\mu}$  magnetic moment
$\rho$  density
$\rho_c$  critical density
$\rho_r$  reduced density ($= \rho / \rho_c$)
$\sigma$  intermolecular force constant, the collision diameter
$\sigma$  magnetic field distribution width
$\tau_w$  radio-frequency pulse width
$\vec{\omega}$  nuclear magnetic moment angular velocity
$\Omega^{(1.1)*}$  collision integral
1. INTRODUCTION

1.1 Objectives of the Research

This work is part of a continuing research program on the study of diffusion in fluids. This specific investigation presents self diffusion coefficients in an equimolar binary mixture of methane and carbon tetrafluoride, as well as in pure carbon tetrafluoride, which were experimentally determined by the pulsed nuclear magnetic resonance (NMR) technique. Since both hydrogen and fluorine nuclei possess magnetic moments, the NMR technique can be used to conduct the self diffusion studies on both components.

The measurements cover moderately dense and dense gas regions, at temperatures above the critical. Specifically, this dissertation reports the following:

(1) Experimental self diffusion coefficients of carbon tetrafluoride have been measured from $-30^\circ C$ to $75^\circ C$ from 20 atm to 440 atm,

(2) The activation energy for self diffusion in carbon tetrafluoride has been determined to be $-480\pm 5$ cal/mole at a density of 0.1 gm/cm$^3$.

(3) Force constants for CF$_4$ have been determined for the
Lennard-Jones (6-12) and the modified Buckingham (6-exp) potentials, using these self diffusion data and independent second virial coefficient data simultaneously.

(4) A corresponding states representation of the self diffusion coefficients of CF$_4$ agrees with the data with an average error of $\pm 6\%$.

(5) Self diffusion coefficients have been measured for methane and carbon tetrafluoride in an equimolar mixture of the two components. The measurements cover temperatures from 0°C to 75°C and pressures from 56 atm to 500 atm.

(6) Mutual diffusion coefficients have been calculated from measured self diffusion coefficients for the above mixture using the theory of Bearman.$^2$

(7) The behavior of the composition dependence of the mutual and self diffusion coefficients in the CF$_4$ - CH$_4$ mixture has been examined and show qualitative agreement with that determined by Woessner et al.$^{46}$

1.2 Review of Related Work

Theoretical studies of diffusion phenomena in fluids have been developed from different bases. These studies have attempted to relate the diffusion coefficient to
molecular properties by statistical mechanical approaches and to calculate mutual diffusion coefficients from self diffusion coefficients. The kinetic theory of diffusion in dilute gases, as developed independently by Chapman and Enskog in 1922, has been reported by Chapman and Cowling.  

During the last forty years there have been several approaches to the theoretical study of diffusion in dense fluid systems. It was proposed that self diffusion coefficients could be correlated based on the corresponding states principle, but no attempts to develop a correlation from existing data were made at that time.

The Eyring dense gas theory, based on the theory of absolute reaction rates, showed very poor agreement between calculated and observed coefficients of diffusion. A modification of the dilute gas kinetic theory has been developed by Enskog for dense gases and further modified by Slattery and Bird. The experimental results of Dawson showed only qualitative agreement with their modified theory.

A rigorous kinetic theory of dense gases, based on the Liouville equation, was developed by Kirkwood and others; and an equivalent equation was derived by Douglass. In these deviations it is assumed that the molecules are
point particles and that the forces between them are two body forces.

Bearman\(^2\) developed a statistical mechanical theory of diffusion in liquids and compared it to some earlier theories developed from other viewpoints, namely those of Eyring\(\textit{et al.}\)\(^{16}\), Hartley and Crank,\(^{22}\) and Gordon.\(^{18}\) Bearman showed that, although there are some differences in the earlier derivations, the equations are basically equivalent and are valid for regular solutions.

Interest in self diffusion increased after the availability of radioactive tracers and the development of experimental methods for measuring their concentration.\(^{14,35,41}\)

At a somewhat later date the pulsed NMR method for measuring self diffusion coefficients was discovered.\(^{4,19,37}\)

Bearman\(^1\) derived equations, based on statistical mechanics, which related self diffusion coefficients, mutual diffusion coefficients, friction factors, and molar volumes in binary liquid solutions. Based on these relationships, Van Geet and Adamson\(^{43,44}\) obtained semi-empirical equations for predicting diffusion coefficients of mixtures of n-alkanes at any composition when the self diffusion coefficients of the pure components are known; and their experimental results for \(n-C_{8}H_{18}\), \(n-C_{12}H_{26}\), and \(n-C_{18}H_{38}\) showed good agreement with their predictions.
2. THEORETICAL BACKGROUND

Ordinary diffusion has been defined as the transfer of a molecular specie from one region to another because of a gradient in the concentration. It is formally described by the phenomenological relations, known as Fick's laws:

\[ \text{Flux} = -D \frac{\partial c}{\partial z} \]  \hspace{1cm} (1)

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} \]  \hspace{1cm} (2)

where \( c \) is the local concentration of the diffusing specie and \( D \) is the diffusion coefficient.

For a system at equilibrium, self diffusion is defined as the diffusion of the molecules of the different components within the system. Its measurement depends on somehow tagging one of the components, e.g., through the use of radioactive tracers. Self diffusion is caused by the random motion of the molecules and is described by Fick's laws applied to the trace component. In this work the nuclear spin states of the samples provide the tag for observing self diffusion by means of spin echo nuclear magnetic resonance.
The coefficient of self diffusion is best defined by the basic equation

$$D = \frac{\overline{r^2}}{6t}$$

(3)

where $r^2$ is the mean square net distance a molecule moves in time $t$. The coefficient defined by this equation may be shown to be the same as that defined by Fick's laws but has the appeal that no concentration gradients are necessary.

2.1 **Self Diffusion in Dilute Gases**

The rigorous kinetic theory of dilute gases (the Chapman-Enskog theory) has been presented in a monograph by Chapman and Cowling. It is based on knowledge of the distribution function and is developed for cases where only binary collisions are considered. Additional assumptions are that the molecules are monatomic, that the dimensions of the containing vessel are large compared to the mean free path of the molecules, and that the molecular diameter is small compared to the mean free path. The Chapman-Enskog equations are applicable only in the dilute gas region where all of the above assumptions are justifiable. The final result, as presented by Hirschfelder, Curtiss, and Bird, for mutual diffusion in a binary solution is:
\[ D_{12} = 0.0026280 \left( \frac{\sqrt{T^3(M_1 + M_2)/(2M_1M_2)}}{p \sigma^2 \Omega^{(1,1)*}_{12} (T^*)} \right) \]  \hspace{1cm} (4)

where \( D_{12} \) = mutual diffusion coefficient, \( \text{cm}^2/\text{sec} \)

\( p \) = pressure, \( \text{atm} \)

\( T \) = temperature, \( ^\circ \text{K} \)

\( T_{12}^* \) = \( kT/\epsilon_{12} \)

\( M_1, M_2 \) = molecular weights

The interaction parameters are defined by the combination rules

\[ \sigma_{12} = (\sigma_1 + \sigma_2)/2 \text{ and } \epsilon_{12} = \sqrt{\epsilon_1 \epsilon_2} \]

\( \sigma, \epsilon/\kappa \) = parameters in the intermolecular potential function, in \( \AA \) and \( ^\circ \text{K} \), respectively.

The collision integral, \( \Omega^{(1,1)*} \), which is a function of \( (kT/\epsilon) \), is tabulated\(^{25}\) for various intermolecular potentials.

If Equation (4) is applied to a one component system, the following expression is obtained for self diffusion:

\[ D_1^o = 32.027 \times 10^{-6} \left( \frac{\sqrt{T M}}{p \sigma^2 \Omega^{(1,1)*}_{11} (T^*)} \right) \]  \hspace{1cm} (5)

where \( D_1^o \) = self diffusion coefficient of specie (1) in pure (1), \( \text{cm}^2/\text{sec} \)
\[ \rho = \text{density, gm/cm}^3 \]

\[ (T^*) = kT/\epsilon \]

2.2 Self Diffusion in Dense Gases

Most of the theories of diffusion in dense gases do not give satisfactory results or, due to their complexity, cannot be solved for practical applications. A rigorous kinetic theory of dense gases has been developed by Irving and Kirkwood\textsuperscript{28} on the basis of the Liouville equation.

An equivalent derivation has also been given by Douglass \textit{et al.}\textsuperscript{10} and Longuet-Higgins and Pople,\textsuperscript{31} who expressed the self diffusion coefficient in terms of the velocity correlation function. The equation for diffusion was obtained by assuming an exponential decay of the velocity correlation function. This derivation is based on a hard-sphere model and is good to high densities. But it does not include intermolecular attractive forces. The result is:

\[ D_1^0 = \left( \frac{3}{4} \right) \left( \frac{nRT}{M} \right)^{1/2} \left[ \frac{(PV)}{(RT)} - 1 \right]^{-1} \]  \hspace{1cm} (6)

However, Equation (6) is inadequate for describing self diffusion behavior in real molecules due to the omission of the intermolecular attractive forces.
The development of semi-empirical relations for the prediction of self diffusion coefficients at high densities is justified by the absence of an applicable comprehensive theoretical treatment. Correlations based on the principle of corresponding states attempt to predict the properties of one substance from measured values of another. This principle has been applied in the study of self diffusion coefficients.

By rearranging Equation (5), which was developed from the kinetic theory of dilute gases, it can be seen that the diffusivity-density product is constant at constant temperature; therefore, the study of self-diffusion is simplified by examining the behavior of the product \((\rho D)\). The temperature dependence can be factored out by reducing \((\rho D)\) with respect to \((\rho D)_o\) --- the low density value given by Equation (5). On the basis of the Douglass equation for high densities [Equation (6)], the ratio \((\rho D)/(\rho D)_o\) is given by: 8

\[
\frac{(\rho D)}{(\rho D)_o} = K \rho \left[ \frac{pV}{RT} - 1 \right]^{-1}
\]  \hspace{1cm} (7)

where \(K\) is a constant. Replacing \((pV)/(RT)\) in Equation (7) with the volume virial expansion gives

\[
\frac{(\rho D)}{(\rho D)_o} = K \rho \left[ 1 + \frac{B}{V} + \frac{C}{V^2} + \ldots - 1 \right]^{-1}
\]
\[
= K \rho \left[ B \rho + C \rho^2 + \ldots \right]^{-1}
\]  \hspace{1cm} (8)
Inversion of the polynominal results in:

\[
\frac{\rho D}{(\rho D)\,_o} = K \left[ \text{constant terms} + \ldots \right] \tag{9}
\]

As the density is reduced, \((\rho D)\) approaches \((\rho D)\,_o\); i.e., as \(\rho \to 0\), \((\rho D)/(\rho D)\,_o \to 1\) and \((\rho b') \to 1\). This leads to the correlation

\[
\frac{\rho D}{(\rho D)\,_o} = 1 + b\,\rho + c\,\rho^2 + d\,\rho^3 + \ldots \tag{10}
\]

or, in terms of the reduced density

\[
\frac{\rho D}{(\rho D)\,_o} = 1 + b_r\,\rho_r + c_r\,\rho_r^2 + d_r\,\rho_r^3 + \ldots \tag{11}
\]

where \(\rho_r = \rho/\rho\,_c\).

While the dilute gas density-diffusivity product \((\rho D)\,_o\) depicts the effect of binary collisions only, the coefficients \(b_r, c_r, \text{etc.}\), account for the effect of ternary, quadruiple, and higher-order collisions. Detailed inspection\(^\text{3,17}\) of the quadruple interactions accounting for the coefficient \(c_r\) revealed both that this coefficient would be infinite and that higher-order terms would be divergent.

To alleviate the mathematical difficulty of an infinite coefficient, some investigators\(^\text{6,29}\) have suggested that \(c_r\) be replaced by \((c_r' \, \ln \rho_r + c_r'')\), which gives
\[
\frac{(\rho D)}{(\rho D)_o} = 1 + b_r \rho_r + c_r^1 \rho_r^2 \ln\rho_r + c_r^2 \rho_r^3 + \ldots
\]

No expressions have yet been suggested for higher order terms. The diffusion coefficient is no longer an analytic function of the density, but the first density correction \(b_r\) is the same as in Equation (11). Similar expressions have been obtained for thermal conductivity and viscosity. \(^3\)

Recently, Hanley et al. \(^20\) analyzed previously published experimental data on thermal conductivity and viscosity of several monatomic and diatomic gases as a function of density and temperature. The analysis covered temperatures from 20 to 350\(^o\)K and densities from 40 to 800 amagat. They found that the experimental data were more consistent, under the conditions investigated, with the logarithmic function terminated at the \(\rho_r^2\) term than with a cubic polynomial. However, they emphasize that this is not a proof that the logarithmic expansion is correct.

In this work the power series expansion given by Equation (11), terminated at the \(\rho_r^3\) term, was found to agree with the experimental data on self diffusion of CF\(_4\) with an average error of \(+6\%\).

2.3 **Self Diffusion in Binary Mixtures**

The self diffusion in a mixture is the diffusion of a
trace of a substance identical with one of the constituents in a system in equilibrium. Using a statistical mechanical approach, Bearman\(^1\) obtained relationships between self diffusion coefficients and mutual diffusion coefficients in a binary mixture. The two basic assumptions in the derivation are: The molecules have pairwise additive central forces dependent only upon the distance separating the centers of mass of the molecular pairs and not upon their relative orientations, and the frictional forces are linearly related to the relative velocities of the molecules. This leads to expressions for the ratios of the friction coefficients in terms of integrals of the distribution function perturbations. If it is also assumed that the volumes are additive and that the radial distribution functions are independent of composition, it is possible to evaluate the integrals and then establish the following relationships:

\[
D_1 V_1 = D_2 V_2 \quad , \quad D_1 = \left(D_{12}/\alpha_{12}\right) \left(V_2/V\right) \tag{13}
\]

where \(D_1\) and \(D_2\) are the self diffusion coefficients of each component in the mixture, \(D_{12}\) is the mutual diffusion coefficient at the same composition, \(V_1\) and \(V_2\) are the respective molar volumes, and \(V\) is the molar volume of the solution.

The coefficient \(D_1\) (or \(D_2\)) involves collisions between molecules of component 1 (or 2) with molecules of both components, while
the coefficient $D_{12}$ involves only collisions between unlike molecules. Also, it is possible to define mixture diffusion coefficients $D_{11}$ (or $D_{22}$), which are the effects only of collisions among molecules of component 1 (or 2). The factor $\alpha_{12}$ is defined in terms of the mole fraction, $x$, the chemical potential, $\mu$, and the activity, $a$, by:

\[
\alpha_{12} = \frac{x_1}{RT} \frac{d\mu_1}{dx_1} = \frac{x_2}{RT} \frac{d\mu_2}{dx_2}
\]

\[\mu_1 = \mu^0_1(T,P) + RT \ln a_1\]

\[\therefore \alpha_{12} = \frac{x_1}{a_1} \frac{da_1}{dx_1}\]  

(14)

(15)

(16)

The last assumptions regarding the additivity of the volumes and the composition independence of the radial distribution functions are closely satisfied by "regular" solutions, which are defined as having zero excess entropy; \(^{24,36}\) i.e., their entropy equals that of an ideal solution. In other words, they are mixtures for which the molecular motions are completely random and in which the entropy of mixing results only from the increase in randomness caused by mixing. This type of solution is usual for mixtures of non-polar, reasonably symmetrical and chemically similar molecules. Also, differences in molecular sizes do not contribute appreciably to the entropy of mixing. \(^{23}\) Since both $\text{CF}_4$ and $\text{CH}_4$ are non-polar and have a tetrahedral configuration, it would
be reasonable to assume that they form a regular solution. To verify this assumption, however, the excess entropy of the mixture was calculated. The calculation, which utilized entropy data reported by Douslin for the CF₄–CH₄ system, is given in detail in Appendix B. It was found that the relative excess entropy, $\frac{S^E}{\Delta S} \text{fig. 12}$, throughout the temperature and pressure ranges of this investigation does not exceed 2.5%.

A qualitative representation of the relationships between the mutual and self diffusion coefficients is given in Figure 1. It embodies the following phenomenological considerations:

- as $x_1 \to 0 \ (x_2 \to 1)$, $D_1 \to D_1^\infty \to D_{12}^\infty$, and $D_2 \to D_2^\infty$
- as $x_1 \to 1 \ (x_2 \to 0)$, $D_2 \to D_2^\infty \to D_{12}^\infty$, and $D_1 \to D_1^\infty$

where $D_1^\infty$ and $D_2^\infty$ are self diffusion coefficients at infinite dilution.

Since the volumes have been assumed to be additive; i.e., $V = x_1V_1 + x_2V_2$, Equation (13) can be used to derive the relationship between the mutual and self diffusion coefficients in the mixture:

$$D_{12} = \alpha_{12} \left( D_1 x_2 + D_2 x_1 \right) \tag{17}$$

The activities needed to calculate the factor $\alpha_{12}$ [Equation (16)] were derived from p-V-T data by Douslin of the methane-carbon
tetrafluoride system. Details are presented in Appendix A.

2.4 Theory of Diffusion Measurement by Pulsed NMR

The measurement of self diffusion coefficients by means of NMR is based on observation of the "spin echoes". These are radio frequency signals received from the sample under study which follow pulses of an applied oscillating magnetic field. The sample, which must contain atomic nuclei with non-zero spin, is also subjected to a constant magnetic field and a linear field gradient. The method, first discovered by Hahn, was later clarified and improved by Carr and Purcell, who introduced a modified sequence of the oscillating magnetic field pulses.

The NMR technique is based on the fact that the nuclei of many atoms possess an intrinsic angular momentum or spin. If such nuclei are subjected to a magnetic field they behave as small magnets with a specific magnetic moment. This nuclear magnetic moment, \( \vec{\mu} \), of a nucleus with angular momentum \( \vec{\alpha} \) is given by:

\[
\vec{\mu} = \gamma \vec{\alpha}
\] (18)

where \( \gamma \) is the gyromagnetic ratio.

In the absence of an external magnetic field the magnetic moments in a sample are randomly oriented. If now a magnetic
field, \( \vec{H}_z \), parallel to the z-axis, is applied to the sample, the magnetic moments will precess about the z-axis. The equation of motion of the nuclei is:

\[
\frac{d\vec{\mu}}{dt} = \gamma (\vec{\mu} \times \vec{H}_z)
\]  

(19)

The precession angular velocity, \( \vec{\omega} \), is in the negative sense for \( \gamma > 0 \), and is given by:

\[
\vec{\omega} = -\gamma \vec{H}_z
\]  

(20)

The nuclear moments in the sample give rise to a polarization field, which at equilibrium will be parallel to \( \vec{H}_z \). If the polarization field is tilted, it will precess about \( \vec{H}_z \) at angular velocity \( \vec{\omega} \). This rotating field will induce a voltage in a coil of wire wound around the sample, which can be amplified and detected.

The static field \( \vec{H}_z \), applied along the z-axis, is not perfectly homogeneous throughout the sample. Its magnitude \( H_z \) is distributed about some average value \( H_{z_0} \) with width \( \sigma \). Similarly, \( \omega \) is distributed about \(-\gamma H_{z_0}\) with width \( \gamma \sigma \). In a coordinate system rotating about the z-axis with velocity \(-\gamma H_{z_0}\), the distribution of precessional velocities is centered about zero.

An oscillating field \( \vec{H}_1 \) in the x-y plane is now applied
by means of a radio frequency pulse (A) through a coil perpendicular to $\vec{H}_Z$. This will have the effect of a magnetic vector $\vec{H}_1$ rotating in the x-y plane. If the radio frequency is \[- \gamma H_{Z_0}/(2\pi) \], then $\vec{H}_1$ will appear stationary in our rotating coordinate system. It is assumed that $\vec{H}_1$ lies along the x-axis.

By transforming to a rotating coordinate system we have eliminated the effect of $\vec{H}_Z$. But, because of the inhomogeneity of $H_z$, an incremental field, $\Delta \vec{H}_Z$, proportional to the field magnitude distribution width, $\sigma$, is still in effect. When $\vec{H}_1$ is applied, the nuclear magnetic moments will precess about the resultant vector of $\Delta \vec{H}_Z$ and $\vec{H}_1$. However, if the magnitude of $\vec{H}_1$ is large enough ($H_1 \gg \sigma$) and its duration, $\tau_w$, is short enough \[\tau_w \ll 1/(\gamma \sigma)\], the nuclear magnetic moments will precess approximately about the x-axis. If $H_1$ and $\tau_w$ are chosen such that \( \gamma H_1 \tau_w = \pi/2 \) radians, the magnetic moments will be left along the y-axis. After $H_1$ is turned off, half the magnetic moments fan out clockwise, the other half counter-clockwise in the x-y plane. This is because of the inhomogeneity in $H_z$. The net magnetic moment along the y-axis dies out after a time depending on the shape of the distribution of the magnitude of the magnetic field $H_z$. A highly homogeneous magnetic field will give slow decays and
a lesser homogeneous field will give more rapid decays. An observer in a non-rotating frame would see a net magnetic moment precessing about the z-axis and decaying in amplitude to zero. This is called the "free induction decay."

To produce a "spin echo," another $H_1$ pulse, twice as long as the first one is applied after a time $t$. This pulse (B) will rotate the nuclear magnetic moments through $180^\circ$ around the x-axis. Since the distribution of the precession frequencies is the same as before, the magnetic moments will converge on the minus y-axis. An observer in the stationary frame sees a rotating magnetic vector grow to a maximum and then die out again as the moments pass each other and diverge again. This is the "spin echo." Chains of echoes may be formed by repeating the $180^\circ$ pulse. The time between the $180^\circ$ pulses is commonly twice the time between the $90^\circ$ pulse and the first $180^\circ$ pulse. This pulse sequence is known as the Carr-Purcell sequence.

If a linear magnetic field gradient is superimposed on the field $\mathbf{H}_z$, the molecular diffusion affects the distribution-in-phase of the precessing moments. It can be shown that in the case of a two pulse sequence ($90^\circ$ and $180^\circ$), the amplitude of the echo will be:

$$A = A_o \exp \left( -\frac{t}{T_2} - \gamma^2 G^2 D t^3/12 \right)$$  \hspace{1cm} (21)
where $T_2$ is the spin-spin relaxation time and $t$ is the time between the pulses. The ratio of the amplitudes corresponding to the magnetic field gradient on to off will be:

$$ \frac{A_{\text{on}}}{A_{\text{off}}} = \exp \left(-\gamma^2 G^2 D \frac{t^3}{12}\right) $$

(22)

or

$$ \ln \left(\frac{A_{\text{on}}}{A_{\text{off}}}\right) = -\gamma^2 G^2 D \frac{t^3}{12} $$

(23)

This ratio is measured at several different time lapses, and the logarithm of the ratio is plotted against $t^3$. A straight line is obtained whose slope is

$$ \text{slope} = -\gamma^2 G^2 D/12 $$

(24)

Since $\gamma$ and $G$ are known quantities, $D$ can be calculated. Since the distribution-in-phase of the precessing moments is affected by the movement of the molecules resulting from all collisions, the coefficient $D$ measured by this method is actually $D_1^0$ in the case of the pure component (Section 2.1) and $D_1$ or $D_2$ in the mixture (Section 2.3).

If convection takes place within the sample, the spin echo will be affected. The presence of convection can be checked by two tests:

(1) The $\ln \left(\frac{A_{\text{on}}}{A_{\text{off}}}\right)$ used in the calculation would contain $t^2$ terms and, when plotted against $t^3$, would not give a straight line.

(2) The odd-numbered echoes in a Carr-Purcell sequence would be attenuated from the envelope given by the even-numbered echoes.
3. EXPERIMENTAL EQUIPMENT AND PROCEDURE

Self diffusion coefficients of methane and carbon tetra-fluoride were measured in the pure components and in an equi-molar mixture of the two components by the pulsed nuclear magnetic resonance technique. The sample container was carefully designed for precise control and measurement of both temperature and pressure. A single coil wound around the sample space served both for transmitting the pulses and for receiving the resulting signals. The pulses were generated by a spectrometer system, and the signals were amplified and displayed on an oscilloscope where they were photographed for measuring the amplitudes. The major vertical magnetic field, \( H_z \), was provided by a super-conducting magnet, and the field gradient by two opposing magnetic coils.

3.1 Spectrometer System

The pulsed NMR spectrometer used in this work is shown diagramatically in Figure 2. It was originally built for use in this laboratory by NMR Specialties, Inc., (Model PS-60). It was employed for measuring self diffusion coefficients of methane and was described in detail.\(^7\) The system consists of the following components:

A time mark generator (Tektronix Type RM 181), with a
frequency tolerance of 0.03%, provides basic time marks at intervals of 1, 10, 100, 1000, and 10,000 microseconds. The selected marker is fed into the programmer.

The programmer controls the lengths and separation of the radio frequency pulses that are produced by the RF unit. It consists of a binary scaler which provides time intervals that are powers of two times the basic interval from the time mark generator.

The pulse sequence used in the experiments consists of only two pulses, A (90°) and B (180°). The pulses are triggered automatically after the interval as selected by a third interval selector (the repetition rate switch). Alternatively, the pulses can be triggered manually by means of a reset button. The reset pulse causes the start of another pulse sequence.

The pulses from the programmer are fed into the RF unit, where they turn on amplifiers supplying 60 megacycles (mc). When the amplifiers are off, they block the passage of the 60 mc. The 60 mc sine wave is generated in the RF unit (NMR Specialties Model P-118A) by a continuously-running crystal oscillator.

The output from the second stage amplifier (gated power amplifier NMR Specialties Model P-103A) is transmitted (XMTR,
Figure 4) to the coil in the sample probe. The same coil also serves for receiving the signals (echoes) from the sample. It is made of three and one half turns of brass shim stock, 4 mm wide and 0.25 mm thick.

The receiver (RCVR, Figure 4) is a high-gain, tuned (60 mc) amplifier (NMR Specialties Model P-100A). It has a 90 decibel (db) voltage gain with an output of 5 volts rms. It is possible to reduce the gain by placing various amounts of attenuation in the circuit. In ordinary operation, the output is fed through a diode detector and low-pass filter for display on an oscilloscope. However, it is possible to pass the unfiltered output through a phase-sensitive detector, where it is mixed with a continuous 60 mc signal, thus giving improved signal-to-noise ratios.7

The oscilloscope used is a Tektronix Type 561 A with a Tektronix Type 3A1 vertical amplifier and a Tektronix Type 3B3 time base. The oscilloscope display is photographed with a Tektronix C-12 camera with a 1:0.85 lens and a projected graticule.

3.2 Magnet System

The homogeneous magnetic field is generated by a solenoid at liquid helium temperature. The coil becomes superconducting and the current circulates indefinitely.
The magnet system was made by Westinghouse Electric Corp., and the details are described in the Westinghouse Cryogenics Systems instruction manual. 45

A schematic diagram of the Dewar and solenoid is given in Figure 3. The vertical Dewar consists of a number of co-axial annular vessels for vacuum, liquid nitrogen, and liquid helium. It is fabricated from non-magnetic stainless steel, aluminum, and copper; and it is liquid nitrogen shielded. Unlike most Dewars, this Dewar has a coaxial central bore open at both ends. The probe containing the sample cell, discussed in Section 3.4, is placed in this central bore. The liquid helium storage capacity above the superconducting solenoid is 12.5 liters (0.39 liters/inch of height) and the liquid nitrogen capacity is 26.5 liters. The Dewar O.D. is 10" and the overall length is 60". The I.D. of the central bore is 1.71".

The solenoid windings are of 0.010" diameter niobium-25% zirconium wire. The magnet is rated at 25,000 gauss at a current of 16.3 amperes. In general, the magnet will produce a field given by the formula:

\[ H = 1534 \ I \]  

(25)

where \( H \) is the field in gauss and \( I \) is the current in amps.
A short length of superconducting wire is connected between the ends of the solenoid in close proximity to a heater. This enables the magnet to operate in either persistent or normal (non-superconducting) mode. The connecting wire is submerged, together with the solenoid, in the liquid helium. When the heater near the wire is off, both the solenoid and the wire are at superconducting temperature (about 4\(^\circ\)K). If the heater is turned on, the connecting wire becomes normal, and the current in the solenoid will be controlled by the power supply. After the current has been adjusted to give the desired field as governed by Equation (25), the heater is turned off and the current circulates indefinitely in the persistent mode in a closed circuit of the solenoid and wire.

The current from the power supply can be adjusted to a few parts per million using a fine adjustment potentiometer. Up to 25 amperes can be supplied at voltages less than 6 volts. The power supply also controls the current for the persistent switch heater. A current of only 24 milliamperes will drive the persistent switch normal.

3.3 Magnetic Field Gradient

In addition to the homogeneous magnetic field, a small linear field gradient superimposed on it is required for NMR diffusion measurements. The field gradient is produced by a
pair of coils outside the magnet Dewar and coaxial with the superconducting solenoid. The two coils are connected in series such that their magnetic fields are opposed. They are located such that the point midway between them, where the gradient is most linear, is at the same level as the middle of the solenoid, where the field is most homogeneous (Figure 3). Further vertical adjustment may be achieved by sliding the coils up and down, then setting them at the location of maximum linearity, as described in Section 3.6, by fastening screws on a clamping ring.

The field gradient coils are spaced 15 cm apart. Each coil has 18 turns of 14 gauge wire on a 30 cm diameter. The gradient was determined by measuring the field along the axis between the coils with a Hewlett-Packard flux gate magnetometer at different coil currents. The average value of 0.0888 gauss/cm per ampere was obtained at currents between 4 and 15 amperes.

The current was supplied to the coils by a Kepco constant current power supply and was measured by a Weston d.c. ammeter, accurate to within 0.5%.

3.4 Sample Probe

The sample fluid was contained in a cylindrical probe, which was constructed of non-magnetic beryllium-copper alloy
and was designed for working pressures up to 1000 atm. The electrical connections were dropped through the central bore of the magnet Dewar and attached to the probe. The probe was then inserted into the Dewar from the bottom, with the fluid connections for the probe emerging at the bottom of the Dewar. This probe insertion operation usually required two people.

A sketch of the sample probe is shown in Figure 4. Its chief components are the bomb and a beryllium-copper plug (0.93" diameter) which fills most of the bomb interior. The sample space was a horizontal 9/16" bore near the top of the plug, so located that the sample would be at the center of the superconducting solenoid, where the magnetic field is expected to be most homogeneous. Two semi-circular cross-sections of 1/8" diameter channels down opposite sides of the plug connected the sample space to the sample lines. The sample space was insulated from the plug by a glass tube, into which the RF coil was fitted. The glass tube had an I.D. of 11.3 mm, an O.D. of 13.9 mm, and a length of 19.2 mm. A small portion of loose glass wool was placed inside the RF coil, and glass wool was also placed along the fluid channels; the glass wool acted as a baffle to minimize convection. (See Chapter 4.)

One end of the RF coil was grounded to the bomb, and the other was connected to the outside leads through a tuning
circuit as shown in Figure 4.

The temperature was controlled by circulating a fluid through the spiral coolant channel in the bomb, as shown in Figure 4. The coolant fluid, isohexanes for temperatures below 0°C and silicone oil #7 for higher temperatures, was circulated through a reservoir bath where the temperature was controlled by a Bayley Instrument Co. (Model 250) proportional controller using a 100 watt heater. In addition, a 750 watt heater connected through a Powerstat was used to supply an adjustable amount of heat at a constant rate. For operation below room temperature, cooling was provided by circulating the refrigerant from a one-stage Freon-12 refrigerator through coils in the bath. The bath was equipped with a stirrer and a pump submerged in the fluid to circulate the coolant through the sample probe. The submersion of the pump in the bath eliminated lubrication and leak problems, and also helped minimize bath temperature fluctuations that could arise from heat losses if the pump were outside the bath.

The sample temperature was measured by means of a copper-constantan ten-junction thermopile placed in the vicinity of the coil. It was supplied by Science Products Corp. and complied with the NBS calibration as given in Appendix C. The thermopile EMF was measured with a Type K-3 Leeds & Northrup
Universal Potentiometer. It was possible to control the temperature and measure it to within ±0.02°C.

The sample probe was wrapped with an Armaflex foam rubber sheet for insulation. The exposed part below the Dewar was insulated with styrofoam cakes. The empty space in the central bore of the Dewar above the probe was filled with a 20" high layer of silica gel for moisture absorption and then a 25" layer of Vermiculite granules for insulation.

A Ruska Type high pressure, positive displacement pump was used to pressurize the system. A Heise Bourdon gauge was used to measure pressures above 2000 psi, with an accuracy within the reading error (±2 psi). Below 2000 psi, the pressure was measured with a Ruska Instrument Corporation (Type 2455) dead-weight gauge to within ±0.2 psi.

3.5 Sample Gases

The carbon tetrafluoride used in the experiments was supplied by E.I. du Pont de Nemours and Company, with a purity of 99.87%. The methane for the mixture was obtained from the Matheson Company with a specified purity of more than 99.9%. The equimolar mixture was prepared from these samples by the Matheson Company, whose gas analysis determined the methane composition in the mixture to be 0.494 mole fraction, with a tolerance of ±2% of this amount. The balance was assumed to
be carbon tetrafluoride. By measuring the exact density of the mixture, and using Douslin's data on the concentration dependence of the density, the mole fraction of CF$_4$ was found to be 0.506 mole fraction. This agrees with the above analysis.

3.6 Procedure

Self diffusion measurements were made for pure carbon tetrafluoride and for methane and carbon tetrafluoride in an approximately equimolar mixture of the two. The experimental procedure, after complete positioning of the apparatus components, electrical leads, and flow lines, is given below.

The liquid nitrogen and liquid helium chambers in the magnet Dewar were checked for dryness. Any water that might have condensed into them was syphoned out, and the chambers dried by flowing dry nitrogen gas through them.

For two days before taking data for each experimental run, the magnet Dewar was evacuated using a diffusion pump with a vacuum fore pump. The Dewar was then flushed with dry nitrogen and re-evacuated. The evacuation valve (Figure 3) was then closed and the diffusion pump turned off. Additional vacuum was later achieved through cryopumping resulting from the liquid helium cool-down.

The Dewar was pre-cooled by filling the helium chamber with liquid nitrogen from the supply tank. The solenoid was
kept immersed in the liquid nitrogen for about one hour. Then, for economy, the liquid nitrogen was transferred from the liquid helium chamber into the liquid nitrogen chamber. For this purpose a piece of rubber tubing was temporarily connected between the helium chamber top opening and the nitrogen inlet tube (Figure 3). The transfer was then carried out by slightly pressurizing the liquid helium chamber with helium gas. Additional liquid nitrogen was added to the nitrogen chamber until the level was above the liquid helium chamber. Make-up liquid nitrogen was added about twice every twenty-four hours.

Immediately after the helium chamber had been emptied of liquid nitrogen, liquid helium was transferred from a 100 liter storage tank into the helium chamber. This was done with a flexible bellows, stainless steel, vacuum insulated transfer tube. Before introducing it into the Dewar, the tube was cooled by allowing some helium to escape through it into the atmosphere, until liquid helium started coming out. Then it was quickly lowered into the Dewar fitting. The transfer was carried out at a moderate rate (about 1 psig excess pressure in the storage tank) over a period of about ten minutes. Occasionally, the helium storage tank needed pressurizing to re-establish the excess pressure. This was done by connecting it to a helium gas cylinder through a
pressure regulator. The transfer was continued until the liquid helium level (measured by means of a "bubbler") was about 15" above the solenoid. The transfer tube was then withdrawn from the Dewar and tank. Helium make-up was carried out about once a day, and a 100 liter liquid helium container lasted for about a week.

At the start of the pre-cooling of the Dewar, the temperature controller was turned on, the bath fluid was circulated through the probe, and the temperature was allowed to reach equilibrium. As time permitted, preliminary adjustments were made during the Dewar preparations. The controller was adjusted until the exact predetermined temperature was obtained. Along with the control heater, it was necessary to supply the bath with a constant rate of heating or cooling, depending on the temperature. This was achieved with a Powerstat control of resistance heating and/or refrigeration with a mechanical refrigerator.

In the meantime the spectrometer was turned on and the RF pulses were checked by displaying them on a fast scope (Tektronix Type 454). If the pulses were rectangular and their power level was satisfactory (about 600 volts rms at the output of the power amplifier), then the next step was to search for resonance.
A sample of gas was introduced into the probe. CF\textsubscript{4} at about 800 psi provided good conditions for finding resonance. The magnet power supply was then turned on. Resonance was first searched for by examining the free induction decay signal after a 90° pulse. Pulse B was turned off and pulse A was allowed to trigger at a repetition rate of about 2 pulses per second, with a width of about 10 \( \mu \text{sec} \). The oscilloscope was set at 0.2 volt/cm and 0.2 or 0.5 msec/cm and allowed to trigger internally.

The probe circuit was tuned with the tuning rod attached to a variable capacitor (Figures 3 and 4) to resonate at 60 mc. This was carried out by maximizing the output signal.

Next, the magnetic field was varied with the fine knob of the power supply until resonance was found. Close to resonance small wiggles appeared at the tail of the decaying signal. Fine adjustment gave rise to the resonance exponential-type decay. The magnet was then switched to the persistent mode.

The width of the 90° pulse (pulse A) was adjusted to its exact value which corresponds to the first maximum of the decay amplitude as the pulse width was increased. At this pulse width the oscillating magnetic field \( H_1 \) aligns the nuclear magnetic moments in the sample entirely along the
y-axis (Section 2.4). The oscilloscope was then set at a sweep rate of 2 msec/cm and pulse B (180°) was turned on, and its width adjusted to twice the A pulse width. At the correct width, pulse B rotates the magnetic moments through 180° around the x-axis. An echo appeared after a time interval equal to the separation between pulse A and pulse B. The exact width of the B pulse was adjusted to obtain the maximum echo amplitude. This same method was used to check and re-adjust the A pulse width.

The last step prior to an experimental run was the adjustment of the axial positions of the sample probe and the field gradient coils relative to the magnetic field for maximum field homogeneity and gradient linearity. It was necessary to move both positions simultaneously, upwards or downwards using a trial and error approach, until a configuration was reached where the echo amplitude was not affected by reversing the orientation of the field gradient. Furthermore, turning on the field gradient should not displace the signal from resonance.

About every other day during an experimental run it was necessary to re-check to determine that the magnetic field was still exactly at resonance. This was done by looking at the echo with the phase sensitive detector which beat the
nuclear precession frequency of the echo against the oscillator frequency. If these frequencies did not match precisely, adjustment of the magnetic field was required by the procedure discussed in Section 3.2. For normal operation, the signal was passed through the diode and filter, rather than through the phase-sensitive detector. (See Section 3.1.) With all the above adjustments performed, the system was ready for use.

To calculate a self diffusion coefficient, data of the ratio of the echo amplitude with and without a field gradient at different pulse separations, are needed as governed by Equation (23). Hence, photographs were taken of about ten different echoes for each set of conditions (temperature, pressure, and composition). The photographs were taken first with the gradient off. The photographs with the gradient on were taken for the gradient in each direction and the results averaged. After the completion of each experimental run, the amplitudes were read from the pictures, and the diffusion coefficient was calculated by means of a computer program from the slope of the straight line fit by the least-squares method to the plot of the logarithm of the amplitude ratios vs. $t^3$, the cube of the time between the pulses. The pulse separations were chosen such that the logarithm of the amplitude ratio varied between zero and one. A long enough
interval between photographs was left in order to allow for relaxation. An interval of about 30 sec was sufficient at high pressures; shorter intervals were sufficient at lower pressures.

Since in the mixture self diffusion coefficients had to be measured for both methane and carbon tetrafluoride, separate experimental runs were carried out with the magnetic field tuned for proton resonance and then for fluorine nuclei resonance. Measurements for mixture self diffusion were made first for methane. The magnitude of the field at 60 mc is 14,092 gauss for protons and 14,979 gauss for fluorine nuclei. These correspond to the power supply settings of 3;6;6;740 and 3;8;9;824, respectively.

For each temperature, the experiments were started at high pressures, then the sample gas was bled out to lower pressures, each time waiting to re-establish pressure and temperature equilibrium. Measurements were carried out down to the lowest densities possible, that would still produce a good signal-to-noise ratio. With the mixture it was not possible to go to as low a density as with the pure components because the signal was only about half as strong.
4. RESULTS AND DISCUSSION

The experimental data obtained in this work include self diffusion coefficients of carbon tetrafluoride in the pure component at temperatures of -30, -20, -10, 0, 25, 50, and 75°C for pressures ranging between 20 and 440 atm. The data also include self diffusion coefficients of methane and carbon tetrafluoride in an approximately equimolar mixture. These measurements were taken at temperatures of 0, 25, 50, and 75°C for pressures between 57 and 500 atm. Experimental results are given in Tables 1, 2, and 3, and are presented graphically as (ρD) vs. ρ in Figures 5 through 19.

The scope of measurements at the low density end was limited by the sensitivity of the apparatus where signals became too weak for accurate measurement. Consequently, it will be noted that the mixture data do not cover densities as low as those of the pure component, due to the fact that only about half of the molecules in the mixture contributed to the signal.

The densities of CF₄ and the mixture at 0°C and above were determined from the observed temperatures and pressures using p-V-T data from Douslin. The measurements in the mixture did not include temperatures below 0°C since no mixture p-V-T data were available below 0°C. Densities
of pure CF$_4$ at temperatures below 0°C were calculated from an equation of state by Martin and Bhada.\textsuperscript{33}

Early in the course of the experiments at low temperatures, particularly at temperatures near the critical, erratic and inconsistent behavior of the echo signals was observed which was suspected to be due to convection. This was remedied by improving the insulation of the sample probe and by placing a glass wool baffle (Section 3.4) in the sample cell. A test was then performed using the Carr-Purcell sequence (Section 2.4) and no convection or erratic signals could be detected.

4.1 Self Diffusion of Pure Carbon Tetrafluoride

The ($\rho D$) vs. log $\rho$ isotherms for pure CF$_4$ (Figures 5 through 11) show the expected constant ($\rho D$) at low densities, up to a reduced density of about 0.4, or a density of about 0.25 gm/cm$^3$. Then the density-diffusivity product begins decreasing sharply at densities typical of compressed fluids and liquids. No anomalies were observed, and the diffusivity varied smoothly throughout the density ranges investigated. The constant ($\rho D$) sections of the curves are relatively short since no data could be taken at reduced densities lower than 0.2, where the signal-to-noise ratios ceased to be large enough.
**Effect of Temperature:** Smoothed values of $(\rho D)$ from Figures 5 through 11 were used to prepare cross plots of log $(\rho D)$ at constant density vs. reciprocal temperature in Figures 20 through 23. Cross plots are not shown for the high density region, because the high sensitivity of $(\rho D)$ to the density causes a large scatter to appear. According to the Arrhenius relation, applicable to the constant $(\rho D)$ region,

$$D = A \exp \left[ \frac{E}{(RT)} \right]$$  \hspace{1cm} (26)

where $E$ is the activation energy and $A$ is a constant; a straight line is to be expected from the plot of log $D$ vs. reciprocal absolute temperature. At the lowest density of 0.1 gm/cm$^3$ (Figure 20), from the straight line shown, an activation energy $E = -480 \pm 5$ cal/mole was calculated. The straight line corresponding to $\rho = 0.2$ gm/cm$^3$ (Figure 21) has the same slope as that corresponding to 0.1 gm/cm$^3$, and thus would give the same activation energy.

**Force Constants:** The low density self diffusion coefficients were used to calculate intermolecular force constants $\epsilon/k$ and $\sigma$ of CF$_4$ for the Lennard-Jones (6-12) and the modified Buckingham (6-exp) potentials. For each of these potentials, and with the experimental values of the diffusivities at given temperatures, Equation (5), the Chapman-Enskog relation,
constitutes an equation in the two unknowns $\sigma$ and $\epsilon/k$, which may be represented by a curve in a $\sigma$ vs. $\epsilon/k$ plot. Any pair of parameters lying on the curve will satisfy the experimental data when the corresponding potential is used.

Now, if another property is used to calculate $\sigma$ and $\epsilon/k$, another curve will be generated which may intersect the diffusivity curve. The point of intersection of the two curves determines regionalized values of the parameters which satisfy both properties.

It is possible to generate two curves that do not intersect from the data on two properties for a particular intermolecular potential. There is always an experimental error associated with experimental data. The corresponding effect on the $\sigma$ vs. $\epsilon/k$ curve will be a band rather than a line for the relationship. Since this effect is present for both properties, the actual point of intersection will be an "area of intersection," whose size will be directly related to the magnitudes of the experimental error.

In this work the smoothed CF$_4$ self diffusion coefficients at $\rho = 0.1$ gm/cm$^3$ were used to determine one curve for the intermolecular force constants for each potential. The property used to determine the other curve was the second virial coefficient data obtained from the literature.\textsuperscript{11,13,32,38}
For the L-J (6-12) potential, values of $\sigma$ and $\varepsilon/k$ given below were deemed sufficient to determine the curve for the second virial coefficient:

<table>
<thead>
<tr>
<th>$\varepsilon/k$, $^\circ$K</th>
<th>$\sigma$, Å</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>152.5</td>
<td>4.70</td>
<td>32</td>
</tr>
<tr>
<td>152.1</td>
<td>4.70</td>
<td>13</td>
</tr>
<tr>
<td>151.5</td>
<td>4.744</td>
<td>38</td>
</tr>
</tbody>
</table>

For the 6-exp potential, second virial coefficient data by Douslin\textsuperscript{11} were used to calculate the curve with $\alpha = 15$. Standard tables\textsuperscript{25} provided the necessary functions for the two potentials. The experimental errors resulted, in both potentials, in a variation of about $\pm 2.5\%$ in the values of $\sigma$ calculated from the self diffusion coefficients, and a variation of about $\pm 1.5\%$ in the values of $\sigma$ calculated from the second virial coefficients. The calculated curves are presented in Figures 26 and 27 with the variation shown as light lines flanking each curve. The force constants lie within the area of intersection of the bands. The points of intersection of the curves themselves correspond to the following values of the force constants for $\text{CF}_4$:

<table>
<thead>
<tr>
<th></th>
<th>L-J (6-12)</th>
<th>6-exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$, Å</td>
<td>4.706</td>
<td>4.642</td>
</tr>
<tr>
<td>$\varepsilon/k$, $^\circ$K</td>
<td>152.1</td>
<td>170</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>-</td>
<td>15</td>
</tr>
</tbody>
</table>
It is better to determine the force constants from an equilibrium property and a transport property rather than from two transport properties. The reason is that, while an equilibrium curve intersects a transport curve at a well-defined point, two transport curves may overlap, or they may be parallel.\textsuperscript{27} Thus, the effect of the experimental error on the values of the force constants is less in the first case than in the second.

**Corresponding States Correlation:** The experimental data were used to determine the coefficients of the correlation given in Section 2.2 by Equations (10) and (11) using the least squares method. The correlation was terminated with the $\rho^3$ term. In the least squares calculations the experimental point, $T = -20^\circ C$, $\rho = 0.6915 \text{ gm/cm}^3$, had an error in $(\rho D)$ of 22\%, whereas the remainder of the data had errors of less than 15\%. The average error for this calculation was 7.2\%. When this point was omitted, the average error was 6.04\% and the maximum error for any point was 12\%. With this omission the values of the coefficients in the correlation are:

\begin{align*}
b &= -0.0417274 \\
c &= -0.265870 \\
d &= -0.0543426
\end{align*}

The units of $D$ are $\text{cm}^2/\text{sec}$ and those of $\rho$ are $\text{gm/cm}^3$. 
Written in terms of the reduced density, the coefficients are:

\[ b_r = -0.026263 \]
\[ c_r = -0.105323 \]
\[ d_r = -0.013549 \]

The curve in Figure 31 represents the correlation, while the points are the experimental data. Figure 32 compares the correlation in its reduced density form with data from the literature of the diffusivities of dense gases other than carbon tetrafluoride. In these comparisons the \((\rho D)_0\) value was taken from the sources referenced in Figure 32. The agreement appears to be better in the lower and higher density regions than in the intermediate densities.

Figure 32 also shows the correlation of Dawson et al.\(^8\) based on the methane self diffusion coefficients. The deviation between this correlation and the \(\text{CF}_4\) correlation of this work seems to be most pronounced at reduced densities somewhat above unity. Other data with low molecular weight compounds appear to agree better with the methane correlation than with the carbon tetrafluoride correlation. High molecular weight data were available only for the liquid state, and the self diffusion of liquid octane\(^{44}\) seems to agree better with the carbon tetrafluoride correlation, although at densities typical
of liquids the two correlations tend to coincide.

4.2 **Self Diffusion in an Equimolar Mixture of CH₄ and CF₄**

Self diffusion measurements of methane and carbon tetrafluoride in an approximately equimolar mixture of the two were carried out in separate runs for each component. The \((\rho D)\) vs. \(\log \rho\) isotherms, where \(\rho\) is the mixture density, for \(\text{CH}_4\) self diffusion coefficients in the mixture are shown in Figures 12 through 15. Similar isotherms for \(\text{CF}_4\) are shown in Figures 16 through 19. No data were taken for the mixture at temperatures below 0°C because no density data were available at those temperatures. In the region investigated, the density-diffusivity product appears to decrease less sharply with density than in the case of the pure component. No data were available at low enough densities to verify any constant \((\rho D)\) behavior.

**Effect of Temperature:** Smoothed values of \((\rho D)\) of methane from Figures 12 through 15 were used to prepare cross plots of \(\log (\rho D)\) at constant density vs. reciprocal absolute temperature in Figure 24. Cross plots are shown for methane self diffusion in the mixture for mixture densities of 0.3, 0.4, and 0.5 gm/cm³. Similar cross plots were prepared for \(\text{CF}_4\) self diffusion in the mixture from Figures 16 through 19 and are shown in Figure 25 for mixture densities of 0.2, 0.3, and
0.4 gm/cm$^3$. Unlike the lines drawn for pure CF$_4$ at low densities, these higher density lines are not straight. As mentioned above, no meaningful data could be taken for the mixture at lower densities.

**Calculation of $D_{12}$ from $D_1$ and $D_2$:** Equation (17) is used to calculate mutual diffusion coefficients in the equimolar mixture from the measured values of self diffusion coefficients of carbon tetrafluoride and methane. The factor $\alpha_{12}$ was computed according to Equation (16), with the activities derived from p-V-T data of Douslin.$^{12}$ Values of $\alpha_{12}$ are given in Figure A-5. The resulting curves of the mutual diffusion coefficients are plotted on Figure 28 as $(\rho D_{12})$ vs. $\rho$ of the mixture.

Following the arguments in Section 2.3, the diffusivities $D_1$, $D_2$, $D_{12}$, $D_1^0$, $D_2^0$, $D_1^\infty$, and $D_2^\infty$ are interrelated as described graphically in Figure 1. Experimental verification of these relationships would require diffusivities of the two components at infinite dilution and in the pure components, as well as self and mutual diffusion coefficients at several compositions. It was not possible to measure the infinite dilution diffusivities with the present NMR technique, and the only data available in the literature is one point at a low pressure.$^{27}$ The self diffusion data of methane,$^8$ together with the data obtained
in this work, can be used in a qualitative comparison of the various diffusivities. Table 4 presents a compilation of smoothed data at the 4 experimental temperatures for 5 selected pressures over the experimental range. Figure 29 is typical for all the data in Table 4. It will be noticed that at \( x_1 = 0.5 \), the mutual diffusion coefficient as calculated from Equation (16) is less than either self diffusion coefficient in the mixture. The correction factor \( \alpha_{12} \) which is appreciably less than unity is responsible for this behavior.

Although not enough data are available to show the composition dependence of the mutual diffusion coefficient, an approximate curve has been drawn through the three existing points (Figure 29). This curve has the same general form as that given by Woessner et al.\textsuperscript{46} for the composition dependence of \( D_{12} \) in the methane-propane system, calculated using the same theory as in this study. Figure 30 was prepared from the figure of Woessner et al.\textsuperscript{46} by changing the units for diffusion to those used in this study. It can be seen in both cases that the curve remains almost constant at high and medium concentrations of the heavy component, then rises sharply at high concentrations of the light component.
4.3 Sources of Error

The following are the uncertainties associated with each of the quantities measured for determining the self diffusion coefficient.

The temperature was measured to within $\pm 0.02^\circ C$ and the pressure above 2000 psi to within $\pm 0.2$ psi (Section 3.4). With these errors the density could be determined with an uncertainty of $\pm 0.3\%$. This is small compared to the uncertainty of the diffusion data.

The error in the field gradient results from the error in measuring the current and the error in the calibration of the gradient field. These amount to $\pm 1.5\%$; and, since the gradient is squared in the diffusion calculation, the resulting error will be $\pm 3\%$.

Most of the error was introduced by the echo amplitudes. In some of the experimental series of approximately 30 photo-records, 2 or 3 erratic responses were observed, which usually had to be discarded. The probable causes for the fluctuations are instabilities in the electronics and the background noise. The error due to noise increased at low densities where the signal was weak. When the signal-to-noise ratio became too small, no reliable measurements could be taken. Since one data point contained about ten echoes, part of the
echo error was averaged out by the least squares fit. The average maximum total uncertainty in a data point is thus ±6%.

4.4 Suggestions for Future Work

The results of this work did not complete the quantitative picture of the dependence of the various diffusion coefficients on the composition in the $\text{CF}_4$–$\text{CH}_4$ system. Lower density measurements could not be carried out, especially in the mixture, due to the limited sensitivity of the present equipment.

For future work with this apparatus it is recommended that diffusivities be measured in mixtures of several other compositions and at wider density ranges. This would require a still higher sensitivity. To achieve this and other improvements in the equipment the following modifications should be considered:

1) A new sample probe should be built with a larger sample space to produce stronger NMR signals.

2) An RF coil should be designed with a larger number of turns which would give a stronger RF field and would also be more sensitive for detecting the signal.

3) The building material close to the coil (the upper third of the plug, Figure 4) should not be metallic, to avoid distortion of the RF field. Plastic materials are also
unsuitable, because they contain hydrogen or fluorine atoms which might interfere with the NMR signal. Glass-like materials should be considered.

4) The magnetic field gradient coils should be modified to achieve better homogeneity of the gradient field.⁴⁰

5) A higher gain receiver should be used while minimizing the noise through better electrical shielding of the spectrometer.
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<td></td>
</tr>
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<td></td>
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<td>CH$_4$, D$_2$</td>
<td>CF$_4$, D$_1$</td>
<td>CH$_4$, D$_2$</td>
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<td>cm$^2$/sec</td>
<td>cm$^2$/sec</td>
<td>cm$^2$/sec</td>
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<td>cm$^2$/sec</td>
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<td></td>
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**T = 50°C**

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<td>cm$^2$/sec</td>
<td>cm$^2$/sec</td>
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<td></td>
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<td>Pure Component</td>
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<td>----------------</td>
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</tr>
<tr>
<td>atm</td>
<td>cm&lt;sup&gt;2&lt;/sup&gt;/sec</td>
<td>cm&lt;sup&gt;2&lt;/sup&gt;/sec</td>
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*Computed from correlation.*
FIGURE I - QUALITATIVE RELATIONSHIP BETWEEN MUTUAL AND SELF DIFFUSION COEFFICIENTS
FIGURE 2 - PULSED NMR SPECTROMETER BLOCK DIAGRAM
FIG. 3 - MAGNET DEWAR WITH SAMPLE CELL AND GRADIENT COILS IN PLACE
FIGURE 4 - SAMPLE PROBE
Figure 5 - Density-diffusivity product vs. density for pure CF₄ at 75°C
Figure 6 - Diffusivity Product vs. Density for Pure CF4 at 50°C

T = 50°C
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AT 25°C
FIGURE 8 - DENSITY-DIFFUSIVITY PRODUCT VS. DENSITY FOR PURE CF₄ AT 0°C
FIGURE 9 - DENSITY-DIFFUSIVITY PRODUCT VS. DENSITY FOR PURE CF$_4$
AT -10°C
Figure 10: Density-Diffusivity Product vs. Density for Pure CF₄ at -20°C
FIGURE II: DENSITY-DIFFUSIVITY PRODUCT VS. DENSITY FOR PURE CF₄ AT -30°C
Figure 12: Density-diffusivity product vs. density for CH₄ self diffusion in an equimolar mixture of CH₄ and CF₄ at 75°C.
Figure 13 - Density-Diffusivity Product vs. Density for CH₄ self diffusion in an equimolar mixture of CH₄ and CF₄ at 50 °C.
Figure 14 - Density-Diffusivity Product vs. Density for CH₄ Self Diffusion in an Equimolar Mixture of CH₄ and CF₄ at 25°C
$T = 0^\circ C$

**Figure 15** - Density-Diffusivity Product vs. Density for CH$_4$ Self Diffusion in an Equimolar Mixture of CH$_4$ and CF$_4$ at 0°C.
Figure 17 - Density-diffusivity product vs. density for CF$_4$ self diffusion in an equimolar mixture of CH$_4$ and CF$_4$ at 50°C.
FIGURE 16 - DENSITY-DIFFUSIVITY PRODUCT VS. DENSITY FOR CF₄ SELF DIFFUSION IN AN EQUIMOLAR MIXTURE OF CH₄ AND CF₄ AT 75 °C
FIGURE 18 - DENSITY-DIFFUSIVITY PRODUCT VS. DENSITY FOR CF₄ SELF DIFFUSION IN AN EQUIMOLAR MIXTURE OF CH₄ AND CF₄ AT 25°C
Fig. 20—Smoothed density-diffusivity product vs. temperature for pure CF₄.

\[ \rho = 0.1 \, \text{gm/cm}^3 \]
$\rho = 0.2 \text{ gm/cm}^3$

FIG. 21 - SMOOTHED DENSITY-DIFFUSIVITY PRODUCT VS. TEMPERATURE FOR PURE CF$_4$, $\rho = 0.2 \text{ gm/cm}^3$
$\rho = 0.25 \text{ gm/cm}^3$

FIG. 22 - SMOOTHED DENSITY-DIFFUSIVITY PRODUCT VS. TEMPERATURE FOR PURE CF$_4$, $\rho = 0.25 \text{ gm/cm}^3$
$\rho = 0.3 \text{ gm/cm}^3$

FIG. 23 - SMOOTHED DENSITY-DIFFUSIVITY PRODUCT VS. TEMPERATURE FOR PURE CF$_4$,
$\rho = 0.3 \text{ gm/cm}^3$
FIG. 24 - SMOOTHED DENSITY-DIFFUSIVITY PRODUCT VS. TEMPERATURE FOR CH₄ SELF DIFFUSION IN AN EQUIMOLAR MIXTURE OF CH₄ AND CF₄
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FIG. 26 - FORCE CONSTANTS OF L-J (6-12) POTENTIAL FOR CARBON TETRAFLUORIDE

FIG. 27 - FORCE CONSTANTS OF 6-EXP POTENTIAL FOR CARBON TETRAFLUORIDE
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FIGURE 30 - MUTUAL DIFFUSION COEFFICIENT IN CH₄ - C₃D₈ SYSTEM
(Woessner, et al.⁴⁶)
FIGURE 31 - CF₄ SELF DIFFUSION DATA PRESENTED IN REDUCED FORM SHOWING EXPERIMENTAL DATA AND CORRELATION
FIG. 32 - COMPARISON BETWEEN THIS CORRELATION AND OTHER DATA
APPENDIX A

Calculation of the Factor $\alpha_{12}$

The factor $\alpha_{12}$ which appears in Equation (17) is related to the chemical potential as follows: $^1, 2, 44, 46$

$$\alpha_{12} = \frac{x_1}{RT} \frac{d\mu_1}{dx_1} \quad (A-1)$$

where $\mu_1 = \mu^0_1 + RT \ln a_1$

Differentiating and substituting, one obtains:

$$\alpha_{12} = \frac{x_1}{a_1} \frac{d a_1}{dx_1} \quad (A-2)$$

The activities of the $\text{CF}_4 - \text{CH}_4$ mixture were calculated by two alternative methods from the thermodynamic properties of the mixture as reported by Douslin. $^{12}$ One method utilizes the volumetric data while the other utilizes Gibbs' excess free energy. The results of the two methods are in very good agreement.

**Method 1: Activities from Volumetric Data**

The pressure dependence $^{26}$ of the fugacity of component 1 in a mixture is given by the equation:

$$\left( \frac{\partial \ln f_1}{\partial p} \right)_T = \frac{\bar{V}_1}{RT} \quad (A-3)$$
where $f_1$ = fugacity of component 1 in the mixture.

$V_1$ = partial molal volume of component 1 (taken here as CF<sub>4</sub>). Integration gives:

$$\ln \frac{f_1}{x_p} = -\frac{1}{RT} \int_{p^*}^{p} \frac{1}{\bar{V}_1} \, dp$$  \hspace{1cm} (A-4)

where $p^*$ = low pressure at which $f_1^* = x_1 p^*$, and $\bar{V}_1$ = partial residual molal volume of component 1. Taking the fugacity at standard state $f_1^0$ as 1 atm, we have $a_1 = \frac{f_1}{f_1^0} = f_1$.

The calculation procedure is as follows:

1. Calculate $\alpha$ from p-V-T data for the mixture at different compositions from the equation

$$\alpha = \frac{RT}{p} - \frac{1}{\rho}$$

2. Calculate $\bar{V}_1$ from $\alpha$ by the method of tangent intercepts, which is illustrated in Figure A-1.

3. Calculate $a_1 = f_1$ from Equation (A-4) by graphical integration, which is illustrated in Figure A-2.

The results at $p = 120$ atm and $T = 75^\circ C$ are given in Table A-1.

**Method 2: Activities from Free Energies**

Douslin<sup>12</sup> reports the excess free energy for the CF<sub>4</sub>-CH<sub>4</sub> mixture:
\[ \Delta G = G - G^0 = RT \ln (\gamma_p) \quad (A-5) \]

where \( \gamma \) is the activity coefficient of the mixture.

The partial molal excess free energy is obtained from the molal excess free energy by the method of tangent intercepts (Figure A-3), then the activity \( \gamma \) is calculated from \( \Delta \tilde{G}_1 \).

\[ \Delta G_1 = RT \ln \frac{\frac{f_1}{f_1^0 x_1}}{x_1} \quad (A-6) \]

The results for \( p = 120 \) atm and \( T = 75^\circ C \) are given in Table A-2.

The activities were plotted vs. the mole fraction (as in Figure A-4) and \( \alpha_{12} \) was calculated graphically according to Equation (A-2). The values thus obtained are plotted in Figure (A-5).
### TABLE A-1

**ACTIVITIES OF CF₄ IN CH₄ - CF₄ MIXTURE**

*BY METHOD 1, p = 120 atm, T = 75°C*

<table>
<thead>
<tr>
<th>x₁</th>
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<th>0.50</th>
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<td>mole fraction CF₄</td>
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<table>
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<th>4.545</th>
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<tr>
<td>liter/gm mole</td>
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<table>
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|    |     |      |      |      |       |
### TABLE A-2

ACTIVITIES OF CF₄ IN CH₄ - CF₄ MIXTURE

BY METHOD 2, \( p = 120 \) atm, \( T = 75^\circ C \)

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<th>0.75</th>
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<td>cal/gm mole</td>
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<tr>
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<td>( a_1 )</td>
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FIG. A-1 RESIDUAL MOLAL VOLUME OF A CF₄ - CH₄ MIXTURE AT 75°C AND 120 ATM

T = 75°C

P = 120 ATM

INTERCEPTS CORRESPOND TO Χ₁
FIG. A-3 MOLAL EXCESS FREE ENERGY OF A CF$_4$-CH$_4$ MIXTURE AT 75 °C AND 120 ATM
FIG. A-4  ACTIVITY OF CF₄ IN A CF₄-CH₄ MIXTURE AT 75°C AND 120 ATM
FIG. A-5  THE FACTOR $\alpha_{12}$ FOR AN EQUIMOLAR MIXTURE OF CF$_4$ AND CH$_4$
APPENDIX B

Calculation of Excess Entropy of Mixing of Equimolar Mixture of Methane and Carbon Tetrafluoride

The entropy of an equimolar regular solution, $S_{12}$, is given by:

$$ S_{12} = 0.5 S_1 + 0.5 S_2 - R \ln 0.5 $$  \hspace{1cm} (B-1)

where $S_1$ and $S_2$ are the entropies of the pure components. Douslin$^{12}$ reports the values of $\Delta S_1$, $\Delta S_2$, and $\Delta S_{12}$ defined by:

$$ S_1 = S_1^0 - \Delta S_1 , \quad S_2 = S_2^0 - \Delta S_2 $$  \hspace{1cm} (B-2)

$$ S_{12} = S_{12}^0 - \Delta S_{12} $$  \hspace{1cm} (B-3)

where $S_1^0$, $S_2^0$, and $S_{12}^0$ are the standard state entropies. In the case of $S_1^0$ and $S_2^0$, the standard state is the pure component at one atmosphere. As to $S_{12}^0$, the standard state is the ideal gas mixture at one atmosphere. In an equimolar mixture $S_{12}^0$ is given by:

$$ S_{12}^0 = 0.5 S_1^0 + 0.5 S_2^0 - R \ln 0.5 $$  \hspace{1cm} (B-4)
Combining Equations (B-1) and (B-2), we have:

\[ (S_{12})_{\text{regular}} = 0.5 S_1^0 + 0.5 S_2^0 - 0.5 \Delta S_1 - 0.5 \Delta S_2 - R \ln 0.5 \]  

(B-5)

and from Equations (B-3) and (B-4)

\[ (S_{12})_{\text{real}} = 0.5 S_1^0 + 0.5 S_2^0 - R \ln 0.5 - \Delta S_{12} \]  

(B-6)

Hence, the excess entropy:

\[ S_{12}^E = (S_{12})_{\text{real}} - (S_{12})_{\text{regular}} = 0.5 \Delta S_1 + 0.5 \Delta S_2 - \Delta S_{12} \]  

(B-7)

The relative excess entropy of the \( \text{CF}_4 - \text{CH}_4 \) equimolar mixture, \( S_{12}^E / \Delta S_{12} \), was calculated at the temperatures and pressures covered by the self diffusion experiments. The results are shown in Figure B-1. The relative excess entropy does not exceed 2.5%.
FIG. B-1  RELATIVE EXCESS ENTROPY OF EQUIMOLAR CF₄ - CH₄ MIXTURE
APPENDIX C

Calibration of Copper-Constantan Thermopile

The copper-constantan thermopile used for temperature measurement in this work was supplied by Science Products Corporation, Dover, New Jersey, who certified that the 10-junction thermopile was prepared from the same spools of wire used in the preparation of a similar 25-junction thermopile calibrated for the Company by the National Bureau of Standards under NBS Test No. 18548. The NBS calibration was conducted with one end of the thermopile maintained at 0°C and the other end at the temperatures listed in Table C-1. The Company asserted that the same calibration would be determined regardless of the number of junctions in thermopiles from the same spools of wire. Table C-1 gives the data obtained by NBS on the 25-junction thermopile. This calibration was used in this work.

TABLE C-1

CALIBRATION OF THERMOPILE

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<td>- 50.00</td>
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<td>200.00</td>
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REFERENCES

REFERENCES (continued)


REFERENCES (continued)


REFERENCES (continued)


