

APPLICATIONS OF HYDRODYNAMIC THEORY TO
MULTICOMPONENT LIQUID DIFFUSION

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ABSTRACT

APPLICATIONS OF HYDRODYNAMIC THEORY TO MULTICOMPONENT LIQUID DIFFUSION

by Terence K. Kett

Hydrodynamic theory is applied to multicomponent diffusion of non-electrolytes. Generalized equations are derived for the flows, diffusion coefficients, and the phenomenological coefficients for non-associating systems. Similar equations are derived for associating systems but only for the simplest ternary cases where either one component associates with itself to form dimers or where two components associate with each other to form dimers. The theory indicates that under the condition of constant partial molar volumes, Onsager's reciprocal relations are valid for non-associating systems and for the associating systems with the additional assumption that the partial molar volume of the associated species is equal to the sum of the partial molar volumes of the species making up the dimer.

Four ternary systems are studied in this investigation. Experimental diffusion and phenomenological coefficients are obtained using a Mach-Zehnder interferometric technique for the systems dodecane-hexadecane-hexane and diethyl ether-chloroform-carbon tetrachloride. Experimental data for the systems toluene-chlorobenzene-bromobenzene and acetone-benzene-carbon tetrachloride

were taken from the literature. Diffusion and phenomenological coefficients for all four systems are also calculated from equations derived from hydrodynamic theory. The coefficients obtained by the two methods are compared and for the non-associating systems show excellent agreement. For the acetone-benzene-carbon tetrachloride system in which the actual associated species present is not clearly known, reasonable agreement among the diffusion coefficients was evident. The other associating system could not justifiably be compared since satisfactory activity data was not available.

Experimental evidence from this investigation verified within the limits of experimental accuracy that Onsager's reciprocal relations are valid for non-associating systems. In addition, it demonstrated the applicability of hydrodynamic theory to multicomponent diffusion. For associating systems where the degree of association is not clearly known, it indicated that hydrodynamic theory can be applied as a predictive theory in obtaining reasonable multicomponent diffusion coefficients. Based on this evidence, it can be concluded that hydrodynamic theory should play a major role in describing multicomponent diffusion.

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By
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To my Mother and Father

and

my wife, Betty

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INTRODUCTION

Throughout the last twenty years, interest has gradually increased in the area of multicomponent diffusion. There is voluminous literature available on binary diffusion that has built up since Fick²¹ presented his equation defining a diffusion coefficient. However, it was not until Onsager^{37,38} presented equations describing the flux of each component as the linear sum of every concentration gradient multiplied by a diffusion coefficient that any reasonable attempt to describe multicomponent liquid diffusion was made. Even so, no reasonable experimental work in this area was introduced until Baldwin, Dunlop, Fujita and Gosting^{3,22} in 1955 presented equations similar to Onsager's along with experimental techniques for obtaining the diffusion coefficients. This was certainly a major contribution in this area and furnished the impetus for renewed interest and consequent improvements in multicomponent diffusion.

Since that time Gosting, et. al.,^{19,21,23} have periodically developed improved experimental techniques with optical methods utilizing a Gouy interferometer. Burchard and Toor⁷ have also adapted the diaphragm cell method to obtain the multicomponent diffusion coefficients. With these methods, ternary diffusion data have become increasingly available enabling the study of both electrolytic and non-electrolytic multicomponent systems.^{7,12,18,19,22,35,41,44,45,49}

The equations presented by Baldwin, Dunlop and Gosting³ describing multicomponent liquid diffusion for an N component system are

$$J_i = - \sum_{j=1}^{N-1} D_{ij} \frac{\partial C_j}{\partial x} \quad i = 1, \dots, N - 1 \quad (1)$$

where J_i is the one-dimensional flux of component i in moles/cm.²/sec., D_{ij} is a diffusion coefficient in cm.²/sec., and $\partial C_j / \partial x$ is the concentration gradient of component j in the x direction in moles/cm.³/cm. Concentration gradients are used because they render themselves more easily to experimental measurement but in actuality the negative gradient of chemical potential is considered the driving force for the flows, J_i .

From irreversible thermodynamic^{9,13} considerations, the flows J_i are also related by the following expression

$$J_i = \sum_{j=1}^{N-1} L_{ij} Y_j \quad i = 1, \dots, N - 1 \quad (2)$$

where the L_{ij} are phenomenological coefficients. If in these expressions, both the fluxes J_i and the thermodynamic forces Y_j are independent and the sum of their products appears in the expression for the rate of entropy production then under these conditions,²⁸ the theory of irreversible thermodynamics says that the L_{ij} should satisfy the following relations, known as Onsager's reciprocal relations, namely,

$$L_{ij} = L_{ji} \quad (3)$$

A strong emphasis in most multicomponent diffusion studies has been placed in trying to verify these reciprocal relations. This verification has been conclusively shown in a number of cases such as

heat conduction in anisotropic crystals, thermoelectricity, electrokinetic effects, and e.m.f. and transference in electrolyte solutions.³⁴ However, this verification has not been shown in isothermal diffusion without some doubt because of the limitations in the experimental techniques employed.

The phenomenological coefficients, L_{ij} , can be related to the diffusion coefficients, D_{ij} , and therefore if the Onsager reciprocal relations can be verified, the experimental quantities necessary to describe diffusion will be reduced considerably. This explains the interest in the verification. Up till now, verification has only been possible by experimental means and; consequently, because the experimental techniques have been of limited accuracy, question concerning the verification has been justified.

In this research, hydrodynamic theory of Hartley and Crank²⁷ is extended to multicomponent diffusion in non-electrolytes. Generalized equations for the flows J_i are obtained in terms of concentration gradients, chemical potential gradients, and the forces Y_j . In addition, expressions for the phenomenological coefficients are obtained in terms of the diffusion coefficients, D_{ij} , and in terms of friction coefficients, σ_i . This theory shows that the reciprocal relations are valid for non-associating liquid systems and this is verified experimentally. In addition, experimental evidence is provided which supports the hydrodynamic theory.

THEORY

Hydrodynamic Model

The hydrodynamic theory of Hartley and Crank²⁷ considers molecular diffusion of liquid solutions in a closed container. They proposed that diffusion of a particular species could occur in two ways. First, by random molecular motion and secondly by flow of the entire medium itself. The latter Hartley and Crank called mass flow. Since these two methods of movement of a species can occur at the same time, both effects must be taken into account when experimentally studying the overall diffusion process.

The interpretation of molecular motion in a liquid can best be explained by assuming that the liquid molecules oscillate within a cage or hole formed by its neighboring molecules. The molecule performing this oscillatory motion, will occasionally acquire sufficient energy to overcome the potential energy barrier of this hole and migrate to another hole. Because of the energy required before a molecule can make this jump, typically less than 1% of the total number of molecules are undergoing this motion at any given time. It can be seen, however, that in this way diffusion of a species is occurring. This type of motion, often referred to as intrinsic diffusion, can occur regardless of whether concentration gradients exist or not. However, if a concentration gradient of a component

does exist, there will be a net movement of that component to reduce the gradient.

The other means by which a particular species can flow from one point in the container to another is by flow of the medium itself. It is easy to see in the case of a liquid solution flowing continuously through a container with open ends, such as a pipe, how a particular species can move from one point to another. It is simply carried along by the bulk solution itself. It was unfortunate that Hartley and Crank referred to a "mass flow" as contributing to the overall diffusion of a species since this implied the flow just described. Actually this bulk motion referred to by Hartley and Crank can occur in a closed container. In order to study molecular diffusion experimentally, the system is closed to enable free diffusion to take place.

To obtain an understanding of how a flow of the medium takes place in a closed container and how this contributes to the diffusion of a species, consider a coordinate fixed reference plane somewhere in the container. Now if there are different components in the solution, the molecules will have different sizes and shapes. Hence when a component of type "i" migrates by molecular motion across this reference plane in the closed volume, an increase in volume necessarily occurs unless there is a compensating flow back across the plane. This compensating flow is what Hartley and Crank called the bulk motion and what is referred to here as the flow of the medium.

Let us now look at the plane across which no net flow of material is occurring. In the case of a pure liquid where all the

species are alike, the velocity of this plane relative to fixed coordinates is zero. This follows because there would be just as many molecules diffusing by hole migration (intrinsically) across a coordinate-fixed plane in one direction as there would be in the opposite direction. Thus for a pure liquid, any coordinate-fixed plane satisfies the condition of no net flow across it.

The same analysis can be applied to a solution of uniform concentration. The concentration of any component would be the same on either side of a coordinate fixed plane located anywhere in the container. Since the concentration is the same on either side, the number of molecules of component "i" crossing the plane by hole migration would be the same as the number of component "i" molecules crossing in the opposite direction. The same applies to all the other components in the solution. Hence, the plane across which no net flow occurs corresponds to any coordinate fixed plane as long as the solution is uniform.

It follows that if the solution is not uniform, the velocity of the plane across which no net flow occurs will not be zero relative to fixed coordinates. In this case, the number of molecules of "i" crossing a coordinate-fixed plane by hole migration will not be equal to those migrating across in the opposite direction. The same follows for the other components. Since each component will generally have a different rate of migration, there will tend to be an accumulation on one side of the coordinate fixed plane unless there is a compensating flow back. Even if the molar volumes of each component are the same, there still will be build up if the rates are different. For nonuniform

solutions, only in the case of equal constant molar volumes and equal rates of hole migration will the velocity of the plane across which no net flow occurs be zero. In further discussions, this velocity with respect to fixed coordinates will be referred to as the velocity of the medium, $v_{m,c}$.

Hydrodynamic Flow Equations

If a molecule in solution is assumed to diffuse at a constant rate, the sum of the forces acting on it must be zero. The driving force per molecule and the resisting force per molecule must be equal and opposite. The question arises as to what are these forces.

It is generally accepted that the driving force for diffusion is the negative gradient of chemical potential, $-\nabla\mu_i$. Intuition says that a particular component will diffuse in such a direction as to reduce its gradient of concentration. In binary solutions this is the case, but in solutions of 3 or more components this does not always follow even though eventually the solution will become uniform throughout. For example, if the velocity of the medium is greater than the intrinsic rate of a particular component it is possible for the net flux of that component to be in the opposite direction to its negative gradient of concentration. Eventually the velocity of the medium slows down as the concentration gradients decrease and the intrinsic rate of the component surpasses it. Gibbs²⁴ has shown that at equilibrium the chemical potential should be the same throughout and hence a system not at equilibrium always tends to equalize the chemical potential. This

applies whether a particular component is present in more than one phase or whether it is present in various subsystems of one phase. The negative gradient of concentration, introduced by Fick²¹ in mathematically describing the diffusion process, is generally used in diffusion equations because it lends itself more easily to experimental measurement.

The resisting force for diffusion is a more controversial subject; however, certain conclusions regarding its description can be drawn. The overwhelming experimental evidence^{4,25,39,45} indicates that it is proportional to the viscosity of the medium. Attempts have also been made to correlate it to the radius or some power of the radius of the diffusing molecule.^{4,20,31,39,45} Although indeed it has been shown that the size of the molecule is a factor, no universal relation to the size has been found. In addition, Bidlack⁴ has shown that shape should be an important consideration. Based on these observations let us define the resisting force as follows

$$F_{i,r} = -f_i N \eta u_{i,m} = -\sigma_i \eta u_{i,m} \quad (4)$$

where $F_{i,r}$ is the resisting force per molecule of component i to intrinsic diffusion, f_i is a coefficient which is a function of the size and shape of the diffusing molecule and includes effects of the medium, η is the viscosity of the medium, N is Avogadro's number, $u_{i,m}$ is the velocity of species i with respect to the velocity of the medium. The proportionality factor, $\sigma_i = f_i N$ will be referred to as the friction coefficient of component i . The negative sign is a result of the velocity of i being in the opposite direction to the force.

The driving force for diffusion as discussed earlier is given by

$$F_{i,d} = -\nabla\mu_i \quad (5)$$

where $F_{i,d}$ is the driving force for intrinsic diffusion of i and $\nabla\mu_i$ is the gradient of chemical potential of component i . For one-dimensional diffusion in the x -direction, equation 5 becomes

$$F_{i,d} = -\frac{\partial\mu_i}{\partial x} \quad (6)$$

Since the driving force is equal and opposite to the resisting force,

$$-\frac{\partial\mu_i}{\partial x} = \sigma_i \eta u_{i,m} \quad (7)$$

Multiplying both sides by C_i , the concentration of i , and rearranging gives

$$J_i^m = C_i u_{i,m} = -\frac{C_i}{\sigma_i \eta} \frac{\partial\mu_i}{\partial x} \quad (8)$$

where J_i^m is the flux of component i with respect to the velocity of the medium (i.e., the intrinsic flux of i).

The chemical potential of the i^{th} constituent may be written as

$$\mu_i = \mu_i^0 + RT \ln a_i \quad (9)$$

where μ_i^0 is a function of T and P , R is the gas constant, and a_i is the activity of i . At constant T and P , substituting equation 9 into equation 8 yields

$$J_i^m = - \frac{C_i}{\sigma_i \eta} \left(\frac{\partial \ln a_i}{\partial x} \right)_{T,P} = - \frac{C_i RT}{\sigma_i \eta} \left(\frac{\partial \ln a_i}{\partial C_i} \right)_{T,P} \left(\frac{\partial C_i}{\partial x} \right)_{T,P} \quad (10)$$

$$J_i^m = - \frac{RT}{\sigma_i \eta} \left(\frac{\partial \ln a_i}{\partial C_i} \right)_{T,P} \left(\frac{\partial C_i}{\partial x} \right)_{T,P}$$

In order to obtain an expression for the velocity of the medium with respect to fixed coordinates, $v_{m,c}$, a volume flux balance across a coordinate-fixed plane is made. If we consider the case where the partial molar volumes of each component are assumed constant and the system is closed, then the volume flux across a coordinate fixed plane must be zero. In other words every time a certain volume of molecules diffuses across the plane, an equal volume of solution must come back in order to keep the total volume constant. Since the system is closed, the only way this could not happen is if the molar volumes changed. However they are assumed constant, thus the volume flux crossing the plane due to intrinsic diffusion plus the volume flux crossing this plane due to the flow of the medium must be zero. That is for an N-component system

$$\sum_{i=1}^N \bar{V}_i J_i^m + v_{m,c} = 0 \quad (11)$$

where \bar{V}_i is the partial molar volume. Since J_i^m has units of moles/cm.²/sec. and \bar{V}_i has units of cm.³/mole, notice that $v_{m,c}$ has units of velocity, cm./sec.

Equation 11 applies only for the case of constant partial molar volumes and a closed system. What about the case where the molar

volumes are not constant? Again, an expression for the velocity of the medium relative to fixed coordinates, $v_{m,c}$, can be obtained by looking at a volume flux balance across a coordinate fixed plane. In this case, however, there are three contributions. There is a flux of volume due to the intrinsic motion relative to the medium, there is a volume flux as a result of the flow of the medium, and there is a volume flux across this coordinate plane because the total volume is changing. Physically what happens is that a certain volume of material diffuses across this plane due to intrinsic motion. As a result of this, to relieve any hydrostatic pressure which might build up since the system is closed, the medium itself flows back. However, because of this diffusion, the concentrations have changed and thus if the molar volumes are functions of concentrations, the total volume may have changed thus producing a net volume flux across the coordinate fixed plane. The net volume flux relative to a fixed coordinate plane is given by $\sum_{i=1}^N \bar{V}_i J_i^m + v_{m,c}$ which does not equal zero in this case but rather

$$\sum_{i=1}^N \bar{V}_i J_i^m + v_{m,c} = v_{V,c} \quad (12)$$

where $v_{V,c}$ is the net volume flux relative to fixed coordinates resulting from the change in volume. It follows that $v_{V,c}$ is the velocity of the plane across which the net volume flux is zero.

From equations 11 and 12, expressions for $v_{m,c}$ can be obtained. These are

$$v_{m,c} = - \sum_{i=1}^N \bar{V}_i J_i^m \quad (13)$$

for the condition of constant molar volumes and

$$v_{m,c} = - \sum_{i=1}^N \bar{V}_i J_i^m + v_{V,c} \quad (14)$$

for the condition of varying molar volumes.

The diffusion process that is studied experimentally consists of both intrinsic diffusion and the flow of the medium. It is desirable then to obtain expressions for the overall diffusion flux relative to fixed coordinates of each component. These are obtained by summing both contributions. Hence

$$J_i^c = J_i^m + C_i v_{m,c} \quad (15)$$

where J_i^c is the overall flux of component i relative to fixed coordinates. Most experimental data reported in the literature are considered using overall fluxes relative to the velocity of a plane across which the net volume flux is zero, that is relative to $v_{V,c}$. Therefore

$$J_i^V = J_i^m + C_i (v_{m,c} - v_{V,c}) \quad (16)$$

where J_i^V is the total flux of i with respect to this volume flux plane.

From equation 14, it follows that equation 16 becomes

$$J_i^V = J_i^m - C_i \sum_{j=1}^N \bar{V}_j J_j^m \quad (17)$$

For the case of constant molar volumes, equation 16 becomes

$$J_i^V = J_i^m + C_i v_{m,c} \quad (18)$$

and substitution of equation 13 into equation 18 gives the same result as in the case of varying molar volumes. That is,

$$J_i^V = J_i^m - C_i \sum_{j=1}^N \bar{V}_j J_j^m \quad (17)$$

Substituting equation 8 into equation 17 gives J_i^V in the desired form.

$$J_i^V = - \frac{C_i}{\sigma_i \eta} \frac{\partial \mu_i}{\partial x} + \frac{C_i}{\eta} \sum_{j=1}^N \frac{C_j \bar{V}_j}{\sigma_j} \frac{\partial \mu_j}{\partial x} \quad (19)$$

Throughout the rest of this report, the superscript V will be dropped. All fluxes, unless specifically designated, will refer to the volume flux plane.

Current Flow Equations in Terms of Concentration Gradients

As mentioned earlier, the flow equations required to interpret diffusion experiments are generally written in terms of concentration gradients. For systems of two components, diffusion of either component is completely described by Fick's²¹ first law. For one-dimensional flow this law is

$$J_i = - D_{AB} \left(\frac{\partial C_i}{\partial x} \right)_t \quad i = A, B \quad (20)$$

In this equation, J_i is the flux of component i, and $(\partial C_i / \partial x)_t$ is the concentration gradient, at position x and time t. The same diffusion coefficient D_{AB} applies to both components.

In systems with three or more components, the flow of each component depends not only on its own concentration gradient but also on the concentration gradients of other components present. There is interaction of the flows. As a result, Onsager^{37,38} first proposed a description of this case by expressing the flow of each component as

the sum of every negative concentration gradient multiplied by a diffusion coefficient. Thus for a system of N components, his formulated equations were

$$J_i = - \sum_{j=1}^N D_{ij} \frac{\partial C_j}{\partial x} \quad i = 1, \dots, N \quad (21)$$

with N^2 diffusion coefficients, D_{ij} . He then showed that only $(N - 1)^2$ diffusion coefficients are necessary to describe the flows however.

This can easily be seen in the case of a constant volume system. It follows for a closed system that

$$\sum_{i=1}^N C_i \bar{V}_i = 1 \quad (22)$$

and if in addition the molar volumes are constant that

$$\sum_{i=1}^N \bar{V}_i J_i = 0 \quad (23)$$

Equation 22 follows from a material balance on the system with each $C_i \bar{V}_i$ factor representing the fraction of the total volume contributed by component i . It is not necessary that the partial molar volumes be constant for equation 22 to be valid. Equation 23 results from the assumption of a closed volume system with no volume change on mixing for which the net volume flux must be zero. From equation 22, the number of terms in each flux equation can be reduced from N to $N - 1$. Similarly with equation 23, one of the fluxes J_i can be eliminated from equation 21. Thus there are $N - 1$ independent fluxes and $N - 1$ independent concentration gradients for an N component system.

Baldwin, Dunlop, and Gosting³ therefore presented a set of flow equations for an N component system as follows

$$J_i = - \sum_{j=1}^N D_{ij} \left(\frac{\partial C_j}{\partial x} \right)_t \quad i = 1, \dots, N \quad (24)$$

This set of flow equations defines $(N - 1)^2$ diffusion coefficients, D_{ij} , for a system of N components, as required by Onsager's theory; however, these coefficients differ from those defined by Onsager in equation 21. They are related to certain combinations of Onsager's N^2 coefficients. These combinations can easily be found by applying equation 22 to eliminate the concentration gradient of the N^{th} component in equation 21, and then comparing corresponding coefficients of like concentration gradients in equation 24. These relationships, first obtained by Dole,¹⁴ are

$$D_{ij} = \mathcal{D}_{ij} - \frac{\bar{V}_j}{\bar{V}_N} \mathcal{D}_{iN} \quad i, j = 1, \dots, N - 1 \quad (25)$$

where the \mathcal{D}_{ij} are the Onsager diffusion coefficients.

The preferred equations for describing multicomponent diffusion are equations 24, since they are linearly independent and contain gradients of the measurable quantity, concentration, not chemical potential. Baldwin, Dunlop, Fujita, and Gosting^{3,22,23} in a series of articles have discussed in detail various methods of experimentally determining the diffusion coefficients, D_{ij} , for ternary systems. Their techniques involve interferometric methods and the utilization of resulting refractive index gradient curves. Some of these techniques are adapted in this laboratory and are discussed in the experimental section. Solution of the describing equations is

given in Appendix II. Burchard and Toor⁷ modified the diaphragm cell to experimentally measure the ternary diffusion coefficients.

Diffusion and Phenomenological Coefficient Expressions

Non-Associating Systems

It is desirable to obtain expressions for the D_{ij} in terms of the friction coefficients, σ_i . Since experimental values of the D_{ij} and the σ_i can be obtained, a check would then be available on the hydrodynamic theory. These expressions will now be derived here.

Diffusion Coefficient Expressions - It is convenient to first derive expressions for the D_{ij} in terms of the friction coefficients, σ_i , for the ternary case since the terms, equations, and algebraic manipulations are less involved. From this, the generalization to N components is easier to follow.

The flow equations for the ternary case from equation 24 are

$$\begin{aligned} J_1 &= - D_{11} \frac{\partial C_1}{\partial x} - D_{12} \frac{\partial C_2}{\partial x} \\ J_2 &= - D_{21} \frac{\partial C_1}{\partial x} - D_{22} \frac{\partial C_2}{\partial x} \end{aligned} \tag{26}$$

These equations are written in terms of concentration gradients and equations 19 in terms of chemical potential gradients. It would be desirable to have both sets of equations in terms of concentration gradients because then, provided the equations are independent, the coefficients of like terms could be equated.

For the ternary case, the flow equations for two of the components from equations 19 are

$$\begin{aligned}
J_1 &= - \frac{C_1}{\sigma_1 \eta} (1 - C_1 \bar{V}_1) \frac{\partial \mu_1}{\partial x} + \frac{C_1 C_2 \bar{V}_2}{\sigma_2 \eta} \frac{\partial \mu_2}{\partial x} + \frac{C_1 C_3 \bar{V}_3}{\sigma_3 \eta} \frac{\partial \mu_3}{\partial x} \\
J_2 &= \frac{C_1 C_2 \bar{V}_1}{\sigma_1 \eta} \frac{\partial \mu_1}{\partial x} - \frac{C_2}{\sigma_2 \eta} (1 - \bar{V}_2 C_2) \frac{\partial \mu_2}{\partial x} + \frac{C_2 C_3 \bar{V}_3}{\sigma_3 \eta} \frac{\partial \mu_3}{\partial x}
\end{aligned} \tag{27}$$

From the Gibbs-Duhem relation

$$C_1 \frac{\partial \mu_1}{\partial x} + C_2 \frac{\partial \mu_2}{\partial x} + C_3 \frac{\partial \mu_3}{\partial x} = 0 \tag{28}$$

Therefore,

$$\frac{\partial \mu_3}{\partial x} = - \frac{C_1}{C_3} \frac{\partial \mu_1}{\partial x} - \frac{C_2}{C_3} \frac{\partial \mu_2}{\partial x} \tag{29}$$

For the constant volume system, equation 23 gives

$$J_1 \bar{V}_1 + J_2 \bar{V}_2 + J_3 \bar{V}_3 = 0 \tag{30}$$

and therefore only two fluxes are independent. Substitution of equation 29 into equations 27 gives

$$\begin{aligned}
J_1 &= - \frac{C_1}{\eta} \left[\frac{(1 - \bar{V}_1 C_1)}{\sigma_1} + \frac{\bar{V}_3 C_1}{\sigma_3} \right] \frac{\partial \mu_1}{\partial x} - \frac{C_1 C_2}{\eta} \left(\frac{\bar{V}_3}{\sigma_3} - \frac{\bar{V}_2}{\sigma_2} \right) \frac{\partial \mu_2}{\partial x} \\
J_2 &= - \frac{C_1 C_2}{\eta} \left(\frac{\bar{V}_3}{\sigma_3} - \frac{\bar{V}_1}{\sigma_1} \right) \frac{\partial \mu_1}{\partial x} - \frac{C_2}{\eta} \left[\frac{(1 - \bar{V}_2 C_2)}{\sigma_2} + \frac{\bar{V}_3 C_2}{\sigma_3} \right] \frac{\partial \mu_2}{\partial x}
\end{aligned} \tag{31}$$

To convert the gradients of the chemical potential to gradients of concentration, use will be made of the identity

$$\frac{\partial f}{\partial t} = \sum_j \left(\frac{\partial f}{\partial x_j} \right)_x \left(\frac{\partial x_j}{\partial t_i} \right)_t \tag{32}$$

where $f = f(x_1, x_2, \dots, x_n)$

and $x_i = x_i(t_1, t_2, \dots, t_m)$

At constant T and P, for the ternary case

$$\begin{aligned}\mu_1 &= f(C_1, C_2) \\ \mu_2 &= f(C_1, C_2)\end{aligned}\tag{33}$$

The chemical potentials are functions of only two concentrations, C_1 and C_2 , because the third, C_3 , is not independent. This is evident from equation 22 which for the ternary case is

$$C_1 \bar{V}_1 + C_2 \bar{V}_2 + C_3 \bar{V}_3 = 1\tag{34}$$

Applying the identity equation 32 to equations 33 gives

$$\begin{aligned}\frac{\partial \mu_1}{\partial x} &= \left(\frac{\partial \mu_1}{\partial C_1} \right)_{C_2} \frac{\partial C_1}{\partial x} + \left(\frac{\partial \mu_1}{\partial C_2} \right)_{C_1} \frac{\partial C_2}{\partial x} \\ \frac{\partial \mu_2}{\partial x} &= \left(\frac{\partial \mu_2}{\partial C_1} \right)_{C_2} \frac{\partial C_1}{\partial x} + \left(\frac{\partial \mu_2}{\partial C_2} \right)_{C_1} \frac{\partial C_2}{\partial x}\end{aligned}\tag{35}$$

which when substituted into equations 31 and rearranged yields

$$\begin{aligned}J_1 &= - \left[\frac{C_1}{\eta} \left(\frac{(1 - \bar{V}_1 C_1)}{\sigma_1} + \frac{\bar{V}_3 C_1}{\sigma_3} \right) \left(\frac{\partial \mu_1}{\partial C_1} \right)_{C_2} + \frac{C_1 C_2}{\eta} \left(\frac{\bar{V}_3}{\sigma_3} - \frac{\bar{V}_2}{\sigma_2} \right) \left(\frac{\partial \mu_2}{\partial C_1} \right)_{C_2} \right] \frac{\partial C_1}{\partial x} \\ &\quad - \left[\frac{C_1}{\eta} \left(\frac{(1 - \bar{V}_1 C_1)}{\sigma_1} + \frac{\bar{V}_3 C_1}{\sigma_3} \right) \left(\frac{\partial \mu_1}{\partial C_2} \right)_{C_1} + \frac{C_1 C_2}{\eta} \left(\frac{\bar{V}_3}{\sigma_3} - \frac{\bar{V}_2}{\sigma_2} \right) \left(\frac{\partial \mu_2}{\partial C_2} \right)_{C_1} \right] \frac{\partial C_2}{\partial x}\end{aligned}\tag{36}$$

$$\begin{aligned}
J_2 = & - \left[\frac{c_1 c_2}{\eta} \left(\frac{\bar{v}_3}{\sigma_3} - \frac{\bar{v}_1}{\sigma_1} \right) \left(\frac{\partial \mu_1}{\partial c_1} \right)_{c_2} + \frac{c_2}{\eta} \left(\frac{(1 - \bar{v}_2 c_2)}{\sigma_2} + \frac{\bar{v}_3 c_2}{\sigma_3} \right) \left(\frac{\partial \mu_2}{\partial c_1} \right)_{c_2} \right] \frac{\partial c_1}{\partial x} \\
& - \left[\frac{c_1 c_2}{\eta} \left(\frac{\bar{v}_3}{\sigma_3} - \frac{\bar{v}_1}{\sigma_1} \right) \left(\frac{\partial \mu_1}{\partial c_2} \right)_{c_1} + \frac{c_2}{\eta} \left(\frac{(1 - \bar{v}_2 c_2)}{\sigma_2} + \frac{\bar{v}_3 c_2}{\sigma_3} \right) \left(\frac{\partial \mu_2}{\partial c_2} \right)_{c_1} \right] \frac{\partial c_2}{\partial x}
\end{aligned} \tag{36}$$

The chemical potential of the i^{th} constituent can be written as

$$\mu_i = \mu_i^{\circ} + RT \ln a_i \tag{37}$$

where μ_i° is a function of T and P, R is the gas constant, and a_i the activity. Therefore, at constant T and P

$$\begin{aligned}
\left(\frac{\partial \mu_1}{\partial c_1} \right)_{c_2} &= RT \left(\frac{\partial \ln a_1}{\partial c_1} \right)_{c_2} \\
\left(\frac{\partial \mu_1}{\partial c_2} \right)_{c_1} &= RT \left(\frac{\partial \ln a_1}{\partial c_2} \right)_{c_1} \\
\left(\frac{\partial \mu_2}{\partial c_1} \right)_{c_2} &= RT \left(\frac{\partial \ln a_2}{\partial c_1} \right)_{c_2} \\
\left(\frac{\partial \mu_2}{\partial c_2} \right)_{c_1} &= RT \left(\frac{\partial \ln a_2}{\partial c_2} \right)_{c_1}
\end{aligned} \tag{38}$$

Equating coefficients of the corresponding equations 26 and 36 and substituting equations 38 yields the desired expressions for the diffusion coefficients, D_{ij} .

$$\begin{aligned}
D_{11} &= \frac{RT}{\eta} \left[C_1 \left(\frac{(1 - \bar{V}_1 C_1)}{\sigma_1} + \frac{\bar{V}_3 C_1}{\sigma_3} \right) \left(\frac{\partial \ln a_1}{\partial C_1} \right)_{C_2} + C_1 C_2 \left(\frac{\bar{V}_3}{\sigma_3} - \frac{\bar{V}_2}{\sigma_2} \right) \left(\frac{\partial \ln a_2}{\partial C_1} \right)_{C_2} \right] \\
D_{12} &= \frac{RT}{\eta} \left[C_1 \left(\frac{(1 - \bar{V}_1 C_1)}{\sigma_1} + \frac{\bar{V}_3 C_1}{\sigma_3} \right) \left(\frac{\partial \ln a_1}{\partial C_2} \right)_{C_1} + C_1 C_2 \left(\frac{\bar{V}_3}{\sigma_3} - \frac{\bar{V}_2}{\sigma_2} \right) \left(\frac{\partial \ln a_2}{\partial C_2} \right)_{C_1} \right] \\
D_{21} &= \frac{RT}{\eta} \left[C_1 C_2 \left(\frac{\bar{V}_3}{\sigma_3} - \frac{\bar{V}_1}{\sigma_1} \right) \left(\frac{\partial \ln a_1}{\partial C_1} \right)_{C_2} + C_2 \left(\frac{(1 - \bar{V}_2 C_2)}{\sigma_2} + \frac{\bar{V}_3 C_2}{\sigma_3} \right) \left(\frac{\partial \ln a_2}{\partial C_1} \right)_{C_2} \right] \\
D_{22} &= \frac{RT}{\eta} \left[C_1 C_2 \left(\frac{\bar{V}_3}{\sigma_3} - \frac{\bar{V}_1}{\sigma_1} \right) \left(\frac{\partial \ln a_1}{\partial C_2} \right)_{C_1} + C_2 \left(\frac{(1 - \bar{V}_2 C_2)}{\sigma_2} + \frac{\bar{V}_3 C_2}{\sigma_3} \right) \left(\frac{\partial \ln a_2}{\partial C_2} \right)_{C_1} \right]
\end{aligned} \tag{39}$$

For the case of N components, the Gibbs-Duhem relation is

$$\sum_{i=1}^N C_i \frac{\partial \mu_i}{\partial x} = 0 \tag{40}$$

therefore

$$\frac{\partial \mu_N}{\partial x} = - \sum_{i=1}^{N-1} \frac{C_i}{C_N} \frac{\partial \mu_i}{\partial x} \tag{41}$$

The constant volume constraint is given by equation 23

$$\sum_{i=1}^N J_i \bar{V}_i = 0 \tag{23}$$

Thus, there are only N - 1 independent fluxes and N - 1 independent chemical potential gradients. Performing the same algebraic operations as was done for the ternary case gives the generalized flux equations

$$J_i = - \frac{C_i}{\eta} \left[\frac{(1 - \bar{V}_i C_i)}{\sigma_i} + \frac{C_i \bar{V}_N}{\sigma_N} \right] \frac{\partial \mu_i}{\partial x} - \frac{1}{\eta} \sum_{j \neq i}^{N-1} C_i C_j \left(\frac{\bar{V}_N}{\sigma_N} - \frac{\bar{V}_j}{\sigma_j} \right) \frac{\partial \mu_j}{\partial x} \quad (42)$$

$$i = 1, \dots, N-1$$

The same procedure of converting chemical potential gradients to concentration gradients has to be done so that the corresponding coefficients can be equated.

From equation 22 it is obvious that one of the concentrations, C_N , is not independent. Therefore

$$\mu_i = f(C_1, C_2, \dots, C_{N-1}) \quad i = 1, \dots, N \quad (43)$$

and

$$\frac{\partial \mu_i}{\partial x} = \sum_{j=1}^{N-1} \left(\frac{\partial \mu_i}{\partial C_j} \right)_{C_k} \frac{\partial C_j}{\partial x} = \sum_{j=1}^{N-1} \mu_{ij} \frac{\partial C_j}{\partial x} \quad (44)$$

$$i = 1, \dots, N-1$$

$$C_k = C_1 \dots C_{j-1} C_{j+1} \dots C_{N-1}$$

$$\text{where } \mu_{ij} = \left(\frac{\partial \mu_i}{\partial C_j} \right)_{C_k}$$

Substituting equation 44 into equation 42, collecting the coefficients of the $\partial C_j / \partial x$, and equating these with those in equation 24 gives the desired generalized expression for D_{ij} .

$$D_{ij} = \frac{C_i}{\eta} \left[\frac{(1 - \bar{V}_i C_i)}{\sigma_i} + \frac{C_i \bar{V}_N}{\sigma_N} \right] \mu_{ij} + \sum_{k \neq i}^{N-1} \frac{C_i C_k}{\eta} \left(\frac{\bar{V}_N}{\sigma_N} - \frac{\bar{V}_k}{\sigma_k} \right) \mu_{kj} \quad (45)$$

$$i, j = 1, \dots, N-1$$

Phenomenological Coefficient Expressions - It has been found in almost all non-equilibrium situations where thermodynamic variables have meaning that the thermodynamic theory of irreversible processes^{9,13} can be applied successfully. Briefly this theory states that (1) the rate at which entropy is produced within a system undergoing dissipative processes can be written by

$$T\dot{s} = \sum_i J_i X_i \quad (48)$$

where T is the absolute temperature, \dot{s} is the rate of change of entropy created within the system per unit volume; J_i is the generalized flow such as matter (moles \times cm.⁻² \times sec.⁻¹), electricity (faradays \times cm.⁻² \times sec.⁻¹) or heat (cal. \times cm.⁻² \times sec.⁻¹); and X_i are the generalized thermodynamic forces such as chemical potential gradients, temperature gradients, and e.m.f.'s. (2) The flows J_i are related linearly to the forces X_i by

$$J_i = \sum_j L_{ij} X_j \quad (49)$$

where L_{ij} are phenomenological coefficients related to electrical resistances, diffusion coefficients, or heat conductivities, etc.

(3) If the J_i and X_i are mutually independent, then the L_{ij} satisfy the following relations,²⁸ called the Onsager reciprocal relations, that is

$$L_{ij} = L_{ji} \quad (50)$$

More details are given by Miller.^{33,34}

It can be shown that the entropy production for ternary diffusion¹³ is

$$T\dot{s} = - J_1 \frac{\partial \mu_1}{\partial x} - J_2 \frac{\partial \mu_2}{\partial x} - J_3 \frac{\partial \mu_3}{\partial x} \quad (51)$$

However, only two of the fluxes and two of the chemical potential gradients are independent. This is evident because of equations 30 and 29. If these equations are used to eliminate J_3 and $\partial \mu_3 / \partial x$ in equation 51, one obtains

$$T\dot{s} = J_1 Y_1 + J_2 Y_2 \quad (52)$$

where

$$Y_i = - \sum_{j=1}^2 \left(\delta_{ij} + \frac{C_j \bar{V}_i}{C_3 \bar{V}_3} \right) \frac{\partial \mu_j}{\partial x} \quad i = 1, 2 \quad (53)$$

and δ_{ij} is the Kronecker delta. The linear relations according to irreversible thermodynamics are therefore

$$J_1 = L_{11} Y_1 + L_{12} Y_2 \quad (54)$$

$$J_2 = L_{21} Y_1 + L_{22} Y_2$$

and because the J_i as well as the Y_i are independent, the Onsager reciprocal relation $L_{12} = L_{21}$ should be valid. This analysis was first proposed by Miller³³ who from this derived a sufficient condition for which the reciprocal relations could be experimentally checked. This is presented later.

If the Y_i expressions are substituted into equation 52 and the resulting equations rearranged, one gets

$$J_1 = -(L_{11}^\alpha + L_{12}^\gamma) \frac{\partial \mu_1}{\partial x} - (L_{11}^\beta + L_{12}^\delta) \frac{\partial \mu_2}{\partial x} \quad (56)$$

$$J_2 = - (L_{21}^\alpha + L_{22}^\gamma) \frac{\partial \mu_1}{\partial x} - (L_{21}^\beta + L_{22}^\delta) \frac{\partial \mu_2}{\partial x} \quad (56)$$

where

$$\begin{aligned} \alpha &= 1 + \frac{C_1 \bar{V}_1}{C_3 \bar{V}_3} & \beta &= \frac{C_2 \bar{V}_1}{C_3 \bar{V}_3} \\ \gamma &= \frac{C_1 \bar{V}_2}{C_3 \bar{V}_3} & \delta &= 1 + \frac{C_2 \bar{V}_2}{C_3 \bar{V}_3} \end{aligned} \quad (57)$$

Now by equating like coefficients of the independent equations 31 and 56, four linear equations are obtained which can be solved for L_{11} , L_{12} , L_{21} and L_{22} . These equations are given below

$$\begin{aligned} L_{11}^\alpha + L_{12}^\gamma &= \frac{C_1}{\eta} \left[\frac{(1 - \bar{V}_1 C_1)}{\sigma_1} + \frac{\bar{V}_3 C_1}{\sigma_3} \right] \\ L_{11}^\beta + L_{12}^\delta &= \frac{C_1 C_2}{\eta} \left(\frac{\bar{V}_3}{\sigma_3} - \frac{\bar{V}_2}{\sigma_2} \right) \\ L_{21}^\alpha + L_{22}^\gamma &= \frac{C_1 C_2}{\eta} \left(\frac{\bar{V}_3}{\sigma_3} - \frac{\bar{V}_1}{\sigma_1} \right) \\ L_{21}^\beta + L_{22}^\delta &= \frac{C_2}{\eta} \left[\frac{(1 - \bar{V}_2 C_2)}{\sigma_2} + \frac{\bar{V}_3 C_2}{\sigma_3} \right] \end{aligned} \quad (58)$$

Since we are interested in checking L_{12} and L_{21} , only these phenomenological cross coefficients are obtained.

These are

$$L_{12} = \frac{\beta \frac{C_1}{\eta} \left[\frac{(1 - \bar{V}_1 C_1)}{\sigma_1} + \frac{\bar{V}_3 C_1}{\sigma_3} \right] - \alpha \frac{C_1 C_2}{\eta} \left(\frac{\bar{V}_3}{\sigma_3} - \frac{\bar{V}_2}{\sigma_2} \right)}{\gamma\beta - \alpha\delta} \quad (59)$$

$$\gamma\beta - \alpha\delta$$

$$L_{21} = \frac{\delta \frac{C_1 C_2}{\eta} \left(\frac{\bar{V}_3}{\sigma_3} - \frac{\bar{V}_1}{\sigma_1} \right) - \gamma \frac{C_2}{\eta} \left[\frac{(1 - \bar{V}_2 C_2)}{\sigma_2} + \frac{\bar{V}_3 C_2}{\sigma_3} \right]}{\alpha \delta - \gamma \beta} \quad (59)$$

From the definitions of α , β , γ , and δ and equation 34,

$$\gamma \beta - \alpha \delta = - \frac{1}{C_3 \bar{V}_3} \quad (60)$$

Using equations 34, 57, and 60 in equations 59 and rearranging the resulting expressions gives

$$L_{12} = L_{21} = - \frac{C_1 C_2 \bar{V}_1 (1 - \bar{V}_1 C_1)}{\sigma_1 \eta} - \frac{C_1 C_2 \bar{V}_2 (1 - \bar{V}_2 C_2)}{\sigma_2 \eta} + \frac{C_1 C_2 C_3 \bar{V}_3^2}{\sigma_3 \eta} \quad (61)$$

Thus, the hydrodynamic theory predicts that $L_{12} = L_{21}$ for non-associating ternary systems. It should be emphasized that in the development presented here the condition of constant molar volumes was imposed on the system. Hopefully this condition, although appearing necessary now, may be removed in some future work. An encouraging point of interest here is that no activity data are required in order to calculate the phenomenological coefficients.

Miller^{33,34} has obtained expressions for the ternary phenomenological coefficients, L_{ij} , in terms of the ternary diffusion coefficients, D_{ij} . The method involves using equations 35 to obtain equations 56 in terms of concentration gradients. The resulting equation is then compared to equation 26 giving expressions for the D_{ij} in terms of the L_{ij} . These equations are then solved for the L_{ij} in terms of the D_{ij} . These are

$$L_{12} = \frac{aD_{12} - cD_{11}}{ad - bc} \quad (62)$$

$$L_{21} = \frac{dD_{21} - bD_{22}}{ad - bc}$$

where

$$a = \left(1 + \frac{c_1 \bar{v}_1}{c_3 \bar{v}_3} \right) \left(\frac{\partial \mu_1}{\partial c_1} \right)_{c_2} + \frac{c_2 \bar{v}_1}{c_3 \bar{v}_3} \left(\frac{\partial \mu_2}{\partial c_1} \right)_{c_2} \quad (63)$$

$$b = \frac{c_1 \bar{v}_2}{c_3 \bar{v}_3} \left(\frac{\partial \mu_1}{\partial c_1} \right)_{c_2} + \left(1 + \frac{c_2 \bar{v}_2}{c_3 \bar{v}_3} \right) \left(\frac{\partial \mu_2}{\partial c_1} \right)_{c_2}$$

and c and d are the same respectively as a and b except that $(\partial/\partial c_1)_{c_2}$ is replaced by $(\partial/\partial c_2)_{c_1}$.

Substitution of the expressions derived for the diffusion coefficients in terms of the friction coefficients, σ_i , (equations 39) into equations 62 yields the same expressions obtained for the L_{ij} in terms of friction coefficients (equation 61). This should follow since the same principles are used. However, it does serve as a check on the derivations performed in both methods.

The usefulness of equation 62 is apparent since it provides a check on the hydrodynamic approach and on Onsager's reciprocal relations. The diffusion coefficients can be obtained experimentally by the methods of Fujita and Gosting^{22,23} and Burchard and Toor.³ From them, the phenomenological coefficients can be determined. Also, from equations 39 and equation 61, the diffusion coefficients and phenomenological

coefficients can be obtained using experimentally determined friction coefficients. Hence, by comparing the diffusion coefficients and by comparing the phenomenological coefficients, the hydrodynamic approach can be checked.

Also from equations 62, the condition from which the Onsager reciprocal relations can be verified is obtained. Simply by equating L_{12} and L_{21} , one obtains

$$aD_{12} + bD_{22} = cD_{11} + dD_{21} ; \quad ad - bc \neq 0 \quad (64)$$

This relation has been the basis up to this time for experimentally checking the Onsager reciprocal relations.

For the case of N components, expressions for the phenomenological coefficients can be obtained in a similar procedure to that used for the ternary. Extending the analysis to a system of N components and using equations 23 and 41 one obtains

$$J_i = \sum_{j=1}^{N-1} L_{ij} Y_j \quad i = 1, \dots, N-1 \quad (65)$$

where

$$Y_j = - \sum_{k=1}^{N-1} \left(\delta_{jk} + \frac{\bar{V}_j C_k}{\bar{V}_N C_N} \right) \frac{\partial \mu_k}{\partial x} \quad (66)$$

Substituting equation 66 into equation 65 and collecting the coefficients of the $(\partial \mu_k / \partial x)$'s, yields

$$J_i = \sum_{k=1}^{N-1} \sum_{j=1}^{N-1} L_{ij} \left(\delta_{jk} + \frac{\bar{V}_j C_k}{\bar{V}_N C_N} \right) \frac{\partial \mu_k}{\partial x} ; \quad i = 1, \dots, N-1 \quad (67)$$

Now, equating coefficients of equations 42 and 67 gives $(N - 1)^2$ linear equations with $(N - 1)^2$ unknowns, the L_{ij} . These equations are

$$\sum_{j=1}^{N-1} L_{ij} \left(\delta_{kj} + \frac{\bar{v}_j C_k}{\bar{v}_N C_N} \right) = \delta_{ik} \frac{C_k}{\sigma_k \eta} + \frac{C_i C_k}{\eta} \left(\frac{\bar{v}_N}{\sigma_N} - \frac{\bar{v}_k}{\sigma_k} \right); \quad i, k = 1, \dots, N-1 \quad (68)$$

Solving these equations for the cross-phenomenological coefficients (L_{ij} , $i \neq j$), one obtains

$$L_{ij} = L_{ji} = - \frac{C_i C_j}{\eta} \left[\frac{\bar{v}_i}{\sigma_i} (1 - \bar{v}_i C_i) + \frac{\bar{v}_j}{\sigma_j} (1 - \bar{v}_j C_j) \right] + \frac{1}{\eta} \sum_{\substack{k=1, \dots, N-1 \\ k \neq i, j}} \frac{C_i C_j C_k \bar{v}_k^2}{\sigma_k} \quad (69)$$

$i, j = 1, \dots, N-1; i \neq j$

By looking at equation 69 for the binary, ternary, etc., it is evident that a recursion formula exists. That is

$$L_{ij}^{M+1} = L_{ij}^M + \frac{C_i C_j C_{M+1} \bar{v}_{M+1}^2}{\sigma_{M+1} \eta} \quad (70)$$

where the superscripts M and $M+1$ refer to a system of M components and to the same system with one additional component labelled with the subscript $M+1$.

It can now be concluded that hydrodynamic theory predicts that the Onsager reciprocal relations should be valid for non-associating systems with any number of components with constant molar volumes. It should not be concluded that this implies that hydrodynamic theory only applies for the case of constant molar volumes nor should it be concluded that hydrodynamic theory is applicable only to non-associating systems.

Associating Systems

Non-associating systems comprise only a small percentage of the various systems encountered in industry or the laboratory. It would therefore be desirable to apply the hydrodynamic model to associating systems. The difficulty involved here is that the hydrodynamic model deals with distinct particles present in the solution. Intrinsic fluxes for a particular species are derived and the number of friction coefficients required is equal to the number of unlike molecules present. Thus, with non-associating systems, the number of intrinsic fluxes and friction coefficients is equal to the number of components added to form the system. If for example one component, call it A, associates with itself there will be considerably more unlike species present than if A does not associate (i.e., A-A, A-A-A, ..., A_n in addition to just A monomers). In other words, even though only three components are added there could be an infinite number of actual species present requiring an infinite number of flow equations each with an infinite number of terms.

It is only natural in trying to apply the hydrodynamic model to multicomponent associating systems that a simple system be chosen first. This would be a ternary system in which association occurs between two molecules so as to form only dimers, thus introducing four species instead of three. There are two ways in which this is possible: (1) if one component only associates with itself to form dimers and (2) if two components associate with each other, but not with themselves, to form dimers. Anderson^{1,2} successfully studied

these two cases for binary systems in which only dimerization is known to occur. Extension to ternary systems will now be given here.

Solutions Which Form a One:One Complex

Diffusion Coefficient Expressions - If the components added to form the solution are labelled A, B, and C, and A and B form the one:one complex, the four actual species present will be monomers of A, B, and C and the dimer A:B. Let us designate these actual species by 1, 2, 3, and 12 respectively.

From equations 8 and 14, the following relationship is true

$$v_{m,c} - v_{V,c} = \frac{1}{\eta} \left[\frac{C_1 \bar{V}_1}{\sigma_1} \frac{\partial \mu_1}{\partial x} + \frac{C_2 \bar{V}_2}{\sigma_2} \frac{\partial \mu_2}{\partial x} + \frac{C_3 \bar{V}_3}{\sigma_3} \frac{\partial \mu_3}{\partial x} + \frac{C_{12} \bar{V}_{12}}{\sigma_{12}} \frac{\partial \mu_{12}}{\partial x} \right] \quad (71)$$

The flux of component A relative to fixed coordinates is given by the sum of the contributions of the intrinsic fluxes of the monomer (1), complex (12), and the flow of the medium. Therefore, the flux J_A relative to the velocity of the plane across which the net volume flux is zero is

$$J_A = J_1^m + J_{12}^m + (C_1 + C_{12})(v_{m,c} - v_{V,c}) \quad (72)$$

Similarly

$$J_B = J_2^m + J_{12}^m + (C_2 + C_{12})(v_{m,c} - v_{V,c}) \quad (73)$$

From stoichiometry, it follows that

$$\begin{aligned} C_A &= C_1 + C_{12} \\ C_B &= C_2 + C_{12} \\ C_C &= C_3 \end{aligned} \quad (74)$$

where the subscripts A and B refer to the stoichiometric amounts of A and B added to the system. Therefore equations 72 and 73 become

$$\begin{aligned} J_A &= J_A^m + C_A(v_{m,c} - v_{V,c}) \\ J_B &= J_B^m + C_B(v_{m,c} - v_{V,c}) \end{aligned} \quad (75)$$

Substituting equation 71 into equations 75 and rearranging gives

$$\begin{aligned} J_A &= -\frac{C_1}{\sigma_1 \eta} (1 - \bar{V}_1 C_A) \frac{\partial \mu_1}{\partial x} + \frac{\bar{V}_2 C_2 C_A}{\sigma_2 \eta} \frac{\partial \mu_2}{\partial x} + \frac{\bar{V}_3 C_3 C_A}{\sigma_3 \eta} \frac{\partial \mu_3}{\partial x} - \frac{C_{12}}{\sigma_{12} \eta} (1 - \bar{V}_{12} C_A) \frac{\partial \mu_{12}}{\partial x} \\ J_B &= \frac{\bar{V}_1 C_1 C_B}{\sigma_1 \eta} \frac{\partial \mu_1}{\partial x} - \frac{C_2}{\sigma_2 \eta} (1 - \bar{V}_2 C_B) \frac{\partial \mu_2}{\partial x} + \frac{\bar{V}_3 C_3 C_B}{\sigma_3 \eta} \frac{\partial \mu_3}{\partial x} - \frac{C_{12}}{\sigma_{12} \eta} (1 - \bar{V}_{12} C_B) \frac{\partial \mu_{12}}{\partial x} \end{aligned} \quad (76)$$

If the associating reaction can be described by an equilibrium constant involving activities, one gets:

$$K = \frac{a_{12}}{a_1 a_2} \quad (77)$$

This combined with equation 37 can be used to obtain a relation between the gradients of the chemical potential. This relation is

$$\frac{\partial \mu_{12}}{\partial x} = \frac{\partial \mu_1}{\partial x} + \frac{\partial \mu_2}{\partial x} \quad (78)$$

Substituting this result into equations 76 gives

$$\begin{aligned} J_A &= - \left[\frac{C_1}{\sigma_1 \eta} (1 - \bar{V}_1 C_A) + \frac{C_{12}}{\sigma_{12} \eta} (1 - \bar{V}_{12} C_A) \right] \frac{\partial \mu_1}{\partial x} \\ &\quad - \left[\frac{C_{12}}{\sigma_{12} \eta} (1 - \bar{V}_{12} C_A) - \frac{\bar{V}_2 C_2 C_A}{\sigma_2 \eta} \right] \frac{\partial \mu_2}{\partial x} + \frac{\bar{V}_3 C_3 C_A}{\sigma_3 \eta} \frac{\partial \mu_3}{\partial x} \end{aligned} \quad (79)$$

$$\begin{aligned}
J_B = & - \left[\frac{C_{12}}{\sigma_{12}\eta} (1 - \bar{V}_{12}C_B) - \frac{\bar{V}_1 C_1 C_B}{\sigma_1 \eta} \right] \frac{\partial \mu_1}{\partial x} \\
& - \left[\frac{C_2}{\sigma_2 \eta} (1 - \bar{V}_2 C_B) + \frac{C_{12}}{\sigma_{12}\eta} (1 - \bar{V}_{12}C_B) \right] \frac{\partial \mu_2}{\partial x} + \frac{\bar{V}_3 C_3 C_B}{\sigma_3 \eta} \frac{\partial \mu_3}{\partial x}
\end{aligned} \tag{79}$$

From the Gibbs-Duhem relation we can obtain

$$C_1 \frac{\partial \mu_1}{\partial x} + C_2 \frac{\partial \mu_2}{\partial x} + C_3 \frac{\partial \mu_3}{\partial x} + C_{12} \frac{\partial \mu_{12}}{\partial x} = 0 \tag{80}$$

Using equations 74 and 78, this becomes

$$C_A \frac{\partial \mu_1}{\partial x} + C_B \frac{\partial \mu_2}{\partial x} + C_C \frac{\partial \mu_3}{\partial x} = 0 \tag{81}$$

With this relation, $\partial \mu_3 / \partial x$ can be eliminated from equations 79 to give

$$\begin{aligned}
J_A = & - \left[\frac{C_1}{\sigma_1 \eta} (1 - \bar{V}_1 C_A) + \frac{C_{12}}{\sigma_{12}\eta} (1 - \bar{V}_{12}C_A) + \frac{\bar{V}_3 C_A^2}{\sigma_3 \eta} \right] \frac{\partial \mu_1}{\partial x} \\
& - \left[\frac{-\bar{V}_2 C_2 C_A}{\sigma_2 \eta} + \frac{C_{12}}{\sigma_{12}\eta} (1 - \bar{V}_{12}C_A) + \frac{\bar{V}_3 C_A C_B}{\sigma_3 \eta} \right] \frac{\partial \mu_2}{\partial x} \\
J_B = & - \left[-\frac{\bar{V}_1 C_1 C_B}{\sigma_1 \eta} + \frac{C_{12}}{\sigma_{12}\eta} (1 - \bar{V}_{12}C_B) + \frac{\bar{V}_3 C_A C_B}{\sigma_3 \eta} \right] \frac{\partial \mu_1}{\partial x} \\
& - \left[\frac{C_2}{\sigma_2 \eta} (1 - \bar{V}_2 C_B) + \frac{C_{12}}{\sigma_{12}\eta} (1 - \bar{V}_{12}C_B) + \frac{\bar{V}_3 C_B^2}{\sigma_3 \eta} \right] \frac{\partial \mu_2}{\partial x}
\end{aligned} \tag{82}$$

It is desirable at this point to obtain expressions for the D_{ij} in terms of the friction coefficients. Therefore, the chemical potential gradients of the actual species must be converted to gradients of the

stoichiometric concentrations in order to equate corresponding coefficients.

From equation 22, we have

$$C_1 \bar{V}_1 + C_2 \bar{V}_2 + C_3 \bar{V}_3 + C_{12} \bar{V}_{12} = 1 \quad (83)$$

Therefore at constant T and P,

$$\begin{aligned} \mu_1 &= f(C_1, C_2, C_{12}) \\ \mu_2 &= f(C_1, C_2, C_{12}) \end{aligned} \quad (84)$$

However, from the stoichiometric relations, equations 74, equations 84 can be written

$$\begin{aligned} \mu_1 &= f(C_A, C_B) \\ \mu_2 &= f(C_A, C_B) \end{aligned} \quad (85)$$

Hence

$$\begin{aligned} \frac{\partial \mu_1}{\partial x} &= \left(\frac{\partial \mu_1}{\partial C_A} \right)_{C_B} \frac{\partial C_A}{\partial x} + \left(\frac{\partial \mu_1}{\partial C_B} \right)_{C_A} \frac{\partial C_B}{\partial x} \\ \frac{\partial \mu_2}{\partial x} &= \left(\frac{\partial \mu_2}{\partial C_A} \right)_{C_B} \frac{\partial C_A}{\partial x} + \left(\frac{\partial \mu_2}{\partial C_B} \right)_{C_A} \frac{\partial C_B}{\partial x} \end{aligned} \quad (86)$$

For this system, equation 24 is

$$\begin{aligned} J_A &= -D_{AA} \frac{\partial C_A}{\partial x} - D_{AB} \frac{\partial C_B}{\partial x} \\ J_B &= -D_{BA} \frac{\partial C_A}{\partial x} - D_{BB} \frac{\partial C_B}{\partial x} \end{aligned} \quad (87)$$

Substituting equations 86 into equations 82 and equating corresponding coefficients with equations 87 gives the desired results.

$$\begin{aligned}
D_{AA} &= \left[\frac{C_1}{\sigma_1 \eta} (1 - \bar{V}_1 C_A) + \frac{C_{12}}{\sigma_{12} \eta} (1 - \bar{V}_{12} C_A) + \frac{\bar{V}_3 C_A^2}{\sigma_3 \eta} \right] \left(\frac{\partial \mu_1}{\partial C_A} \right)_{C_B} \\
&\quad + \left[-\frac{\bar{V}_2 C_2 C_A}{\sigma_2 \eta} + \frac{C_{12}}{\sigma_{12} \eta} (1 - \bar{V}_{12} C_A) + \frac{\bar{V}_3 C_A C_B}{\sigma_3 \eta} \right] \left(\frac{\partial \mu_2}{\partial C_A} \right)_{C_B} \\
D_{AB} &= \left[\frac{C_1}{\sigma_1 \eta} (1 - \bar{V}_1 C_A) + \frac{C_{12}}{\sigma_{12} \eta} (1 - \bar{V}_{12} C_A) + \frac{\bar{V}_3 C_A^2}{\sigma_3 \eta} \right] \left(\frac{\partial \mu_1}{\partial C_B} \right)_{C_A} \\
&\quad + \left[-\frac{\bar{V}_2 C_2 C_A}{\sigma_2 \eta} + \frac{C_{12}}{\sigma_{12} \eta} (1 - \bar{V}_{12} C_A) + \frac{\bar{V}_3 C_A C_B}{\sigma_3 \eta} \right] \left(\frac{\partial \mu_2}{\partial C_B} \right)_{C_A} \\
D_{BA} &= \left[-\frac{\bar{V}_1 C_1 C_B}{\sigma_1 \eta} + \frac{C_{12}}{\sigma_{12} \eta} (1 - \bar{V}_{12} C_B) + \frac{\bar{V}_3 C_A C_B}{\sigma_3 \eta} \right] \left(\frac{\partial \mu_1}{\partial C_A} \right)_{C_B} \\
&\quad + \left[\frac{C_2}{\sigma_2 \eta} (1 - \bar{V}_2 C_B) + \frac{C_{12}}{\sigma_{12} \eta} (1 - \bar{V}_{12} C_B) + \frac{\bar{V}_3 C_B^2}{\sigma_3 \eta} \right] \left(\frac{\partial \mu_2}{\partial C_A} \right)_{C_B} \\
D_{BB} &= \left[-\frac{\bar{V}_1 C_1 C_B}{\sigma_1 \eta} + \frac{C_{12}}{\sigma_{12} \eta} (1 - \bar{V}_{12} C_B) + \frac{\bar{V}_3 C_A C_B}{\sigma_3 \eta} \right] \left(\frac{\partial \mu_1}{\partial C_B} \right)_{C_A} \\
&\quad + \left[\frac{C_2}{\sigma_2 \eta} (1 - \bar{V}_2 C_B) + \frac{C_{12}}{\sigma_{12} \eta} (1 - \bar{V}_{12} C_B) + \frac{\bar{V}_3 C_B^2}{\sigma_3 \eta} \right] \left(\frac{\partial \mu_2}{\partial C_B} \right)_{C_A}
\end{aligned} \tag{88}$$

It may appear that a considerable problem has been introduced here because of expressions like $(\partial\mu_1/\partial C_A)_{C_B}$. This would appear to involve obtaining activity data of the actual species as a function of the stoichiometric quantities which could be a considerable problem. However, it has been shown by Nikol'skii³⁶ in general and by Prigogine and Defay⁴⁰ for a two-component mixture with association that the chemical potentials of a component and the monomer of that component are equal. They observed that this result depends in no way on any assumption about the manner in which association occurs. Furthermore, it is valid for both associated solutions and associated gases and only depends upon the assumption that the complexes are in thermodynamic equilibrium with each other. Nikol'skii further stated that it is valid for any equilibrium gaseous or liquid mixtures with any reactions occurring in them. It follows from this that

$$\begin{aligned}\mu_1 &= \mu_A \\ \mu_2 &= \mu_B\end{aligned}\tag{89}$$

It should be recalled that from the Gibbs-Duhem equation one can obtain

$$C_A \frac{\partial\mu_A}{\partial x} + C_B \frac{\partial\mu_B}{\partial x} + C_C \frac{\partial\mu_C}{\partial x} = 0\tag{90}$$

In order for both equations 81 and 90 to be valid, the chemical potential of the species must equal the chemical potential of the component.

Activity Expressions Based on the Chemical Model - If activity data are not available we are still faced with the problem of finding values for expressions of the type $(\partial\mu_i/\partial C_j)_{C_i}$. For associating

systems, Dolezalek^{15,16} first proposed the chemical model which states that non-ideality in associated systems results purely from the complexing to form other species. In other words, the actual species present in the solution form an ideal solution. This of course is only an approximation but a reasonable one if the non-ideality is mostly caused by the association. For the system under consideration here, the monomers 1, 2, and 3 and the dimer 12 should therefore form an ideal solution according to the model. Furthermore, if it is assumed that the associated species does not exist in the vapor and the vapor is an ideal gas, then Raoult's law for species 1 says that

$$p_1 = X_1 P_1 = a_A P_A \quad (91)$$

where p_1 is the partial pressure, P_1 the vapor pressure of the pure species, and a_A the activity. Since P_1 and P_A are identical, a_A must equal X_1 , the mole fraction of monomer of A. This analysis can be extended to the other species, therefore the following set of relations relating stoichiometric and true quantities must hold

$$\begin{aligned} a_A &= a_1 = X_1 = \gamma_A X_A \\ a_B &= a_2 = X_2 = \gamma_B X_B \\ a_C &= a_3 = X_3 = \gamma_C X_C \\ a_{12} &= X_{12} \end{aligned} \quad (92)$$

By obtaining expressions for the true mole fractions in terms of the stoichiometric quantities, values for $(\partial \mu_1 / \partial C_A)_{C_B} = (\partial \mu_A / \partial C_A)_{C_B}$ etc., can be obtained. Details of this are given in Appendix III.

Since pure A and pure B have no associated species present and are assumed to exist only in the monomer form, reasonable values for \bar{V}_1 and \bar{V}_2 are the respective partial molar volumes of the pure components A and B.

Phenomenological Coefficient Expressions - It is of interest to check on the Onsager reciprocal relations for this simplest associative case. The rate of entropy production is given by

$$T\dot{s} = -J_1 \frac{\partial \mu_1}{\partial x} - J_2 \frac{\partial \mu_2}{\partial x} - J_3 \frac{\partial \mu_3}{\partial x} - J_{12} \frac{\partial \mu_{12}}{\partial x} \quad (93)$$

Utilizing equations 78 and 81, equation 93 becomes

$$T\dot{s} = - (J_1 + J_{12} - \frac{C_A}{C_C} J_3) \frac{\partial \mu_1}{\partial x} - (J_2 + J_{12} - \frac{C_B}{C_C} J_3) \frac{\partial \mu_2}{\partial x} \quad (94)$$

For this system, equation 23 is

$$J_1 \bar{V}_1 + J_2 \bar{V}_2 + J_3 \bar{V}_3 + J_{12} \bar{V}_{12} = 0 \quad (95)$$

Eliminating J_3 from equation 94 with equation 95 and rearranging gives

$$\begin{aligned} T\dot{s} = & -J_1 \left[\frac{\partial \mu_1}{\partial x} + \frac{C_A \bar{V}_1}{C_C \bar{V}_3} \frac{\partial \mu_1}{\partial x} + \frac{C_B \bar{V}_1}{C_C \bar{V}_3} \frac{\partial \mu_2}{\partial x} \right] - J_2 \left[\frac{\partial \mu_2}{\partial x} + \frac{C_B \bar{V}_2}{C_C \bar{V}_3} \frac{\partial \mu_2}{\partial x} + \frac{C_A \bar{V}_2}{C_C \bar{V}_3} \frac{\partial \mu_1}{\partial x} \right] \\ & - J_3 \left[\frac{\partial \mu_1}{\partial x} + \frac{C_A \bar{V}_{12}}{C_C \bar{V}_3} \frac{\partial \mu_1}{\partial x} + \frac{\partial \mu_2}{\partial x} + \frac{C_B \bar{V}_{12}}{C_C \bar{V}_3} \frac{\partial \mu_2}{\partial x} \right] \end{aligned} \quad (96)$$

From stoichiometry

$$\begin{aligned} J_1 &= J_A - J_{12} \\ J_2 &= J_B - J_{12} \end{aligned} \quad (97)$$

Substituting equations 97 into equation 96 and rearranging yields

$$\begin{aligned}
 T\dot{s} = & -J_A \left[\left(1 + \frac{C_A \bar{V}_1}{C_C \bar{V}_3} \right) \frac{\partial \mu_1}{\partial x} + \frac{C_B \bar{V}_1}{C_C \bar{V}_3} \frac{\partial \mu_2}{\partial x} \right] - J_B \left[\left(1 + \frac{C_B \bar{V}_2}{C_C \bar{V}_3} \right) \frac{\partial \mu_2}{\partial x} + \frac{C_A \bar{V}_2}{C_C \bar{V}_3} \frac{\partial \mu_1}{\partial x} \right] \\
 & - J_{12} \left[\frac{C_A}{C_C \bar{V}_3} (-\bar{V}_1 - \bar{V}_2 + \bar{V}_{12}) \frac{\partial \mu_1}{\partial x} + \frac{C_B}{C_C \bar{V}_3} (-\bar{V}_1 - \bar{V}_2 + \bar{V}_{12}) \frac{\partial \mu_2}{\partial x} \right] \quad (98)
 \end{aligned}$$

Now a reasonable assumption in accordance with the previous assumption of constant volume is that $\bar{V}_{12} = \bar{V}_1 + \bar{V}_2$. If this is the case, equation 98 becomes

$$T\dot{s} = -J_A \left[\left(1 + \frac{C_A \bar{V}_1}{C_C \bar{V}_3} \right) \frac{\partial \mu_1}{\partial x} + \frac{C_B \bar{V}_1}{C_C \bar{V}_3} \frac{\partial \mu_2}{\partial x} \right] - J_B \left[\frac{C_A \bar{V}_2}{C_C \bar{V}_3} \frac{\partial \mu_1}{\partial x} + \left(1 + \frac{C_B \bar{V}_2}{C_C \bar{V}_3} \right) \frac{\partial \mu_2}{\partial x} \right] \quad (99)$$

From the postulate of irreversible thermodynamics, the following equations are valid.

$$\begin{aligned}
 J_A = & -L_{AA} \left[\left(1 + \frac{C_A \bar{V}_1}{C_C \bar{V}_3} \right) \frac{\partial \mu_1}{\partial x} + \frac{C_B \bar{V}_1}{C_C \bar{V}_3} \frac{\partial \mu_2}{\partial x} \right] - L_{AB} \left[\frac{C_A \bar{V}_2}{C_C \bar{V}_3} \frac{\partial \mu_1}{\partial x} + \left(1 + \frac{C_B \bar{V}_2}{C_C \bar{V}_3} \right) \frac{\partial \mu_2}{\partial x} \right] \\
 J_B = & -L_{BA} \left[\left(1 + \frac{C_A \bar{V}_1}{C_C \bar{V}_3} \right) \frac{\partial \mu_1}{\partial x} + \frac{C_B \bar{V}_1}{C_C \bar{V}_3} \frac{\partial \mu_2}{\partial x} \right] - L_{BB} \left[\frac{C_A \bar{V}_2}{C_C \bar{V}_3} \frac{\partial \mu_1}{\partial x} + \left(1 + \frac{C_B \bar{V}_2}{C_C \bar{V}_3} \right) \frac{\partial \mu_2}{\partial x} \right] \quad (100)
 \end{aligned}$$

and

$$L_{AB} = L_{BA} \quad (101)$$

Carrying out the multiplications in equations 100 and equating corresponding coefficients with those in equations 82 and then solving the resulting equations for L_{AB} and L_{BA} gives

$$\begin{aligned}
L_{AB} = & \frac{\left[\frac{c_1}{\sigma_1 \eta} (1 - \bar{v}_1 c_A) + \frac{c_{12}}{\sigma_{12} \eta} (1 - \bar{v}_{12} c_A) + \frac{\bar{v}_3 c_A^2}{\sigma_3 \eta} \right] \frac{c_B \bar{v}_1}{c_C \bar{v}_3}}{- \frac{1}{c_C \bar{v}_3}} \\
& - \frac{\left[- \frac{\bar{v}_2 c_2 c_A}{\sigma_2 \eta} + \frac{c_{12}}{\sigma_{12} \eta} (1 - \bar{v}_{12} c_A) + \frac{\bar{v}_3 c_A c_B}{\sigma_3 \eta} \right] \left(1 + \frac{c_A \bar{v}_1}{c_C \bar{v}_3} \right)}{- \frac{1}{c_C \bar{v}_3}} \\
& (102) \\
L_{BA} = & \frac{\left[- \frac{\bar{v}_1 c_1 c_B}{\sigma_1 \eta} + \frac{c_{12} (1 - \bar{v}_{12} c_B)}{\sigma_{12} \eta} + \frac{\bar{v}_3 c_A c_B}{\sigma_3 \eta} \right] \left(1 + \frac{c_B \bar{v}_2}{c_C \bar{v}_3} \right)}{\frac{1}{c_C \bar{v}_3}} \\
& - \frac{\left[\frac{c_2}{\sigma_2 \eta} (1 - \bar{v}_2 c_B) + \frac{c_{12}}{\sigma_{12} \eta} (1 - \bar{v}_{12} c_B) + \frac{\bar{v}_3 c_B^2}{\sigma_3 \eta} \right] \frac{c_A \bar{v}_2}{c_C \bar{v}_3}}{\frac{1}{c_C \bar{v}_3}}
\end{aligned}$$

Simplification of these expressions gives

$$\begin{aligned}
L_{AB} = L_{BA} = & - \frac{c_1 c_B \bar{v}_1}{\sigma_1 \eta} (1 - \bar{v}_1 c_A) - \frac{c_2 c_A \bar{v}_2}{\sigma_2 \eta} (1 - \bar{v}_2 c_B) \\
& - \frac{c_A c_B \bar{v}_3}{\sigma_3 \eta} (-1 + \bar{v}_1 c_A + \bar{v}_2 c_B) + \frac{c_{12}}{\sigma_{12} \eta} (1 - \bar{v}_{12} c_A) (1 - \bar{v}_{12} c_B) \\
& (103)
\end{aligned}$$

Thus, if the assumption that $\bar{v}_{12} = \bar{v}_1 + \bar{v}_2$ is true, then the hydrodynamic model for associating systems in which a 12 dimer is formed predicts that Onsager's reciprocal relations are valid. It was

attempted to demonstrate the validity of the reciprocal relations for this associating system without using the above assumption, but such attempts were unsuccessful.

Solutions in Which One Component Dimerizes

The method of obtaining the flow equations, diffusion coefficients, and phenomenological coefficients is the same as that just discussed for the case of a one:one complex. For this reason, only the important equations will be given here. The subscripts 1, 2, 3 and 11 will refer to the monomers of components A, B, and C and the A-A complex respectively.

Diffusion Coefficient Expressions - Again, from equations 8 and 14, we have that

$$v_{m,c} - v_{V,c} = \frac{1}{\eta} \left[\frac{C_1 \bar{V}_1}{\sigma_1} \frac{\partial \mu_1}{\partial x} + \frac{C_2 \bar{V}_2}{\sigma_2} \frac{\partial \mu_2}{\partial x} + \frac{C_3 \bar{V}_3}{\sigma_3} \frac{\partial \mu_3}{\partial x} + \frac{C_{11} \bar{V}_{11}}{\sigma_{11}} \frac{\partial \mu_{11}}{\partial x} \right] \quad (104)$$

The flows are given by

$$J_A = J_1^m + 2J_{11}^m + C_A (v_{m,c} - v_{V,c}) \quad (105)$$

$$J_B = J_2^m + C_B (v_{m,c} - v_{V,c})$$

From stoichiometry, it follows that

$$\begin{aligned} C_A &= C_1 + 2C_{11} \\ C_B &= C_2 \\ C_C &= C_3 \end{aligned} \quad (106)$$

The association reaction can be described by an equilibrium constant as follows

$$K = \frac{a_{11}}{a_1^2} \quad (107)$$

From the defining equation for the chemical potential (equation 37) and equation 107, a relation between the gradients of chemical potential can be obtained. This is

$$\frac{\partial \mu_{11}}{\partial x} = 2 \frac{\partial \mu_1}{\partial x} \quad (108)$$

Also the Gibbs-Duhem relation and the stoichiometric relations combined with equation 108 give

$$C_A \frac{\partial \mu_1}{\partial x} + C_B \frac{\partial \mu_2}{\partial x} + C_C \frac{\partial \mu_3}{\partial x} = 0 \quad (109)$$

Using equations 104, 105, 108 and 109, the flow equations become

$$\begin{aligned} J_A = & - \left[\frac{C_1}{\sigma_1 \eta} (1 - C_A \bar{V}_1) + \frac{2C_{11}}{\sigma_{11} \eta} (2 - C_A \bar{V}_{11}) + \frac{C_A^2 \bar{V}_3}{\sigma_3 \eta} \right] \frac{\partial \mu_1}{\partial x} \\ & - \left[- \frac{C_B C_A \bar{V}_2}{\sigma_2 \eta} + \frac{C_A C_B \bar{V}_3}{\sigma_3 \eta} \right] \frac{\partial \mu_2}{\partial x} \end{aligned} \quad (110)$$

$$\begin{aligned} J_B = & - \left[- \frac{C_1 C_B \bar{V}_1}{\sigma_1 \eta} - \frac{2C_{11} C_B \bar{V}_{11}}{\sigma_{11} \eta} + \frac{C_B C_A \bar{V}_3}{\sigma_3 \eta} \right] \frac{\partial \mu_1}{\partial x} \\ & - \left[\frac{C_B}{\sigma_2 \eta} (1 - C_B \bar{V}_2) + \frac{\bar{V}_3 C_B^2}{\sigma_3 \eta} \right] \frac{\partial \mu_2}{\partial x} \end{aligned}$$

For this system, equation 22 is

$$C_1 \bar{V}_1 + C_B \bar{V}_2 + C_C \bar{V}_3 + C_{11} \bar{V}_{11} = 1 \quad (111)$$

and this combined with the stoichiometry relations (equations 106) enables us to write

$$\begin{aligned}
\mu_1 &= f(C_A, C_B) \\
\mu_2 &= f(C_A, C_B)
\end{aligned}
\tag{112}$$

at constant T and P.

Since equations 86 and 87 also apply to this system, equation 86 can be substituted into equation 110 and the coefficients compared to equation 87. This gives

$$\begin{aligned}
D_{AA} &= \left[\frac{C_1}{\sigma_1 \eta} (1 - C_A \bar{V}_1) + \frac{2C_{11}}{\sigma_{11} \eta} (2 - C_A \bar{V}_{11}) + \frac{\bar{V}_3 C_A^2}{\sigma_3 \eta} \right] \left(\frac{\partial \mu_1}{\partial C_A} \right)_{C_B} \\
&\quad + \left[-\frac{C_A C_B \bar{V}_2}{\sigma_2 \eta} + \frac{C_A C_B \bar{V}_3}{\sigma_3 \eta} \right] \left(\frac{\partial \mu_2}{\partial C_A} \right)_{C_B} \\
D_{AB} &= \left[\frac{C_1}{\sigma_1 \eta} (1 - C_A \bar{V}_1) + \frac{2C_{11}}{\sigma_{11} \eta} (2 - C_A \bar{V}_{11}) + \frac{\bar{V}_3 C_A^2}{\sigma_3 \eta} \right] \left(\frac{\partial \mu_1}{\partial C_B} \right)_{C_A} \\
&\quad + \left[-\frac{C_A C_B \bar{V}_2}{\sigma_2 \eta} + \frac{C_A C_B \bar{V}_3}{\sigma_3 \eta} \right] \left(\frac{\partial \mu_2}{\partial C_B} \right)_{C_A} \\
D_{BA} &= \left[-\frac{C_1 C_B \bar{V}_1}{\sigma_1 \eta} - \frac{2C_{11} C_B \bar{V}_{11}}{\sigma_{11} \eta} + \frac{C_A C_B \bar{V}_3}{\sigma_3 \eta} \right] \left(\frac{\partial \mu_1}{\partial C_A} \right)_{C_B} \\
&\quad + \left[\frac{C_B}{\sigma_2 \eta} (1 - C_B \bar{V}_2) + \frac{C_B^2 \bar{V}_3}{\sigma_3 \eta} \right] \left(\frac{\partial \mu_2}{\partial C_A} \right)_{C_B}
\end{aligned}
\tag{113}$$

$$\begin{aligned}
D_{BB} = & \left[-\frac{c_1 c_B \bar{v}_1}{\sigma_1 \eta} - \frac{2c_{11} c_B \bar{v}_{11}}{\sigma_{11} \eta} + \frac{c_A c_B \bar{v}_3}{\sigma_3 \eta} \right] \left(\frac{\partial \mu_1}{\partial c_B} \right)_{C_A} \\
& + \left[\frac{c_B}{\sigma_2 \eta} (1 - c_B \bar{v}_2) + \frac{c_B^2 \bar{v}_3}{\sigma_3 \eta} \right] \left(\frac{\partial \mu_2}{\partial c_B} \right)_{C_A}
\end{aligned} \tag{113}$$

Activities Based on the Chemical Model - If no dimer is assumed to exist in the vapor, then $p_A = p_1$. If in addition the four species form an ideal solution, then the following relations must hold

$$\begin{aligned}
a_A &= a_1 = X_1 = \gamma_A X_A \\
a_B &= a_2 = X_2 = \gamma_B X_B \\
a_C &= a_3 = X_3 = \gamma_C X_C \\
a_{11} &= X_{11}
\end{aligned} \tag{114}$$

It also follows that

$$\frac{\partial \mu_1}{\partial x} = \frac{\partial \mu_A}{\partial x} \tag{115}$$

Also the fact that B and C do not associate means that

$$\mu_2 = \mu_B, \quad \mu_3 = \mu_C \tag{116}$$

$$\bar{v}_2 = \bar{v}_B, \quad \bar{v}_3 = \bar{v}_C \tag{117}$$

$$\sigma_2 = \sigma_B, \quad \sigma_3 = \sigma_C \tag{118}$$

Phenomenological Coefficient Expressions - The rate of entropy production is given by

$$T\dot{s} = - J_1 \frac{\partial \mu_1}{\partial x} - J_2 \frac{\partial \mu_2}{\partial x} - J_3 \frac{\partial \mu_3}{\partial x} - J_{11} \frac{\partial \mu_{11}}{\partial x} \quad (119)$$

If it is assumed that

$$\bar{V}_{11} = 2\bar{V}_1 \quad (120)$$

then using equations 108 and 109 and the relation

$$J_1 \bar{V}_1 + J_2 \bar{V}_2 + J_3 \bar{V}_3 + J_{11} \bar{V}_{11} = 0 \quad (121)$$

equation 119 reduces to

$$\begin{aligned} T\dot{s} = & - J_A \left[\left(1 + \frac{C_A \bar{V}_1}{C_C \bar{V}_3} \right) \frac{\partial \mu_1}{\partial x} + \frac{C_B \bar{V}_1}{C_C \bar{V}_3} \frac{\partial \mu_2}{\partial x} \right] \\ & - J_B \left[\frac{C_A \bar{V}_2}{C_C \bar{V}_3} \frac{\partial \mu_1}{\partial x} + \left(1 + \frac{C_B \bar{V}_2}{C_C \bar{V}_3} \right) \frac{\partial \mu_2}{\partial x} \right] = - J_A Y_A - J_B Y_B \end{aligned} \quad (122)$$

From irreversible thermodynamics,

$$\begin{aligned} J_A &= L_{AA} Y_A + L_{AB} Y_B \\ J_B &= L_{BA} Y_A + L_{BB} Y_B \end{aligned} \quad (123)$$

Now, carrying out the multiplications indicated in equation 123 when

the substitutions are made for the Y's and equating coefficients

with equations 110, L_{AB} and L_{BA} can be obtained. They are

$$\begin{aligned} L_{AB} = L_{BA} = & - \frac{C_1 C_B \bar{V}_1}{\sigma_1 \eta} (1 - C_A \bar{V}_1) - \frac{C_A C_B \bar{V}_B}{\sigma_B \eta} (1 - C_B \bar{V}_B) \\ & - \frac{2C_{11} C_B \bar{V}_1}{\sigma_{11} \eta} (2 - C_A \bar{V}_{11}) + \frac{C_A C_B \bar{V}_C}{\sigma_C \eta} (1 - C_B \bar{V}_B - C_A \bar{V}_1) \end{aligned} \quad (124)$$

Thus if the assumption that $\bar{V}_{11} = 2\bar{V}_1$ is true, then the hydrodynamic model for systems in which one component dimerizes predicts that Onsager's reciprocal relations should hold.

EXPERIMENTAL

Apparatus

The experimental diffusion coefficients for both binary and ternary systems were obtained with an optical diffusimeter. Diffusion took place in a glass-windowed cell immersed in a constant temperature bath and was followed by measuring the refractive index of the solution with a Mach-Zehnder interferometer.⁵¹ Two solutions of slightly different concentrations were carefully flowed one on top of the other into the cell and free diffusion allowed to take place. The concentration was taken as the average of the two solutions. This set-up was similar to the diffusimeter described by Caldwell, Hall, and Babb⁸ and is described in detail by Bidlack.⁴

A diagram and a photograph of the interferometer system are shown in Figures 1 and 2. The components were supported by ordinary laboratory bench carriages located along a continuous rail composed of three optical benches. These in turn were bolted to an I-beam mounted on a concrete block to dampen outside disturbances and vibrations.

Monochromatic light from a Cenco quartz mercury arc lamp source, filtered to isolate the 5461 Å green mercury line, was collimated and then split in amplitude by a half-silvered mirror (mirror 1). Half of the beam was reflected to a full reflecting mirror (mirror 2) and the other half passed through to a full reflecting

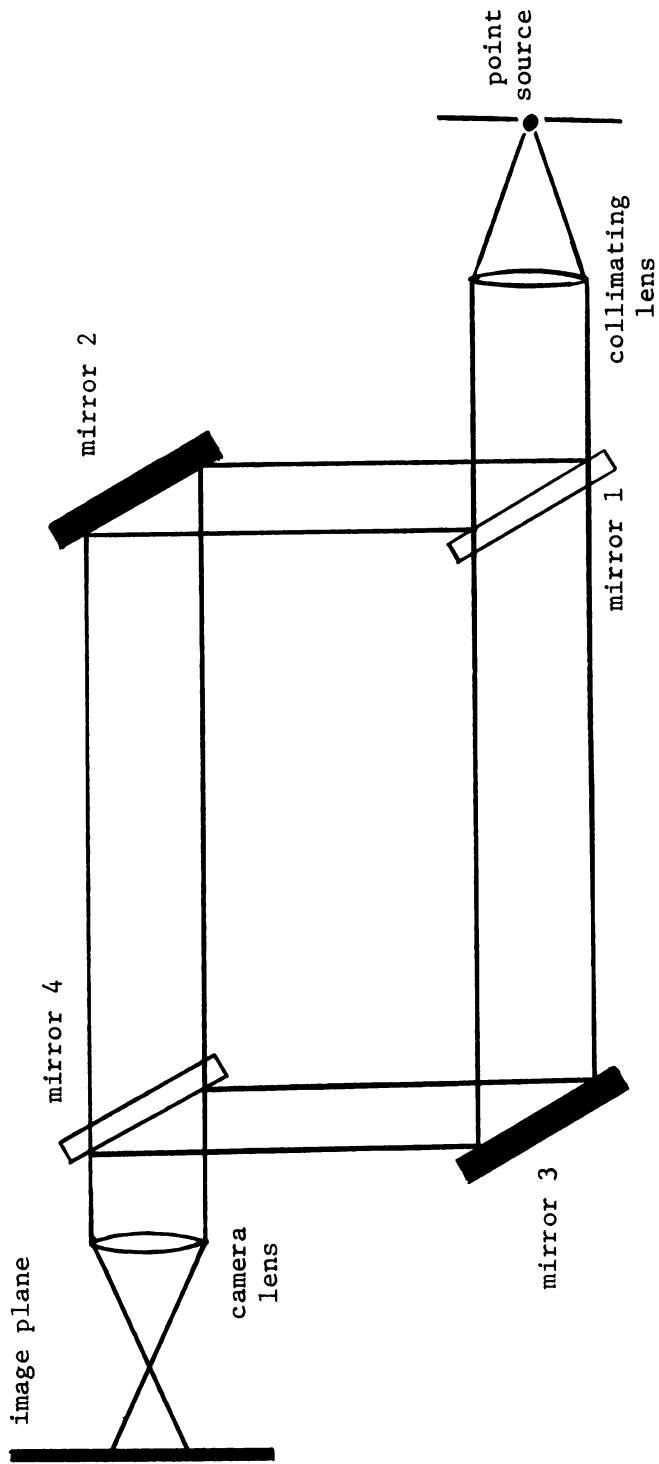


Figure 1. Schematic diagram of interferometer showing position of mirrors.

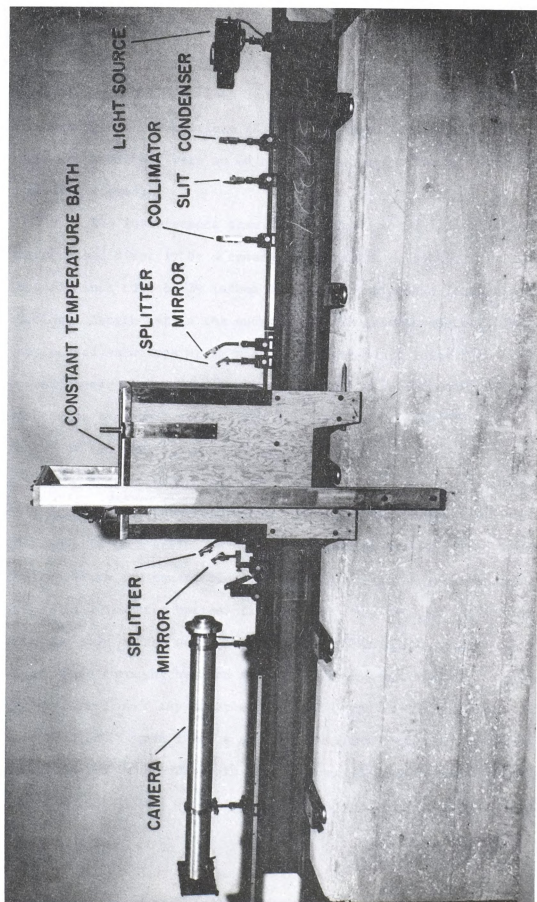


Figure 2. Photograph of Apparatus.

mirror (mirror 3). The two beams were then combined at a half-silvered mirror (mirror 4). Constructive interference of the two beams occurred when the path lengths 1-2-4 and 1-3-4 were equal or differed by a whole multiple of the wavelength of the incident light. The mirrors were so adjusted as to give straight, vertical, parallel fringes.

The interference beam was arranged so that it could be photographed directly by a camera. The camera consisted of a 3 foot long aluminum tube of $3\frac{1}{2}$ inches diameter containing a lens with a 343 mm. focal length set in the end towards the interferometer. The lens was focused on a type M, $3\frac{1}{4} \times 4\frac{1}{4}$ inch Kodak plate located at the opposite end. A lever mechanism on the plate holder enabled fourteen successive exposures to be taken per plate. The magnification factor of the camera was found to be 1.923.⁴

The diffusion cell was fixed in a water bath maintained at $25 \pm 0.03^{\circ}\text{C}$ by a thermoregulator. The water bath consisted of an 18 x 18 x 18 inch stainless steel tank covered with $\frac{3}{4}$ inch plywood and rested on the cement block without touching the interferometer. Two $3\frac{1}{2}$ inch diameter optical flat windows were clamped and sealed into the ends of the water bath and aligned to allow passage of the light beams through the bath and the cell windows. Distilled water was preferred over tap water since it did not cloud up as fast.

In Figures 3 and 4 are shown a photograph and a diagram of the diffusion cell. The main body of the cell consisted of a $\frac{1}{4} \times 3\frac{1}{4}$ inch slot cut into a stainless steel plate with two optically flat

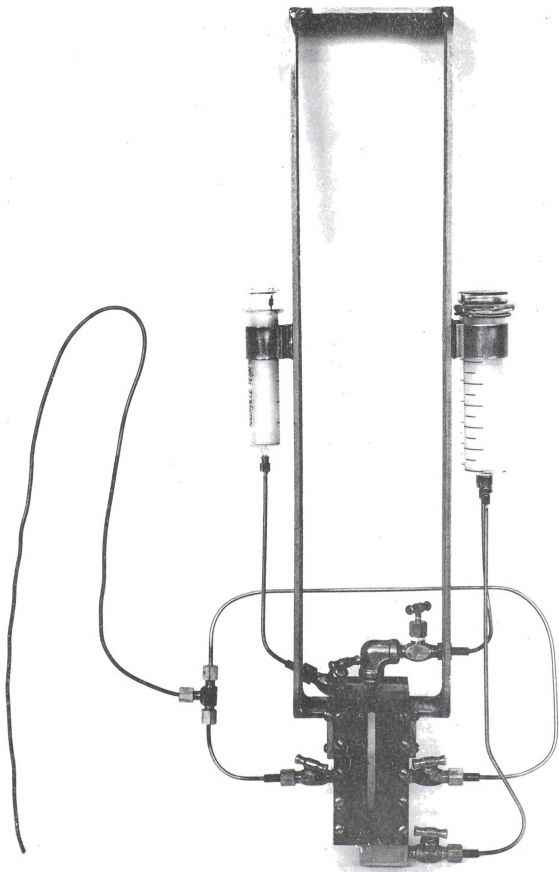


Figure 3. Photograph of the diffusion cell.

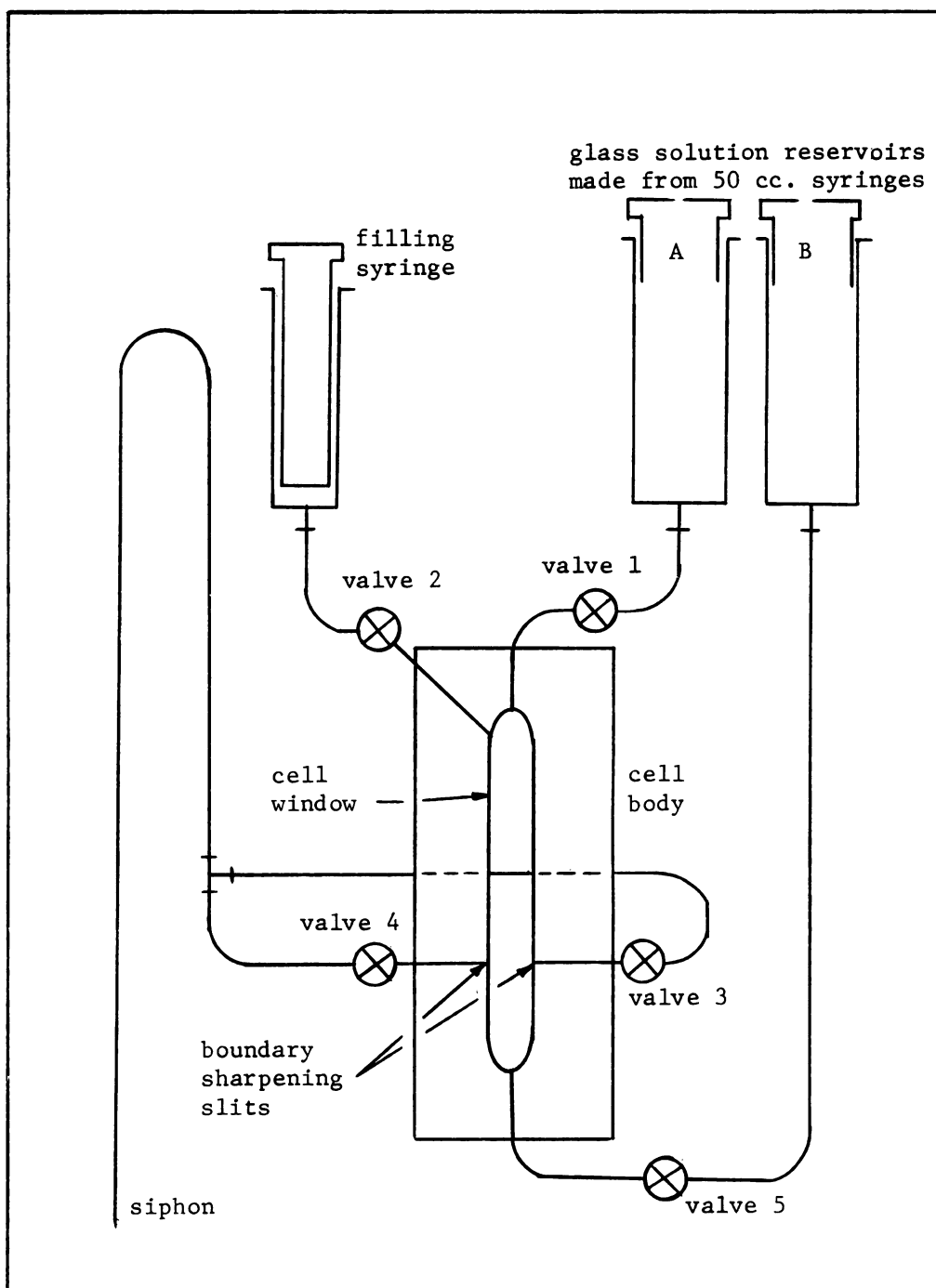


Figure 4. Diagram of diffusion cell.

windows clamped over the slot to form a sealed channel. The channel was situated to allow both light beams to pass through it; thus, a vertical concentration gradient in the solution across one of the beams resulted in a fringe displacement pattern that was a direct plot of refractive index versus distance. All parts of the cell which would be in contact with the liquid solutions were stainless steel or glass to enable the study of most corrosive liquids.

A framework was bolted to the cement block and positioned above the bath so that the cell could be hung from the top and immersed in the bath. Two small position pins were placed on the framework to insure that the cell was always placed in the same position.

The cell was provided with two inlets, one in the top and one in the bottom, and two outlets directly across from each other about one-third the way up the channel sides. Two solutions of slightly different concentrations were then slowly flowed simultaneously into the cell, the denser solution through the bottom inlet and the other through the top, and out the two outlets. A sharp boundary was thus formed between the two layered solutions. This boundary was located in the center of the lower beam. All the valves were then closed and the solution allowed to diffuse freely.

Procedure for Experimental Run

- 1) The light source and water bath heater were first turned on.
- 2) The cell was then placed in a rack away from the rest of the apparatus for convenience in filling.

- 3) All the cell valves except valve 2 were then closed and approximately 25 cc. of the denser solution were placed in reservoir B. Some of this solution was then allowed to flow into the cell through valve 5 until the liquid level was $\frac{1}{4}$ to $\frac{1}{2}$ inches above the outlets. Valve 5 was then closed.
- 4) Valve 4 was next opened slightly and liquid was forced into the exit line by means of the filling syringe plunger until the liquid level in the cell was just above the outlets. Valve 4 was then closed and more solution from the reservoir was passed through valve 5 into the cell as in step 3. More liquid was forced into the exit line through valve 4 and the whole procedure repeated until liquid dripped from the outlet line. This was done to insure that liquid had filled the exit line as far as the tee. Valve 4 was then closed.
- 5) The same procedure of adding liquid to the cell through valve 5 was repeated and exit valve 3 opened. The filling syringe was then used to force liquid into the exit line until the cell liquid level was just above the outlet. At this point, valve 3 was closed.
- 6) Step 5 was repeated until the liquid flowed freely from the exit line by means of a siphon.
- 7) All valves were then closed except valve 1 and 25 cc. of the less dense solution was placed in the filling syringe. Valve 2 was then slowly opened so as to allow the solution to trickle down the side of the cell channel and layer on top of the more dense solution. The solution was allowed to flow this way with valve

- 2 being opened more and more as the solution built up in the cell. After the solution had overflowed up into reservoir A, both valves 1 and 2 were closed.
- 8) The two reservoirs were then filled to approximately equal liquid levels with the appropriate solutions, remembering to always place the more dense in reservoir B.
- 9) At this point the cell was placed in position in the water bath. The reservoir valves, valves 1 and 5, were then opened one full turn followed slowly by valve 3 until the rate of flow from the exit line was one drop every 8 seconds. The opposite outlet valve, valve 4, was then slowly opened until the combined exit flow rate was one drop every 4 seconds. It was important to maintain balanced flow rates into both halves of the cell as well as through both outlets.
- 10) When the boundary had formed satisfactorily, valves 3 and 4 were closed followed as soon as possible by valves 1 and 5. The timer was then started and pictures taken at various times during the run. A series of exposures taken for one run are shown in Figure 5.

Purity of Materials

The chemicals hexane, dodecane, hexadecane, and carbon tetrachloride were obtained in the purest forms available from Matheson, Coleman, and Bell, Co. The hexane and carbon tetrachloride were spectroquality and the dodecane and hexadecane were 99+% (olefin free) quality. The chemicals diethyl ether and chloroform

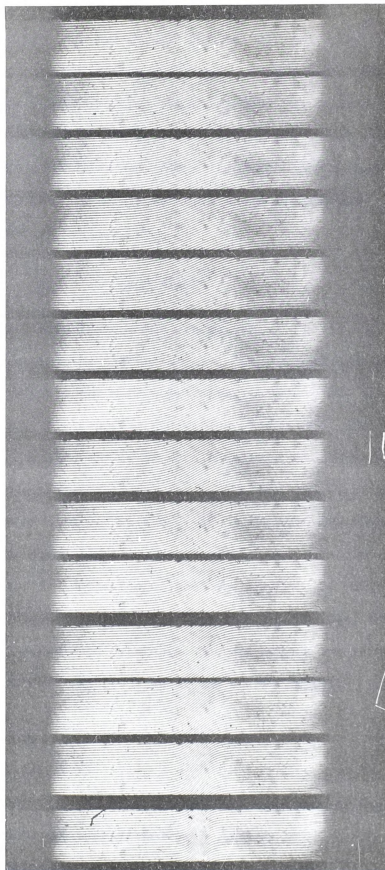


Figure 5. Typical set of photographs taken during diffusion run.

were purchased from the Malinkrodt Chemical Co. and were analytical reagent grade. The chloroform contained a slight impurity of ethanol used as a preservative. This affected the density slightly but showed no noticeable change in the refractive index. The measured values of density and refractive index were compared with those listed in the literature and were found satisfactory. These values are given in Table 1.

Calculations

Calculation of Concentrations and Viscosities

In determining concentrations, various predetermined amounts of each component were weighed out together, and the density of the resulting solution measured with a pycnometer. From the known amounts and the density of each solution, the concentrations were calculated. Volumes calculated on the basis of densities of the pure components agreed within 0.15% of the measured volumes but were lower than the measured values in all cases. The very small differences were an indication of the constancy of the molar volumes.

For systems in which the diffusion coefficients had been experimentally determined by others, concentrations were calculated using the given mole fractions according to the following equation

$$C_i = \frac{X_i}{\sum_{j=1}^3 X_j \bar{V}_j} \quad i = 1, 2, 3 \quad (125)$$

Viscosities of the solutions were experimentally determined using a Cannon-Fenske type viscometer. Kinetic energy effects were taken into account by using an equation of the form

Table 1. Comparison of physical constants with
previous recorded data.

Chemical	Density at 25 °C d (g/cc)		Refractive index at 25 °C n_D	
	This Work	Reference 42	This Work	Reference 42
Hexane	0.6550	0.6549	1.3727	1.3723
Dodecane	0.7450	0.7451	1.4196	1.4195
Hexadecane	0.7698	0.7699	1.4324	1.4325
Carbon Tetrachloride	1.5850	1.5845	1.4570	1.4576
Chloroform	1.4740	1.4795	1.4426	1.4422
Diethyl Ether	0.7075	0.7077	1.3500	1.3499

$$\nu = \frac{\eta}{\rho} = K_1 t - \frac{K_2}{t^2} \quad (126)$$

where K_1 and K_2 are experimental constants determined using liquids of known viscosity and t is the time. The viscosities for the systems reported by other sources when not given were calculated according to the following relationship

$$\ln \eta = \sum_{i=1}^3 X_i \ln \eta_i \quad (127)$$

where X_i is the mole fraction of i and η_i is the viscosity of pure i .

Reduced Second Moment

The fringe pattern obtained by the diffusimeter for each exposure may be considered as a plot of the refractive index versus distance in the cell because the displacement of the fringes is proportional to the refractive index difference. It is also true that

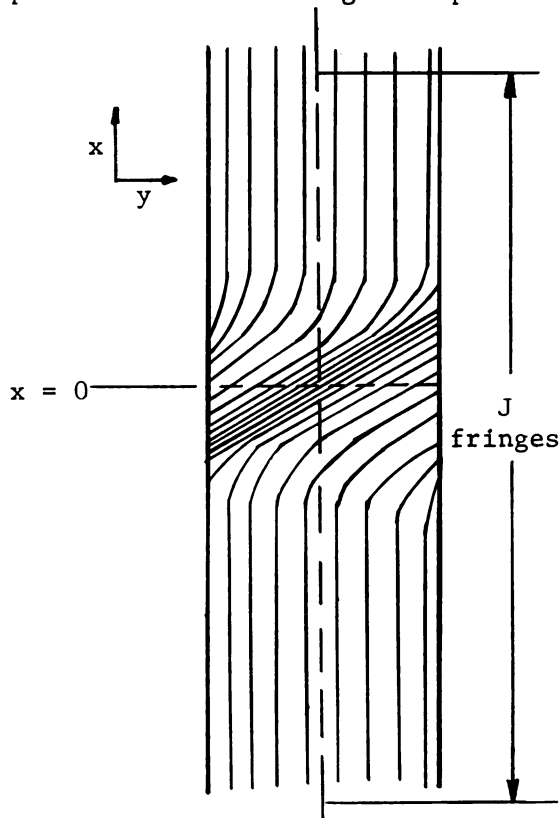
$$n_{x_2} - n_{x_1} = k_1 (j_{x_2} - j_{x_1}) \quad (128)$$

where n_{x_i} is the refractive index

at x_i and j_{x_i} is the number of fringes up to the point x_i .

From equation 128, $k_1 = \Delta n / J$

where J is the total number of fringes and Δn is the total refractive index difference across the boundary. It is desired to obtain a plot of



$(\partial n / \partial x)_t$ versus x for each exposure, since it is the second moment of the refractive index gradient curve that is required. If we look at the center regions of the exposure (near $x = 0$), it is noticed that any curvature in the fringes is small. From equation 128, it follows that the refractive index difference across one fringe is k_1 . Hence in the center regions of an exposure a reasonable value for the refractive index gradient can be obtained by measuring the distance between two fringes. Thus

$$\left(\frac{\partial n}{\partial x} \right)_t \bigg|_{x = \frac{x_{j+1} + x_j}{2}} \approx \frac{k_1}{x_{j+1} - x_j} \quad (129)$$

where x_j and x_{j+1} are the distances to fringe j and $j+1$ respectively and $(\partial n / \partial x)_t$ is the refractive index gradient at $x = (x_{j+1} + x_j) / 2$.

In the outer regions of the exposure ($x \gg 0$, $x \ll 0$), the curvature of the fringes is more pronounced and therefore equation 129 is not a good approximation. In these regions, tangents to the fringes give more accurate values of the refractive index gradient. The tangent at these points gives $\partial y / \partial x$ not $\partial n / \partial x$, therefore a relation between ∂y and ∂n is necessary. This can be obtained by measuring the distance in the y direction between a specific number of fringes. This provides a proportionality constant, k_2

$$k_2 = \frac{y_2 - y_1}{\Delta j} \quad (130)$$

where Δj is the number of fringes between y_2 and y_1 . Using equation 128, equation 130 becomes

$$\Delta n = \frac{k_1}{k_2} \Delta y \quad (131)$$

therefore

$$\left(\frac{\partial n}{\partial x} \right)_t \bigg|_{x_i} = \frac{k_1}{k_2} \tan \theta \bigg|_{x_i} \quad (132)$$

where $\tan \theta \big|_{x_i}$ is the measured tangent of any fringe at point x_i on the exposure and where θ is the angle measured between the tangent line and the x axis.

The values x and y which are measured off an exposure are not the actual distances but rather magnified distances. The camera which records the fringe pattern at various time intervals has a magnification factor, $M = 1.923$, hence $x = x_m/M$ where x_m is the measured distance and x is the actual distance. On this basis, equations 129 and 132 are

$$\left(\frac{\partial n}{\partial x} \right)_t \bigg|_{\frac{x_{j+1,m} + x_{j,m}}{2M}} = M \left(\frac{\partial n}{\partial x_m} \right)_t = \frac{Mk_1}{x_{j+1,m} - x_{j,m}} \quad (133)$$

$$\left(\frac{\partial n}{\partial x} \right)_t \bigg|_{\frac{x_m}{M}} = M \left(\frac{\partial n}{\partial x_m} \right)_t = \frac{Mk_1}{k_2} \tan \theta \bigg|_{\frac{x_m}{M}} \quad (134)$$

The definition of the r^{th} moment is given by

$$m_r = \frac{1}{\Delta n} \int_{-\infty}^{+\infty} x^r \left(\frac{\partial n}{\partial x} \right)_t dx \quad (135)$$

where Δn is the total refractive index difference across the initially sharp boundary. In terms of measured quantities this definition becomes

$$m_r = \frac{1}{M^r \Delta n} \int_{-\infty}^{+\infty} x_m^r \left(\frac{\partial n}{\partial x_m} \right)_t dx_m \quad (136)$$

From the expressions for the refractive index gradients used in the numerical integrations, equations 133 and 134, and the definition of the r^{th} moment, it can be seen that the proportionality constant k_1 cancels. Thus in evaluating the moments, the constant k_1 is not required. It is obvious then that any value chosen for k_1 will not affect the results. If k_1 is chosen as unity in evaluating the refractive index gradients, then

$$\int_{-\infty}^{+\infty} \left(\frac{\partial n}{\partial x} \right)_t dx = \int_{-\infty}^{+\infty} \left(\frac{\partial n}{\partial x_m} \right)_t dx_m = \Delta n = k_1 J = J \quad (137)$$

J can easily be evaluated from each exposure within ± 0.2 fringes. Therefore, since it can also be calculated numerically from equation 137, a check on the numerical calculations is provided.

For the case of $k_1 = 1$, calculation of the value of x_m at the initially sharp boundary can be obtained from

$$x_{c,m} = \frac{1}{J} \int_{-\infty}^{+\infty} x_m \left(\frac{\partial n}{\partial x_m} \right)_t dx_m \quad (138)$$

Notice that the choice of the origin of x used in determining the measured x values will give a different value of $x_{c,m}$. It is shown in Appendix II that if $x_{c,m}$ is taken as the origin, then $m_1 = 0$. This of course follows from equation 138. Since the moments and the diffusion equations are derived on the basis of $x_c = 0$, the values of x used in the determination of m_2 must be equal to $(x_m - x_{c,m})/M$ where x_m is the measured value of x based on any starting point, $x_{c,m}$

is the value of x_m at the boundary based on the same starting point, and M is the magnification factor. The expression for m_2 is therefore

$$m_2 = \frac{1}{M^2 J} \int_{-\infty}^{+\infty} (x_m - x_{c,m})^2 \left(\frac{\partial n}{\partial x_m} \right)_t dx_m \quad (139)$$

The reduced second moment D_{2m} is defined by

$$D_{2m} \equiv \frac{m_2}{2t} \quad (140)$$

In actuality a perfectly sharp boundary will not be formed so that t will not equal the measured time, t_m . Rather

$$t = t_m + \Delta t_{\text{corr.}} \quad (141)$$

Hence equation 140 should be

$$D_{2m} = \frac{m_2}{2(t_m + \Delta t_{\text{corr.}})} \quad (142)$$

Rearrangement of equation 142 gives

$$\frac{m_2}{2} = D_{2m} t_m + D_{2m} \Delta t_{\text{corr.}} \quad (143)$$

Therefore, a plot of $m_2/2$ versus t_m should give a straight line of slope, D_{2m} , and intercept $D_{2m} \Delta t_{\text{corr.}}$. The slope gives the desired value of the reduced second moment, and the intercept provides the time correction, $\Delta t_{\text{corr.}}$. From the latter, the absolute time of diffusion can be determined using equation 141.

Plots of the second moment versus the measured time for the systems studied are given in Figures 12, 13, and 14 of Appendix VI.

It can be seen that they are linear in accordance with equation 143. Tabulations of the time corrections, $\Delta t_{\text{corr.}}$, obtained from these curves are given in Table 15 also in Appendix VI. For convenience the second moments at the various measured times of each run are also provided in Table 14 of Appendix VI.

Reduced Height-Area Ratio

The reduced height-area ratio is defined by

$$\mathcal{D}_A \equiv \frac{(\Delta n)^2}{4\pi t \left[\left(\frac{\partial n}{\partial x} \right)_t \right]_{\text{max}}^2} \quad (144)$$

In terms of measured quantities this becomes

$$\mathcal{D}_A = \frac{(k_1 J)^2}{4\pi t M^2 \left[\left(\frac{\partial n}{\partial x_m} \right)_t \right]_{\text{max}}^2} \quad (145)$$

Again it can be seen from the expressions for the measured refractive index gradients (equations 133 and 134) that k_1 cancels and hence k_1 can be taken as unity in the calculations.

Since there are no minima and only one maximum in the measured refractive index gradient curve, \mathcal{D}_A can be obtained by simply finding the maximum of the measured refractive index gradient curve and substituting this value into equation 145. This maximum which can be obtained either numerically or graphically, decreases as the absolute time, t , increases.

Differential Refractive Index Constants

It was assumed by Gosting, et. al.^{3,19,22,23} and this author that the total refractive index change across the boundary, Δn ,

could be expressed by the equation

$$\Delta n = R_1 \Delta C_1 + R_2 \Delta C_2 \quad (146)$$

where C_i represents the concentration in moles/liter and R_i is the differential refractive index increment of component i . Division of equation 146 by ΔC_1 , gives

$$\frac{\Delta n}{\Delta C_1} = R_1 + R_2 \frac{\Delta C_2}{\Delta C_1} \quad (147)$$

Thus, values of R_1 and R_2 could be obtained from the intercept and slope of a plot of $\Delta n/\Delta C_1$ versus $\Delta C_2/\Delta C_1$.

Δn can be determined either by direct refractive index measurements or from equation 128

$$\Delta n = k_1 J \quad (128)$$

Based on several runs performed in this laboratory, k_1 was found to be 2.10×10^{-5} refractive index units/fringe. To obtain this value larger concentration differences, and thus larger Δn values, were used so as to minimize errors in refractive index measurements. The J values, total fringes, could be obtained directly from the exposures.

It should be pointed out that in the determination of the ternary coefficients, only the ratios of R_1 and R_2 are used. Therefore a value of k_1 is not needed since it cancels in the ratios. The following equation can therefore be used to calculate an R_1' and R_2' from which the correct ratios can be determined.

$$\frac{\Delta J}{\Delta C_1} = R_1' + R_2' \frac{\Delta C_2}{\Delta C_1} \quad (148)$$

where

$$R_1' = \frac{R_1}{k_1}, \quad R_2' = \frac{R_2}{k_1} \quad (149)$$

and

$$\frac{R_1'}{R_2'} = \frac{R_1}{R_2} \quad (150)$$

The latter method is considered more accurate because of the limitations in the refractive index measurements. With small initial concentrations difference chosen to minimize errors resulting from variation of D_{ij} , \bar{V}_i , and R_i with concentration, the Δn values are naturally quite small. In fact, they were in the neighborhood of 0.0005 to 0.0010 indicating that small errors in a refractive index measurement could cause large percentage errors in Δn . The J value, being a strong indicator of refractive index difference, was considered a more accurate measure of Δn .

Diffusion Coefficients

The method used in this laboratory of experimentally determining the diffusion coefficients D_{ij} of a ternary system was very similar to the method outlined by Fujita and Gosting.²² In both methods a refractive index gradient curve at various times during free diffusion is obtained. Using these curves, reduced second moments and reduced height-area ratios are calculated. Plots of the reduced second moments and of the reciprocal square root of

the reduced height-area ratio are then made against the refractive index fraction of one of the components, α_1 . This refractive index fraction is defined by

$$\alpha_1 = \frac{R_1 \Delta C_1}{\Delta n} = \frac{R_1 \Delta C_1}{R_1 \Delta C_1 + R_2 \Delta C_2} \quad (151)$$

The slopes and intercepts at $\alpha_1 = 0$ and $\alpha_1 = 1$ of these plots are then used to calculate the ternary diffusion coefficients.

The linear equations of the reduced second moment, D_{2m} , and of the reciprocal square root of the reduced height-area ratio, $1/\sqrt{D_A}$, with α_1 are

$$D_{2m} = I_{2m} + S_{2m} \alpha_1 \quad (152)$$

$$\frac{1}{\sqrt{D_A}} = I_A + S_A \alpha_1 \quad (153)$$

where S_{2m} and S_A are the slopes and I_{2m} and I_A are the intercepts at $\alpha_1 = 0$. The intercepts at $\alpha_1 = 1$, L_{2m} and L_A , are related to these slopes and intercepts by the following relations

$$L_{2m} = I_{2m} + S_{2m} \quad (154)$$

$$L_A = I_A + S_A \quad (155)$$

The ternary diffusion coefficients in terms of these slopes and intercepts are

$$D_{11} = - \frac{|D_{ij}| + L_{2m} \sqrt{|D_{ij}|} + \frac{L_{2m} I_A S_{2m}}{S_A}}{S_{2m}} \quad (156)$$

$$D_{22} = \frac{|D_{ij}| + I_{2m} \sqrt{|D_{ij}|} + \frac{I_{2m} L_A S_{2m}}{S_A}}{S_{2m}} \quad (157)$$

$$D_{12} = \frac{R_2}{R_1} (I_{2m} - D_{22}) \quad (158)$$

$$D_{21} = \frac{R_1}{R_2} (L_{2m} - D_{11}) \quad (159)$$

where $|D_{ij}|$, the determinant of the ternary diffusion coefficients, is given by

$$|D_{ij}| = D_{11}D_{22} - D_{12}D_{21} \quad (160)$$

The $|D_{ij}|$ is determined from the cubic equation

$$(\sqrt{|D_{ij}|})^3 + \left[I_{2m} - I_A \frac{S_{2m}}{S_A} \right] (\sqrt{|D_{ij}|})^2 - \left(\frac{S_{2m}}{S_A} \right)^2 = 0 \quad (161)$$

The development of these equations and the solution to the describing equations for diffusion are given in Appendix II. A computer program to solve for the roots of equation 161 is given in Appendix V.

Friction Coefficients

Values of the friction coefficients, σ_i , for the systems dodecane-hexadecane-hexane, toluene-chlorobenzene-bromobenzene, and acetone-benzene-carbon tetrachloride were calculated from mutual diffusion of the binaries at infinite dilution and from self diffusion data of each component. Values of the friction coefficients for the system diethyl ether-chloroform-carbon tetrachloride were determined

by Wirth.⁴⁷ For the hydrocarbon system values were determined more exactly using tracer techniques. The necessary diffusion data are provided in Tables 11 and 12. Since the parameter RT/σ_i always appeared together in the calculations, this value was determined for each component rather than σ_i itself. The relationship used in this calculation was

$$\frac{RT}{\sigma_i} = X_i D_i \eta_i + \sum_{\substack{j \\ j \neq i}}^3 X_j D_{ij}^o \eta_j \quad i = 1, 2, 3 \quad (162)$$

where D_i is the self diffusion coefficient of component i in $\text{cm}^2/\text{sec.}$, D_{ij} is the mutual diffusion coefficient of the i - j binary at infinite dilution of component i in $\text{cm}^2/\text{sec.}$, η_i is the viscosity of pure i in $\text{dynes} \times \text{sec.}/\text{cm}^2$, and X_i is the mole fraction of component i at which the diffusion coefficients were measured.

It should be pointed out that equation 162 is more applicable to non-associating systems since the friction coefficients correspond to actual species. With associating systems where there may be more than three species present, the friction coefficients obtained do not correspond to actual species. Rather they are empirical factors for each stoichiometric component. They would therefore give less reliable values for the diffusion and phenomenological coefficients calculated from them.

The parameter RT/σ_i for the hydrocarbon system was obtained from tracer techniques according to the equation

$$\frac{RT}{\sigma_i} = D_i^* \eta \quad (163)$$

where D^* is the tracer diffusion coefficient, η is the viscosity of the solution, and σ_i is the friction coefficient of the tagged species. The concentrations in the tracer runs were the same as those at which the ternary diffusion coefficients were determined. Details on the derivation of equation 163 are given in Appendix I. This procedure could be applied to other non-associating systems if the components could be obtained in tagged form.

Activity Data

Dodecane (1) - Hexadecane (2) - Hexane (3) - Activity data at 20°C for the hydrocarbon binaries hexane-dodecane and hexane-hexadecane were obtained from Bronsted and Koefoed.⁵ Since they concluded that the system exhibited regular solution behavior, the activity data for the ternary system were obtained by a Van Laar fit.⁴³ The equations used were

$$T \ln \gamma_1 = \frac{(C_3 \sqrt{B_{13}} + C_2 A_{23} \sqrt{B_{12}})^2}{(C_1 A_{13} + C_3 + C_2 A_{23})^2}$$

$$T \ln \gamma_2 = \frac{(C_1 A_{13} \sqrt{B_{21}} + C_3 \sqrt{B_{23}})^2}{(C_1 A_{13} + C_3 + C_2 A_{23})^2}$$
(164)

where A_{ij} and B_{ij} are constants obtained from the binaries and C_i is the concentration of i . These constants are tabulated in Table 19 of Appendix VI. Further details on the derivation of required activity expressions are given in Appendix III.

Diethyl Ether (A) - Chloroform (B) - Carbon Tetrachloride (C) - Activity data for this system was calculated on the basis of the

associated chemical model proposed by Wirth⁴⁷ and Anderson.^{1,2} According to their model, diethyl ether and chloroform form a one:one complex and this together with the uncomplexed monomers and the inert carbon tetrachloride species form an ideal solution. The vapor is assumed to be ideal with none of the dimer complex present.

From this model the activities of the species are given by equations 92

$$\begin{aligned}
 a_A &= a_1 = X_1 = \gamma_A X_A \\
 a_B &= a_2 = X_2 = \gamma_B X_B \\
 a_C &= a_3 = X_3 = \gamma_C X_C \\
 a_{12} &= X_{12}
 \end{aligned} \tag{92}$$

where γ is the activity coefficient. Details on the determination of X_1 , X_2 , X_3 , and X_{12} and of $(\partial\mu_i/\partial C_i)_{C_j}$ are given in Appendix III.

Acetone (1) - Benzene (2) - Carbon Tetrachloride (3) - Activity data at 45°C for the acetone-benzene and acetone-carbon tetrachloride binaries are given by Brown and Smith⁵ and for the benzene-carbon tetrachloride binary by Christian, et. al.⁹ These have been fitted to two term Margules equations⁵⁰ and extended to the ternary by the method of Wohl.⁴⁷ The equations used were

$$\begin{aligned}
 C_T^3 \ln \gamma_1 &= C_2^2 \left[A_{12} C_T + 2C_1 (A_{21} - A_{12}) \right] + C_3^2 \left[A_{13} C_T + 2C_1 (A_{31} - A_{13}) \right] \\
 &+ C_2 C_3 \left[C_T (A_{21} + A_{13} - A_{32}) + 2C_1 (A_{31} - A_{13}) \right. \\
 &\left. + 2C_3 (A_{32} - A_{23}) - C_{123} (C_T - 2C_1) \right]
 \end{aligned} \tag{165}$$

$$\begin{aligned}
C_T^3 \ln \gamma_2 = & C_3^2 \left[A_{23} C_T + 2C_2 (A_{32} - A_{23}) \right] + C_1^2 \left[A_{21} C_T + 2C_2 (A_{12} - A_{21}) \right] \\
& + C_1 C_3 \left[C_T (A_{32} + A_{21} - A_{13}) + 2C_2 (A_{12} - A_{21}) \right. \\
& \left. + 2C_1 (A_{13} - A_{31}) - C_{123} (C_T - 2C_2) \right]
\end{aligned} \tag{165}$$

where

$$C_{123} = \frac{1}{2} (A_{21} - A_{12} + A_{13} - A_{31} + A_{32} - A_{23}) \tag{166}$$

and C_i is the concentration of i and the A_{ij} are the binary coefficients. These coefficients are listed in Table 19. Details of the development of the expressions for $(\partial \mu_i / \partial C_j)_{C_i}$ are given in Appendix III. The activity constants determined by Yon and Toor⁵⁰ are given in Table 19 of Appendix VI.

Toluene (1) - Chlorobenzene (2) - Bromobenzene (3) - This system was assumed to be ideal so that for all three components

$$a_i = X_i \tag{167}$$

Error Analysis of Experimental Method

The accuracy in determining binary diffusion coefficients with this apparatus was found to be $\pm 1\%$ by Bidlack.³ He obtained diffusion coefficients for seven aqueous sucrose solutions and compared them with those reported by Gosting and Morris. Diffusion coefficients for aqueous sucrose solutions obtained by this author also were within $\pm 1\%$ of those listed.

It is difficult to specify the accuracy in determining ternary diffusion coefficients. The reason for this is the lack of

reliable ternary data to compare to. The accuracy of the ternary data that are available in the literature is not given for this same reason, only the precision is generally discussed and sometimes not even that. In determining experimental ternary diffusion coefficients in this laboratory, the accuracy is not limited by the apparatus but rather by the readings taken from the photographic plates and in the method of calculations themselves. Because of the former, it is expected that values obtained for the reduced second moment, D_{2m} , and for the reduced height-area ratio, \mathcal{D}_A , can be no better than $\pm 1\%$.

The precision of the data obtained in this laboratory was determined by calculating the variance and confidence limits of the slopes and intercepts of the reduced second moment and reduced height-area ratios. These are listed in Table 2. It was found that the 95% confidence limits on the slopes were considerably larger than the intercepts. The limits on the intercepts in all cases amounted to less than $\pm .95\%$ of the actual value used. The limits on the slopes varied from $\pm 1.6\%$ to $\pm 6\%$, with the average deviation being approximately $\pm 3\%$.

The 95% confidence envelope for each of the least squares fit can be obtained from Table 3. The 95% confidence limits of the ordinate values (D_{2m} and $1/\sqrt{\mathcal{D}_A}$ values) were found to vary from $\pm 0.1\%$ to $\pm 1\%$ of the least squares line through the points.

The variances of the ordinate values were determined according to the equation

Table 2. Variances and 95% confidence limits of the slopes and intercepts of the D_{2m} vs. α_1 and $1/\sqrt{D_A}$ vs. α_1 curves.

Dodecane - Hexadecane - Hexane

Variable	Variance	95% Confidence Limits	Value used in calculations
I_{2m}	1.39×10^{-14}	$\pm 1.12 \times 10^{-7}$	1.192×10^{-5}
S_{2m}	4.31×10^{-15}	$\pm 6.32 \times 10^{-8}$	0.149×10^{-5}
I_A	1.98	± 1.34	2.923×10^2
S_A	0.61	± 0.75	-0.244×10^2

Diethyl Ether - Chloroform - Carbon Tetrachloride

Variable	Variance	95% Confidence Limits	Value used in calculations
I_{2m}	3.21×10^{-15}	$\pm 5.35 \times 10^{-8}$	0.716×10^{-5}
S_{2m}	4.89×10^{-14}	$\pm 2.10 \times 10^{-7}$	1.391×10^{-5}
I_A	1.42	± 1.13	2.890×10^2
S_A	21.6	± 4.42	-0.725×10^2

Table 3. Confidence limits of D_{2m} and $1/\sqrt{D_A}$.

Dodecane (1) - Hexadecane (2) - Hexane (3)

α_1	$D_{2m} \times 10^5$	Confidence limits of $D_{2m} \times 10^5$	$1/\sqrt{D_A}$	Confidence limits of $1/\sqrt{D_A}$
-1.134	0.984	± 0.938	324.7	± 1.12
-0.239	1.203	± 0.380	300.6	± 0.45
0.176	1.197	± 0.121	283.2	± 0.14
1.352	1.411	± 0.612	256.0	± 0.73
-2.416	0.835	± 1.737	350.3	± 2.07
3.599	1.710	± 2.012	206.9	± 2.40
1.257	1.388	± 0.553	261.9	± 0.66

Diethyl Ether (1) - Chloroform (2) - Carbon Tetrachloride (3)

α_1	$D_{2m} \times 10^5$	Confidence limits of $D_{2m} \times 10^5$	$1/\sqrt{D_A}$	Confidence limits of $1/\sqrt{D_A}$
1.002	2.113	± 0.044	218.8	± 0.09
0.623	1.585	± 0.840	243.3	± 1.76
1.317	2.577	± 0.617	193.9	± 1.30
1.150	2.303	± 0.267	203.4	± 0.56

$$s_e^2(y_i) = \frac{\sum_{i=1}^N (Y_i - y_i)^2}{N - 2} \quad (168)$$

where $s_e^2(y_i)$ is the variance of y_i , N is the number of data points used in the least squares fit, Y_i is the ordinate value calculated from the constants of the least squares fit, and y_i is the ordinate value used in determining the least squares fit. The $N - 2$ degrees of freedom result from the use of two quantities, the slope and intercept of the least squares line, which are calculated from the data.

The variances of the slope and intercept were calculated from the following relations:

$$s_e^2(\text{slope}) = \frac{s_e^2(y_i)}{\sum_{i=1}^N (x_i - \bar{x})^2} \quad (169)$$

$$s_e^2(\text{intercept}) = \frac{s_e^2(y_i)}{N} \quad (170)$$

where

$$\bar{x} = \frac{\sum_{i=1}^N x_i}{N} \quad (171)$$

The 95% confidence limits were calculated according to the relation

$$95\% \text{ confidence limits on } z = \pm 0.95 s_e^2(z) \quad (172)$$

where z is a dummy variable.

These equations and error analysis are discussed by Mickley, Sherwood, and Reed.³²

RESULTS AND DISCUSSION

Theoretical

Hydrodynamic theory predicts that the Onsager reciprocal relations are valid for non-associating systems in which the molar volumes are constant. This latter constraint was experimentally maintained by choosing the initial concentration differences as small as possible. An attempt was made to apply hydrodynamic theory to multicomponent associating systems by considering the two simplest cases where association results in a dimer. It was found that Onsager's reciprocal relations would again be valid but with the additional assumption that the molar volume of the dimer be equal to the sum of the molar volumes of the species associating to form the dimer. This assumption was reasonable but not rigorously valid.

It was also found that Miller's equations for the phenomenological coefficients reduced to those derived from the hydrodynamic approach. This was especially encouraging because Miller's equations contain activity expressions but the hydrodynamic equations do not. Activity data for ternary and higher order systems, like diffusion data for these systems, is difficult to obtain and up till now has been a major deterrent in verifying Onsager's reciprocal relations. It was mentioned previously, that Miller's condition for verifying Onsager's reciprocal relations was

derived from his expressions for the phenomenological coefficients. Since these contained activity terms, they also appeared in the condition used for testing the reciprocal relations. It should also be pointed out that the expressions for the diffusion coefficients obtained by the hydrodynamic approach do contain activity terms. When these expressions are substituted into Miller's equations for the phenomenological coefficients, the activity terms drop out.

Experimental

The systems dodecane-hexadecane-hexane and diethyl ether-chloroform-carbon tetrachloride were experimentally studied in this laboratory, while the systems toluene-chlorobenzene-bromobenzene and acetone-benzene-carbon tetrachloride were experimentally studied elsewhere.^{7,41} The hydrodynamic model was applied to all four systems and the reciprocal relations tested when possible.

In the derivation of the equations used to determine experimental diffusion coefficients with optical methods, it was assumed that the dependence of refractive index on the two independent concentrations could be adequately represented by the first three terms of a Taylor expansion (equation II-16, Appendix II). This is a critical assumption since it relates refractive index measurements, which are the basis of optical methods, to the concentrations. Thus, it is important before any confidence in the experimental ternary diffusion coefficients is possible, that the reliability of this assumption be checked. Fortunately, the trend has been in all systems studied that this assumption is valid. By

subtracting the two Taylor expansions representing the refractive index of the two initial solutions used in a run and then rearranging, one obtains

$$\frac{\Delta n}{\Delta C_1} = R_1 + R_2 \frac{\Delta C_2}{\Delta C_1} \quad (147)$$

as was shown in the experimental section. Therefore, provided the R_1 and R_2 are independent of concentration, a plot of $\Delta n/\Delta C_1$ versus $\Delta C_2/\Delta C_1$ should be linear. Since the initial concentration differences are small, the assumption of constant R_1 and R_2 is reasonable. For both systems studied experimentally in this laboratory, such plots exhibited linear behavior. This is shown in Figures 6 and 7.

Non-Associating Systems

Dodecane-Hexadecane-Hexane

The basis of the optical method in determining the diffusion coefficients other than that just discussed is that the reduced second moment, D_{2m} , and the reciprocal square root of the reduced height-area ratio, $1/\sqrt{D_A}$, be linear with the refractive index fraction, α_1 . It is from the intercepts and slopes of these curves that the ternary diffusion coefficients are calculated. For the system dodecane (1) - hexadecane (2) - hexane (3), these curves are given in Figures 8 and 9. It can be seen that linear behavior does occur. The slopes and intercepts of these curves for this hydrocarbon system are presented in Table 16 of Appendix VI. The ternary

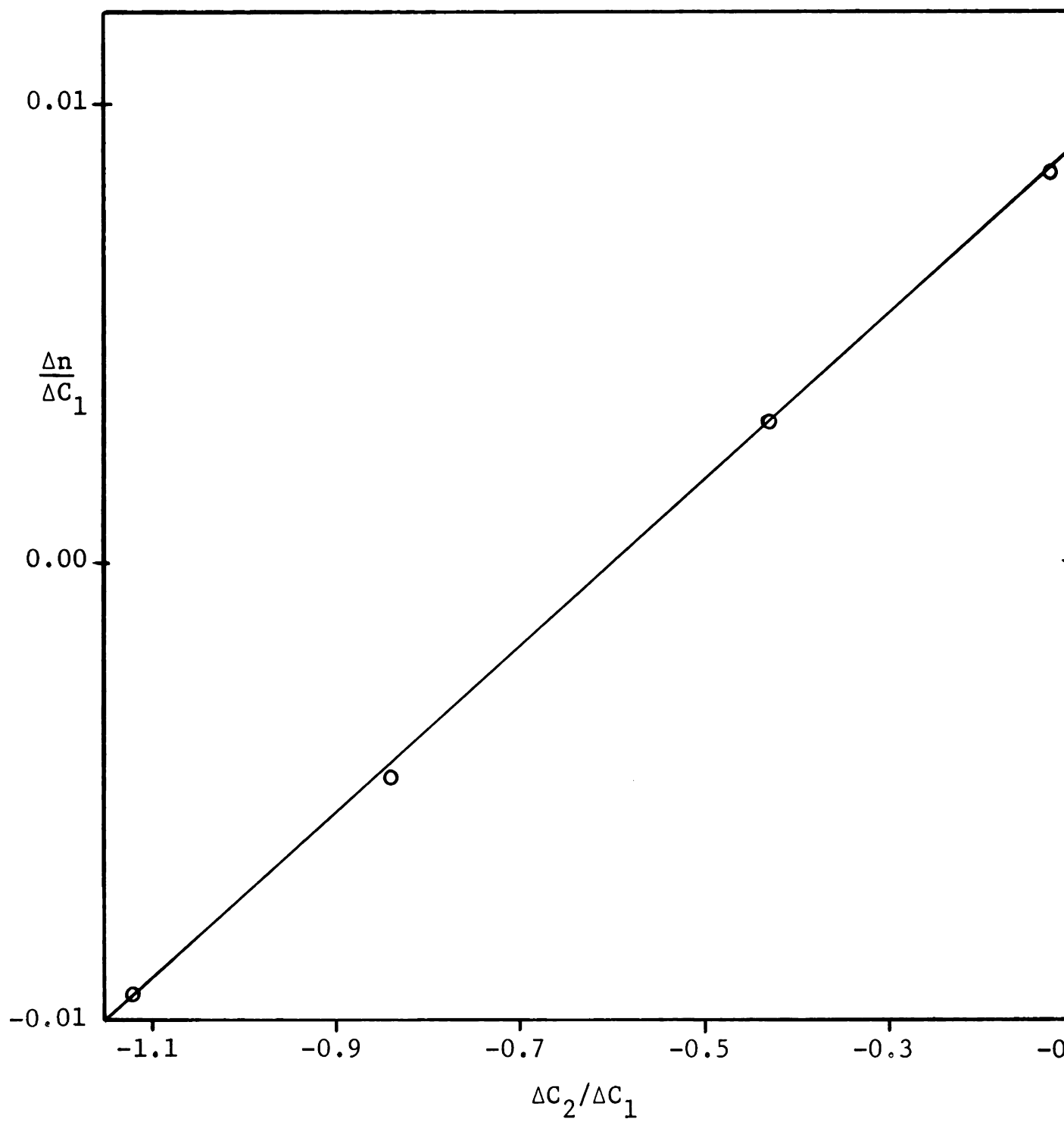


Figure 6. Determination of the differential refractive index increments, R_1 and R_2 , for the system dodecane (1) - hexadecane (2) - hexane (3).

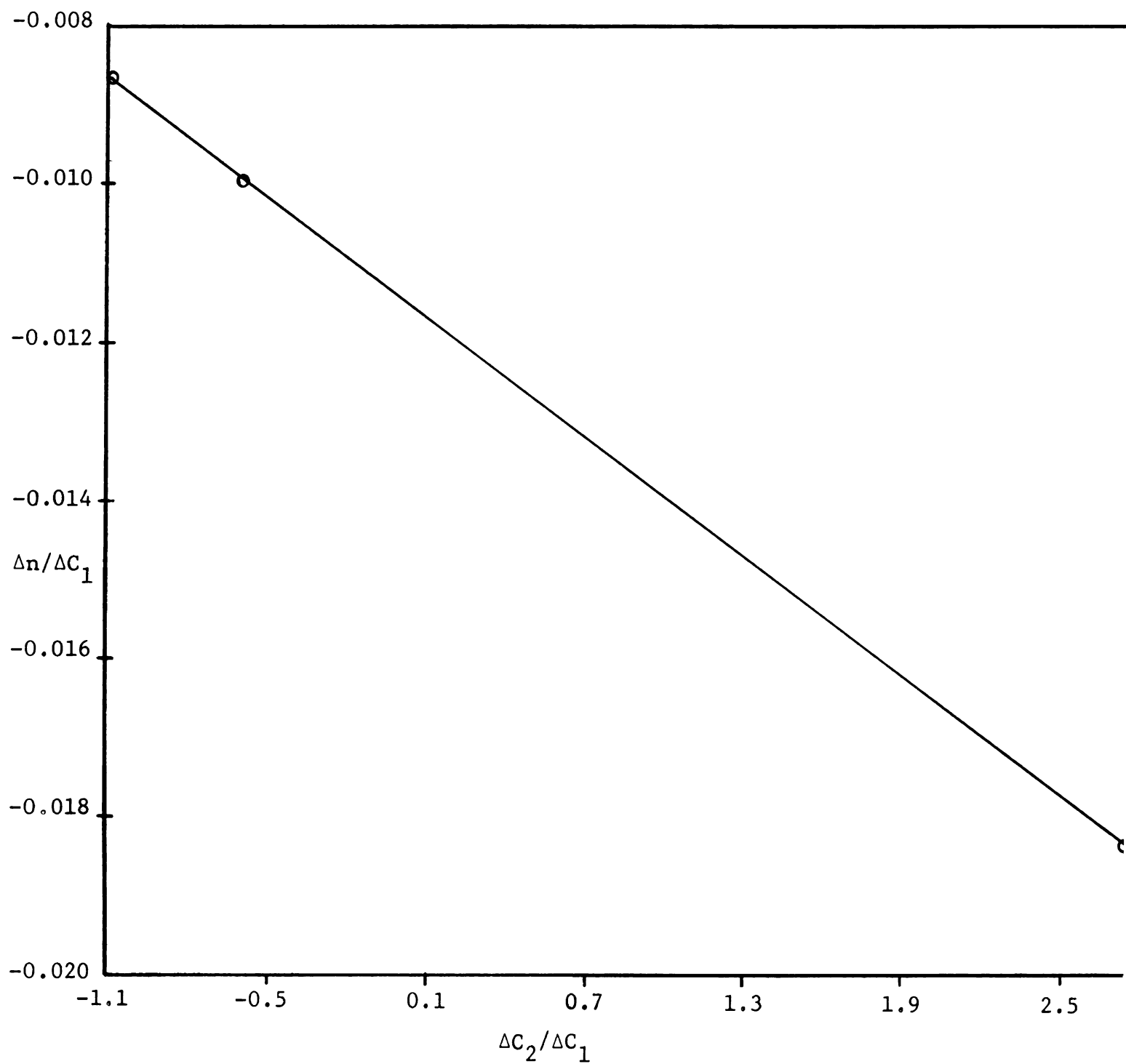


Figure 7. Determination of the differential refractive index increments, R_1 and R_2 , for the system diethyl ether (1) - chloroform (2) - carbon tetrachloride.

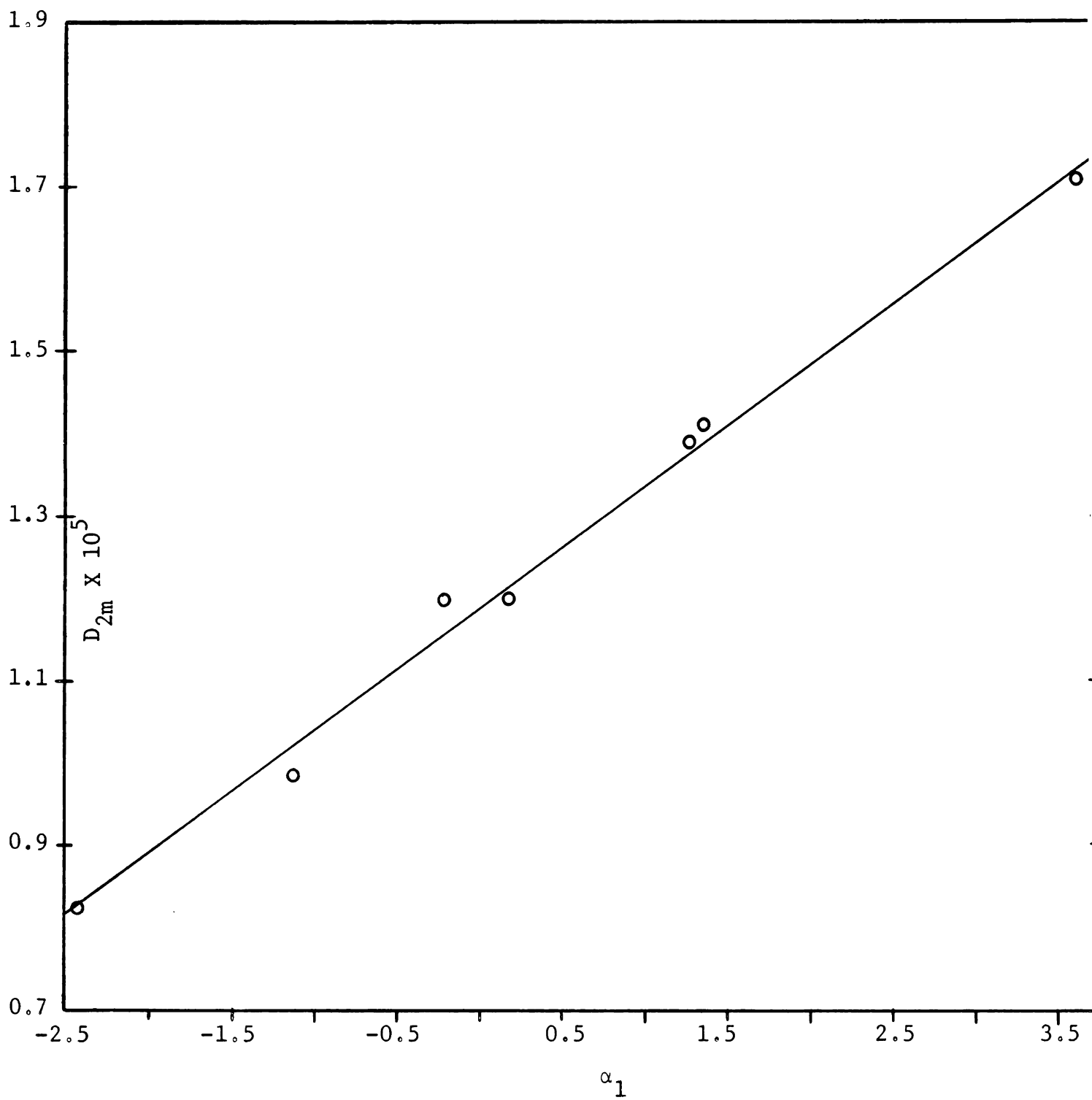


Figure 8. Linear relation of the reduced second moment, D_{2m} , versus the refractive index fraction of dodecane, α_1 , for the system dodecane (1) - hexadecane (2) - hexane (3).

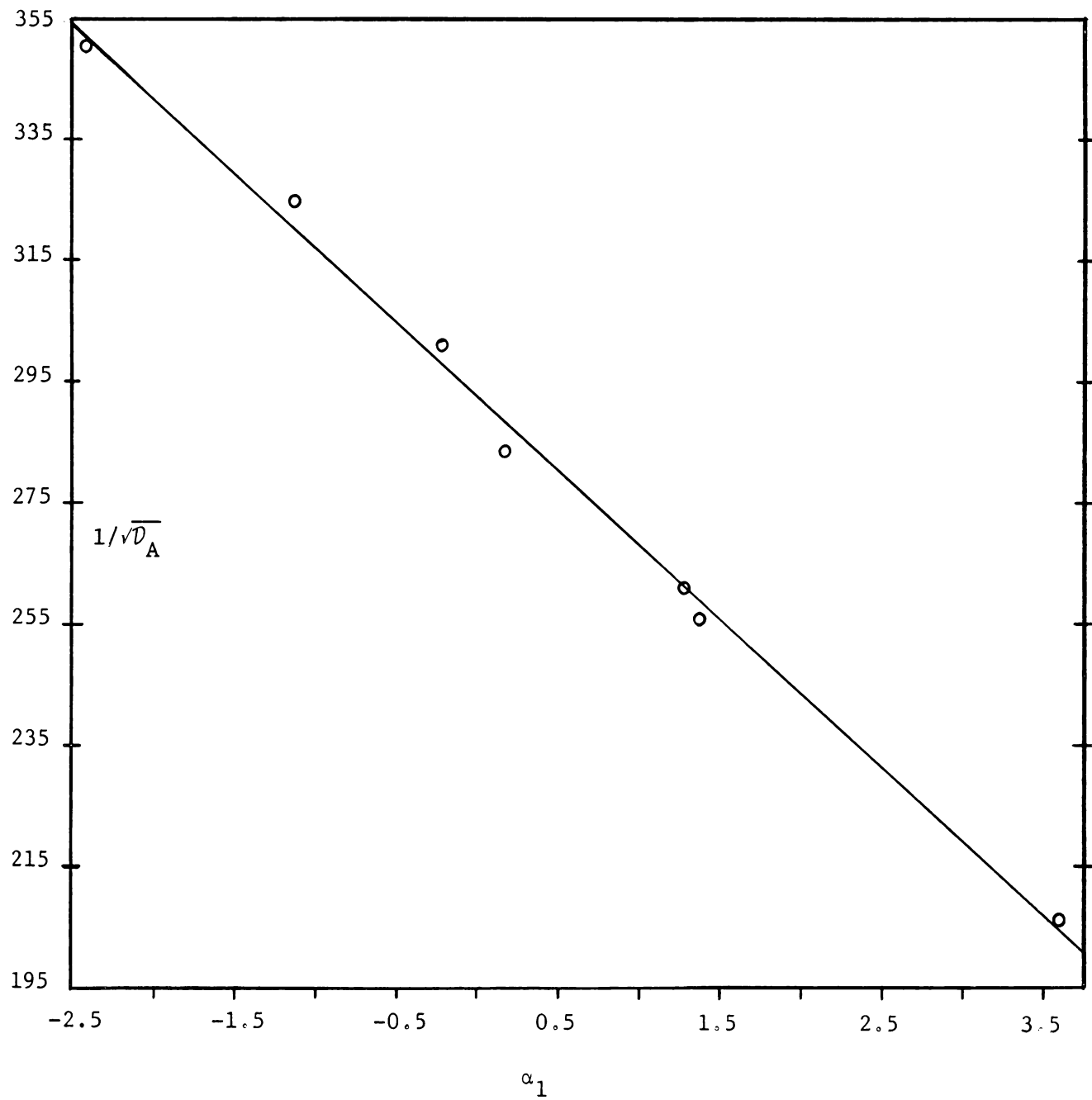


Figure 9. Linear relation of the reciprocal square root of the reduced height-area ratio, $1/\sqrt{D_A}$, versus the refractive index fraction of dodecane, α_1 , for the system dodecane (1) - hexadecane (2) - hexane (3).

diffusion coefficients obtained from these slopes and intercepts along with the phenomenological coefficients calculated from these diffusion coefficients are given in Table 5.

In determining experimental diffusion coefficients and phenomenological coefficients based on the hydrodynamic model, experimental or predictive friction coefficients were required. For the hydrocarbon system, these were obtained both ways. This fulfilled two purposes: (1) to obtain accurate values of the friction coefficients thus placing more confidence on the diffusion and phenomenological coefficients calculated from them and (2) to check on the predictive method of calculating friction coefficients. Values of the friction coefficients calculated by both methods are given in Table 4. Comparison shows that the predicted friction coefficients compared quite favorably with those obtained experimentally by tracer methods. The poorer agreement of the friction factor for hexadecane was probably caused by error in estimating the self diffusion coefficient of the hexadecane. The lack of self diffusion data for hydrocarbons higher than decane is evident from Figure 16. The fact that the molar volumes of the hydrocarbons differed considerably and that friction coefficients for the same component calculated from the infinitely dilute binary diffusion coefficients and self diffusion coefficients differed appreciably indicated that the effects of the other components were strong. Under these conditions, the predictive method for non-associating systems would be the poorest. With this in mind, the agreement between the experimental and predicted friction

Table 4. Comparison of the estimated and the experimentally
determined friction coefficients for the system
dodecane (1) - hexadecane (2) - hexane (3)

$$T = 25^{\circ}\text{C}$$

$$X_1 = 0.350 \quad X_2 = 0.317$$

$(RT/\sigma_1) \times 10^7$ dynes		$(RT/\sigma_2) \times 10^7$ dynes		$(RT/\sigma_3) \times 10^7$ dynes	
Estimated (Equation 162)	Tracer	Estimated (Equation 162)	Tracer	Estimated (Equation 162)	Tracer
1.089	1.118	1.062	0.848	1.899	1.873

Table 5. Comparison of experimental diffusion and phenomenological coefficients with those calculated from friction coefficients for the system dodecane (1) - hexadecane (2) - hexane (3)

$$T = 25^{\circ}\text{C}$$

$$X_1 = 0.350$$

$$X_2 = 0.317$$

$D_{11} \times 10^5$ (cm ² /sec)			$D_{12} \times 10^5$ (cm ² /sec)			$D_{21} \times 10^5$ (cm ² /sec)			$D_{22} \times 10^5$ (cm ² /sec)		
Expt.	Calculated		Expt.	Calculated		Expt.	Calculated		Expt.	Calculated	
	Est. Tracer			Est. Tracer			Est. Tracer			Est. Tracer	
0.968	1.082	1.115	0.266	0.270	0.386	0.225	0.209	0.167	1.031	1.123	0.971

$L_{12} \times RT \times 10^5$			$L_{21} \times RT \times 10^5$		
Experimental	Calculated		Experimental	Calculated	
	Est.	Tracer		Est.	Tracer
-0.453	-0.538	-0.465	-0.444	-0.538	-0.465

coefficients under the least applicable conditions provides reasonable confidence in the predictive method.

The diffusion and phenomenological coefficients calculated from the friction coefficients (equations 39 and 61) are given in Table 5. In comparing the values obtained by optical methods to those predicted from hydrodynamic equations it can be seen that there is good agreement. In fact, the agreement of L_{12} and L_{21} appears to be better than that found by other authors on other systems. This conclusion may not be justified, however, since no comparison between the accuracy of experimental methods can be made. The hydrodynamically obtained values are well within the expected accuracy of the experimental values.

The agreement of the experimental L_{12} and L_{21} and the agreement of these with the $L_{12} = L_{21}$ obtained from the friction coefficients indicates that Onsager's reciprocal relations are valid.

Toluene-Chlorobenzene-Bromobenzene

Experimental diffusion coefficients were obtained by Burchard and Toor⁷ using a modification of the diaphragm cell technique. Based on the fact that this apparatus gives less accurate binary values than the apparatus used in this laboratory, it is reasonable to assume that the ternary diffusion coefficients are less accurate than those obtained in this laboratory.

This system was assumed ideal and on this basis phenomenological coefficients were determined from the diffusion coefficients given by Burchard and Toor. Friction coefficients were obtained by the predictive method. The fact that the molar volumes

were almost equal and that the friction coefficients calculated from the infinitely dilute binary diffusion coefficients were approximately equal, indicated that reasonable values of the friction coefficients could be expected.

Table 6 lists the diffusion and phenomenological coefficients. Excellent agreement between the hydrodynamically obtained values and experimental values can be seen from a comparison. Except for very few cases, the values obtained from friction coefficients were well within the 95% confidence limits. Reasonable agreement between the experimental L_{12} and L_{21} is evident and these agree favorably with those obtained from the hydrodynamic approach. Based on the results, this author feels that Onsager's reciprocal relations are verified for this system.

Associative Systems

Diethyl Ether-Chloroform-Carbon Tetrachloride

For this system plots of the reduced second moment, D_{2m} , and the reciprocal square root of the reduced height-area ratio, $1/\sqrt{\mathcal{D}_A}$, against the refractive index fraction, α_1 , are presented in Figures 10 and 11. It can be seen that these curves exhibit the linear behavior predicted by the experimental equations, 152 and 153. The slopes and intercepts of these curves are given in Table 16 of Appendix VI and the resulting experimental diffusion and phenomenological coefficients are presented in Table 7.

Table 6. Comparison of experimental diffusion and phenomenological coefficients with those calculated from friction coefficients for the system toluene (1) - chlorobenzene (2) - bromobenzene (3)

T = 30 °C											
x_1	x_2	$D_{11} \times 10^5$		$D_{12} \times 10^5$		$D_{21} \times 10^5$		$D_{22} \times 10^5$			
		Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.		
0.25	0.50	1.848 ± 0.066	1.822	-0.063 ± 0.109	-0.019	-0.052 ± 0.093	-0.073	1.797 ± 0.076	1.753		
0.26	0.03	1.570 ± 0.088	1.611	-0.077 ± 0.100	-0.033	-0.012 ± 0.033	-0.006	1.606 ± 0.109	1.580		
0.70	0.15	2.132 ± 0.098	2.069	0.051 ± 0.163	-0.063	-0.071 ± 0.026	-0.039	2.062 ± 0.108	2.071		
0.15	0.70	1.853 ± 0.108	1.819	0.049 ± 0.162	-0.009	-0.068 ± 0.026	-0.072	1.841 ± 0.108	1.750		
0.45	0.25	2.006 ± 0.108	1.883	-0.020 ± 0.026	-0.043	-0.198 ± 0.163	-0.052	1.890 ± 0.108	1.844		
0.18	0.28	1.774 ± 0.107	1.656	-0.037 ± 0.026	-0.019	0.003 ± 0.162	-0.049	1.518 ± 0.107	1.593		

x_1	x_2	$L_{12} \times RT \times 10^5$		$L_{21} \times RT \times 10^5$			
		Experimental	Calculated	Experimental	Calculated		
0.25	0.50	-2.384	-2.248	-2.265	-2.248		
0.26	0.03	-0.145	-0.136	-0.148	-0.136		
0.70	0.15	-2.048	-2.123	-2.175	-2.123		
0.15	0.70	-1.778	-1.856	-1.943	-1.856		
0.45	0.25	-2.212	-2.119	-2.502	-2.119		
0.18	0.28	-0.961	-0.868	-0.758	-0.868		

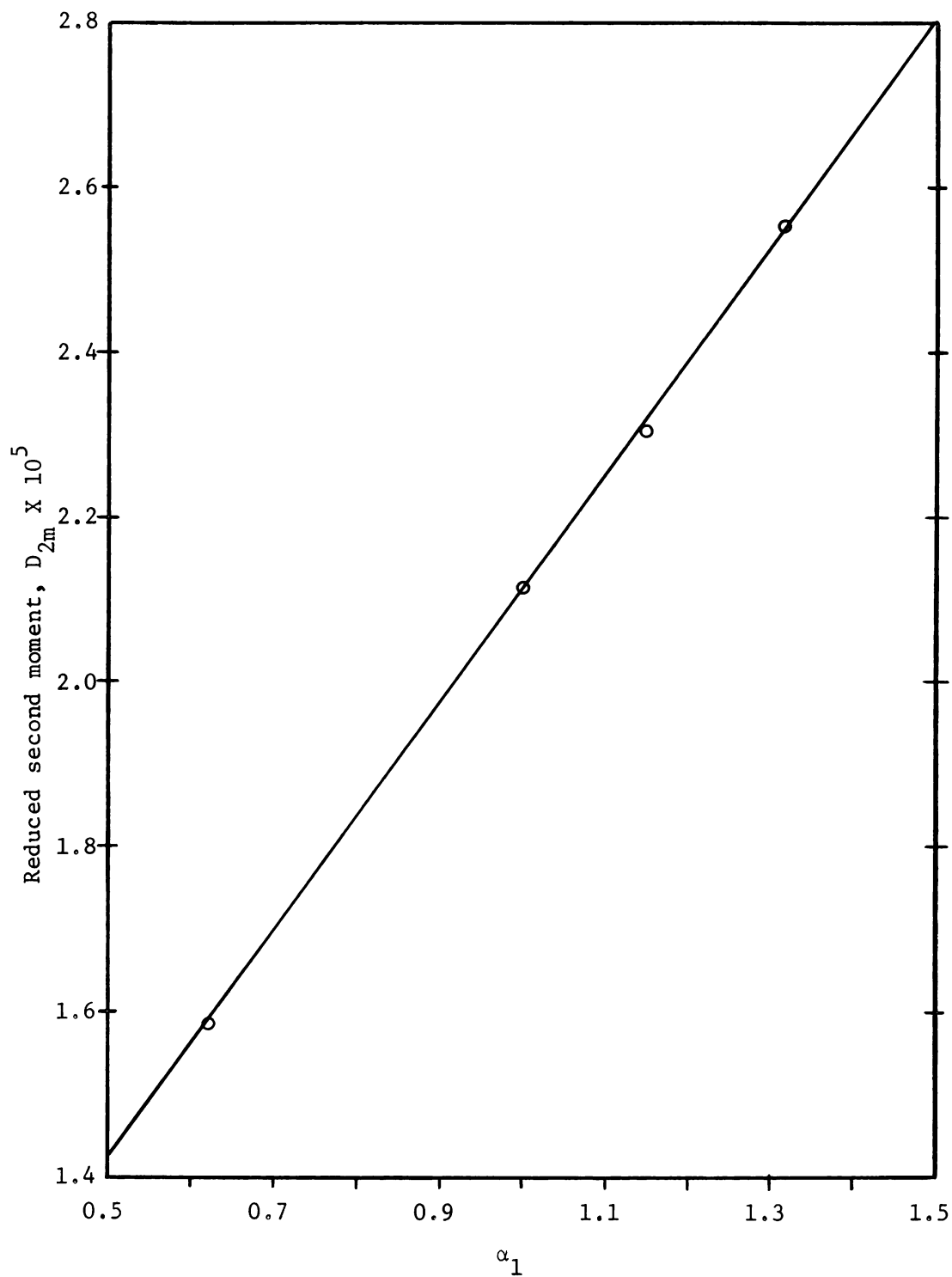


Figure 10. Linear relation of the reduced second moment, D_{2m} , versus the refractive index fraction of diethyl ether, α_1 , for the system diethyl ether (1) - chloroform (2) - carbon tetrachloride (3).

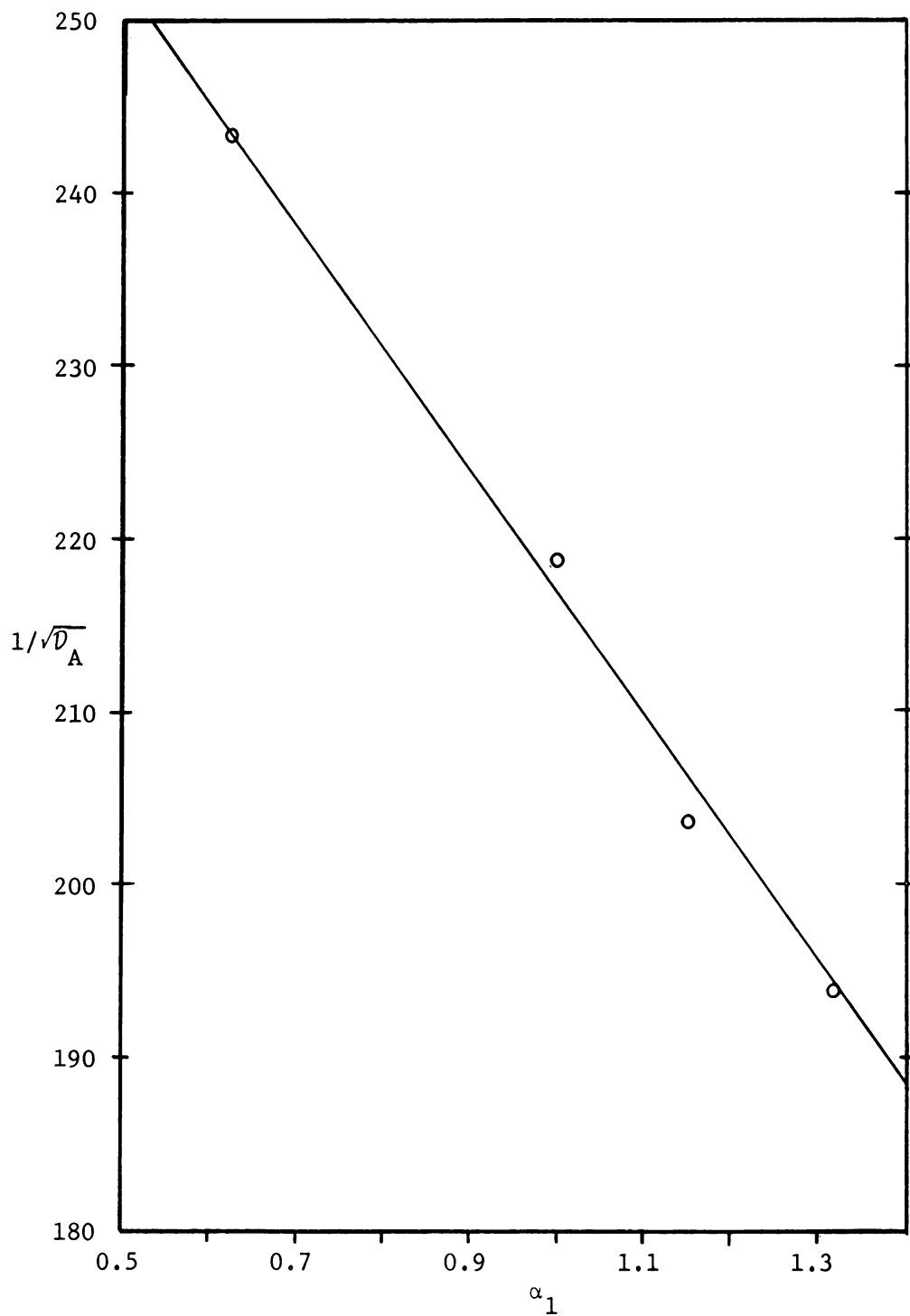


Figure 11. Linear relation of the reciprocal square root of the reduced height-area ratio, $1/\sqrt{D_A}$, versus the refractive index fraction of diethyl ether, α_1 , for the system diethyl ether (1) - chloroform (2) - carbon tetrachloride (3).

Table 7. Comparison of experimental diffusion and phenomenological coefficients with those calculated from friction coefficients for the system diethyl ether(1)-chloroform (2) - carbon tetrachloride (3)

$$T = 25^{\circ}\text{C}$$

$$X_1 = 0.25 \quad X_2 = 0.25$$

$D_{11} \times 10^5$		$D_{12} \times 10^5$		$D_{21} \times 10^5$		$D_{22} \times 10^5$	
Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
2.06	2.76	-0.31	-0.34	0.23	-0.42	2.11	2.23

$L_{12} \times RT \times 10^5$		$L_{21} \times RT \times 10^5$	
Experimental	Calculated	Experimental	Calculated
-0.709	-0.824	0.209	-0.824

The necessity of having reliable activity data is clearly brought out here. No experimentally determined ternary activity data were available for this system. As a result, the associated-model of Wirth⁴⁷ and Anderson^{1,2} was assumed here. This model says that there are four species in solution, the monomers of all three components and the associated dimer of diethyl ether and chloroform. In addition, the model assumes that these four species together form an ideal solution thus assuming that all non-ideality in this solution is caused by the association. For the diethyl ether-chloroform binary, the above model was found by Anderson^{1,2} to be quite good. The importance of assuming that the species form an ideal solution is that then activity data for the components can be obtained without experimentally measuring pressures, etc. The required ternary activity expressions were calculated in Appendix III.

The experimental diffusion coefficients were assumed to be reliable. However, the phenomenological coefficients, calculated from the diffusion coefficients and the required activity expressions, were far from equal. The friction coefficients used to calculate diffusion coefficients were determined by Wirth⁴⁷ and were assumed to be reasonable. These diffusion coefficients did not compare favorably with the experimental diffusion coefficients. It can be seen that reasonable agreement exists between the D_{12} and D_{22} respectively, but this was considered fortuitous.

There were two possible reasons for this disagreement assuming that the experimental work was satisfactory: (1) that the

hydrodynamic approach as applied to associating systems was not correct and/or (2) that the activity data obtained assuming the chemical model was incorrect. It is highly likely that only the latter was the cause. This belief is based on the fact that the vapor-liquid equilibrium data and the mutual diffusion data of the carbon tetrachloride-chloroform binary were not ideal. According to the chemical model, this binary should be ideal since no association has been detected. The equilibrium and diffusion data are presented by Wirth.⁴⁷ It was admitted by Wirth that the diffusion data may not be reliable since difficulties in duplicating it were encountered. In any case, it can easily be seen from his data, that the general trend was far from ideal. If ideal, a plot of $D_{AB} \eta$ versus mole fraction gives a straight line but this plot was quite curved especially in the region towards pure chloroform. The fact that difficulties of duplication were experienced may also reflect the non-idealities of the system. Since the ternary chemical model, assumed to calculate activities, considered this binary as ideal, it is quite reasonable to assume that the activities calculated from this model are in error.

The purpose of studying this system was two-fold, to check the ternary chemical model and the applicability of the hydrodynamic theory as applied to associating systems. It can be concluded from this study that the proposed ternary chemical model is incorrect. Since the validity of the model, or at least partial validity, is necessary in order to experimentally verify the

applicability of the hydrodynamic approach, no justifiable conclusions on the latter can be drawn.

Acetone-Benzene-Carbon Tetrachloride

This system can be classified as an associated system but the actual species present are difficult to predict. However, since experimental data had been collected and activity data for all three binaries were available, it was hoped that some use of the system as a check on the hydrodynamic theory could be made.

To do this, the system was treated as a non-associating system and friction coefficients calculated for each component from binary and self diffusion data. These friction coefficients are not coefficients for any particular species but rather overall factors proposed to give approximate diffusion coefficients for any system. In this sense, friction coefficients calculated in this way serve as a predictive method of obtaining multicomponent diffusion data. In any case, if the hydrodynamic theory could lead to an approximate or predictive method of determining reasonable multicomponent diffusion coefficients, it would certainly provide some faith in the theory.

Friction coefficients were obtained according to equation 162 and the values are recorded in Table 17 of Appendix VI. From these, the ternary diffusion and phenomenological coefficients were obtained and are given in Table 8 along with the experimental values obtained by the diaphragm cell technique. It is evident that indeed the values do compare favorably and are certainly of the right order of magnitude. It is quite possible

Table 8. Comparison of experimental diffusion and phenomenological coefficients with those calculated from friction coefficients for the system acetone (1) - benzene (2) - carbon tetrachloride (3)

T = 25 °C

x_1	x_2	$D_{11} \times 10^5$		$D_{12} \times 10^5$		$D_{21} \times 10^5$		$D_{22} \times 10^5$	
		Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
0.30	0.35	1.887	1.731	-0.213	-0.274	-0.037	-0.029	2.255	2.226
0.15	0.15	1.598	1.532	-0.058	-0.176	-0.083	-0.113	1.812	1.731
0.15	0.70	1.961	2.200	0.013	-0.131	-0.149	-0.251	1.929	2.072
0.70	0.15	2.330	2.366	-0.432	-0.485	0.132	0.146	2.971	3.236
0.09	0.90	3.105	2.499	0.550	-0.071	-0.780	-0.410	1.860	2.065
0.24	0.75	3.069	2.268	0.603	-0.180	-0.638	-0.059	1.799	2.352
0.49	0.50	2.857	2.263	0.045	-0.365	-0.289	0.253	2.471	2.884
0.74	0.25	3.251	2.702	-0.011	-0.563	-0.301	0.252	2.896	3.493
0.895	0.095	3.475	3.162	-0.158	-0.691	0.108	0.122	3.737	3.905

x_1	x_2	$L_{12} \times RT \times 10^5$		$L_{21} \times RT \times 10^5$	
		Experimental	Calculated	Experimental	Calculated
0.30	0.35	-0.283	-0.280	-0.286	-0.280
0.15	0.15	-0.026	-0.041	-0.036	-0.041
0.15	0.70	-0.216	-0.277	-0.243	-0.277
0.70	0.15	-0.461	-0.475	-0.437	-0.475
0.09	0.90	-0.230	-0.230	-0.252	-0.230
0.24	0.75	-0.594	-0.567	-0.604	-0.567
0.49	0.50	-1.068	-0.974	-1.072	-0.974
0.74	0.25	-0.969	-0.943	-0.975	-0.943
0.895	0.095	-0.498	-0.517	-0.496	-0.517

that they are within the experimental accuracy of the method. Only in the case where the concentration of one of the three components is almost zero do the predicted values show any appreciable discrepancy. Better agreement occurs between the main diffusion coefficients, D_{11} and D_{22} , but the cross diffusion coefficients are in the right order of magnitude, and close in comparison, when one considers that they are much smaller and more subject to experimental error. Surprisingly close agreement among the phenomenological coefficients was also obtained.

The fact that this predictive method produced reasonable results is encouraging and indicates that hydrodynamic theory can be applied to multicomponent associating systems with some success. It should be cautioned that the associating system studied was not a particularly strong associating system and thus poorer agreement could be expected in more highly associative systems.

CONCLUSIONS

It can be concluded from this study that hydrodynamic theory should play an important role in describing multicomponent liquid diffusion. It predicts that Onsager's reciprocal relations should be valid for non-associating systems of any number of components. Furthermore, it leads to generalized equations which enable the calculation of diffusion coefficients for quaternary and higher order non-associating systems from friction coefficients, which can be accurately obtained directly from tracer measurements, and activity data. The number of tracer runs required is equal to the number of components in the system. Calculation of diffusion coefficients in this way would eliminate the laborious and time-consuming techniques now available and provide data for systems of higher order than ternary. Such data, currently not available, would be extremely useful in considering multicomponent mass flow problems.

Experimental evidence obtained in this study verifies the Onsager reciprocal relations for non-associating systems within the limits of experimental error. In addition, it demonstrates the validity and applicability of hydrodynamic theory to liquid diffusion. These conclusions were based on the fact that good agreement between the diffusion and phenomenological coefficients obtained by optical

methods and those obtained from friction coefficients was found for the non-associating systems studied.

Hydrodynamic theory applied to simple ternary associating systems in which only dimers are formed indicates that Onsager's reciprocal relations are valid provided the molar volume of the dimer can be considered as the sum of the molar volumes of the species associating to form the dimer. An attempt to describe an associating system by the chemical model which states that the actual species in solution form an ideal solution was not satisfactory. Since ternary activity data were not available and since the model would have predicted the missing activity data, the reciprocal relations for associating systems could not be experimentally verified.

It was found that for associating systems of unknown association reasonable diffusion data could be obtained by treating the system as non-associating and calculating friction factors for each of the chemicals added to form the system. In this way, the hydrodynamic approach served as a useful predictive method. It should be noted however that the predicted data would probably be less reliable in more highly associated systems.

FUTURE WORK

Theoretical

An important area opened up in this study was the application of hydrodynamic theory to associating systems. It would be worthwhile to try to obtain generalized expressions for the fluxes, diffusion coefficients, and phenomenological coefficients in terms of friction coefficients for systems in which there might be dimers, trimers, tetramers, etc., in various combinations among the components. In addition, it is hoped that the hydrodynamic theory can be applied to the simplest associating systems such that the assumption concerning the molar volume of the associating species would not be necessary in order to show that Onsager's reciprocal relations are valid.

A further area of development would be with systems in which the kinds of associated species are not known. It was found in this study for the system acetone-benzene-carbon tetrachloride that using overall friction coefficients for a component gave reasonable diffusion coefficients. Maybe refinement in this area could produce an improved predictive method for associating systems by combining hydrodynamic theory and binary diffusion data.

A critical factor in using hydrodynamic theory is the calculation of friction coefficients. A better understanding of the

effects of composition is certainly needed. Improved methods of determining their values for associated systems at various compositions would also be helpful.

Experimental

There is considerable room for improvement in this area. To obtain ternary diffusion data, time-consuming calculations and lengthy experimental work is required. Considerable error is introduced in the method of calculations which uses the slopes and intercepts from a plot of slopes from other curves and involves differences of small numbers in the same order of magnitude. Improved techniques in taking measurements from the photographic plates are also desirable. The improvement in the experimental area of multicomponent diffusion is not needed so much in the apparatus but rather in the application of the apparatus.

It seems almost ludicrous to speak of development in experimental techniques with quaternary systems when the techniques in ternary systems are not yet well developed, but such data could be extremely useful in checking the hydrodynamic predictions presented in this study for higher order systems. Activity data are a very limiting factor in multicomponent diffusion since they are required and yet are not sufficiently available. In the last few years, more and more ternary data have become available and even some quaternary data have been reported. However, most of these are not collected at constant temperature but rather at constant pressure. It is suggested that careful consideration be

given to the systems chosen before any experimental diffusion work is performed to see that adequate activity data are available. It would of course be convenient if activity data could be collected in conjunction with the multicomponent diffusion studies.

APPENDIX I

Determination of Friction Coefficients

The crux of the hydrodynamic method is obtaining reliable values of the friction coefficients, σ_i . For the non-associating case, these can be obtained directly by tracer techniques.

In tracer diffusion, the concentration is uniform throughout the system and, as a result, the velocities of all reference planes relative to fixed coordinates are zero. That is

$$v_{m,c} = v_{V,c} = 0 \quad (I-1)$$

Thus, equation 16 reduces to

$$J_i^* = J_i^m = - \frac{C_i^*}{\sigma_i^* \eta} \frac{\partial \mu_i^*}{\partial x} \quad (I-2)$$

where the superscript * refers to the tagged species. Substituting for chemical potential from equation 37, equation I-2 becomes

$$J_i^* = - \frac{C_i^*}{\sigma_i^* \eta} RT \frac{\partial \ln a_i^*}{\partial x} \quad (I-3)$$

which can be rearranged to give

$$J_i^* = - \frac{RT}{\sigma_i^* \eta} \frac{\partial \ln a_i^*}{\partial \ln C_i^*} \frac{\partial C_i^*}{\partial x} \quad (I-4)$$

The tracer diffusion coefficient which is measured is defined by

$$J_i^* = - D_i^* \frac{\partial C_i^*}{\partial x} \quad (I-5)$$

Therefore, by comparing equations I-4 and I-5, the measured diffusion coefficient D_i^* is

$$D_i^* = \frac{RT}{\sigma_i^* n} \frac{\partial \ln a_i^*}{\partial \ln C_i^*} \quad (I-6)$$

If we make the reasonable assumption that the physical properties of the labeled species are the same as the unlabeled species, then

$$\sigma_i^* = \sigma_i \quad (I-7)$$

For the case of tracer diffusion,

$$\frac{\partial \ln a_i^*}{\partial \ln C_i^*} = 1 \quad (I-8)$$

Therefore, from equations I-6 and I-8

$$D_i^* = \frac{RT}{\sigma_i n} \quad (I-9)$$

and hence

$$\sigma_i = \frac{D_i^* n}{RT} \quad (I-10)$$

Thus, by tagging each component separately and keeping the concentrations the same as those at which diffusion coefficients, D_{ij} , are

measured, all of the friction coefficients can be determined. If there are N components, N tracer runs would of course be required to obtain the N friction coefficients.

If tagged species are not available, reasonable values of the friction coefficients can be obtained from the infinitely dilute mutual diffusion coefficients of the binaries and the self diffusion coefficients of the binaries and the self diffusion coefficients of the pure components. Hartley and Crank²⁷ and others have shown that

$$D_{AB} = \frac{RT}{\eta} \left(\frac{X_A}{\sigma_B} + \frac{X_B}{\sigma_A} \right) \frac{\partial \ln a_A}{\partial \ln X_A} \quad (\text{I-11})$$

where D_{AB} is the mutual diffusion coefficient of the A-B binary. At infinite dilution of component A, equation I-11 becomes

$$D_{AB}^o = \frac{RT}{\sigma_A \eta_B} \quad (\text{I-12})$$

and therefore

$$\sigma_A = \frac{RT}{D_{AB}^o \eta_B} \quad (\text{I-13})$$

where D_{AB}^o is the mutual diffusion coefficient of the A-B binary at infinite dilution of A and η_B is the viscosity of pure B. In a ternary system, two such values of σ_A can be obtained from the A-B and A-C binaries; similarly, for σ_B and σ_C .

Another value of the friction coefficient can be obtained from the self diffusion coefficient, D_i , of the pure component. Again, Hartley and Crank²⁷ and others have shown that

$$\sigma_i = \frac{RT}{D_i \eta_i} \quad (\text{I-14})$$

In summary, if self diffusion data and binary data at infinite dilution in each component are available, several values for each σ_i can be obtained. These values will be reasonably constant if the friction coefficient is independent of the other species present. A reasonable value of σ_i is therefore a weighted average based on mole fraction. Thus,

$$\sigma_{i, \text{pred.}} = \frac{RT}{D_i \eta_i} + \sum_{\substack{j=1 \\ j \neq i}}^N \frac{RT}{D_{ij}^o \eta_j} X_j \quad i = 1, \dots, N \quad (\text{I-15})$$

where $\sigma_{i, \text{pred.}}$ is the predicted friction coefficient.

Determination of σ_i in associated systems has been described by Wirth⁴⁷. This method also involves tracer techniques.

APPENDIX II

Solution to the Ternary Diffusion Equations and the Experimental Determination of the Diffusion Coefficients²²

Solution to the Diffusion Equations

The flow equations for a ternary system can be obtained from equation 26. They are repeated here for convenience.

$$\begin{aligned} J_1 &= -D_{11} \frac{\partial C_1}{\partial x} - D_{12} \frac{\partial C_2}{\partial x} \\ J_2 &= -D_{21} \frac{\partial C_1}{\partial x} - D_{22} \frac{\partial C_2}{\partial x} \end{aligned} \quad (\text{II-1})$$

To obtain the equations for one-dimensional diffusion in a three-component system, it is first assumed that the diffusion coefficients are all independent of concentration and that no volume change occurs on mixing. These conditions can be approached experimentally by keeping the concentration differences across the initial boundary sufficiently small. By making a material balance on a differential volume element of the diffusion solution, the desired relations are then obtained. These are

$$\frac{\partial C_1}{\partial t} = D_{11} \frac{\partial^2 C_1}{\partial x^2} + D_{12} \frac{\partial^2 C_2}{\partial x^2} \quad (\text{II-2})$$

$$\frac{\partial C_2}{\partial t} = D_{21} \frac{\partial^2 C_1}{\partial x^2} + D_{22} \frac{\partial^2 C_2}{\partial x^2} \quad (\text{II-2})$$

in which C_1 and C_2 are the concentrations of any two components and are functions of position x and time t . D_{11} and D_{22} are the main diffusion coefficients which are generally on the order of mutual diffusion coefficients in binaries, and D_{12} and D_{21} are the cross-term diffusion coefficients which are considerably smaller than the main coefficients. For free diffusion a sharp boundary is formed at $t = 0$ between solutions A and B which are above and below respectively the position $x = 0$. As a result, the initial conditions for the two components ($i = 1, 2$) are

$$\begin{aligned} C_i &= \bar{C}_i - \Delta C_i / 2 & x > 0, \quad t = 0 \\ C_i &= \bar{C}_i + \Delta C_i / 2 & x < 0, \quad t = 0 \end{aligned} \quad (\text{II-3})$$

and the boundary conditions are

$$\begin{aligned} C_i &\rightarrow \bar{C}_i - \Delta C_i / 2 & x \rightarrow +\infty, \quad t > 0 \\ C_i &\rightarrow \bar{C}_i + \Delta C_i / 2 & x \rightarrow -\infty, \quad t > 0 \end{aligned} \quad (\text{II-4})$$

Here \bar{C}_i is the mean concentration of each component and ΔC_i is the concentration difference of each component across the diffusing boundary.

They are defined as follows

$$\bar{C}_i = \frac{(C_i)_A + (C_i)_B}{2} \quad (\text{II-5})$$

$$\Delta C_i = (C_i)_B - (C_i)_A \quad (\text{II-6})$$

It is well known that under these initial and boundary conditions, a new variable, y , may be introduced to reduce equations

II-2 to a set of ordinary differential equations. The new variable y is given by

$$y = \frac{x}{(2\sqrt{t})} \quad (\text{II-7})$$

and the set of ordinary differential equations obtained is

$$\begin{aligned} -2y \frac{dC_1}{dy} &= D_{11} \frac{d^2 C_1}{dy^2} + D_{12} \frac{d^2 C_2}{dy^2} \\ -2y \frac{dC_2}{dy} &= D_{21} \frac{d^2 C_1}{dy^2} + D_{22} \frac{d^2 C_2}{dy^2} \end{aligned} \quad (\text{II-8})$$

In addition, equations II-4 - II-6 reduce to

$$\begin{aligned} C_i &\rightarrow \bar{C}_i - \frac{\Delta C_i}{2} & y &\rightarrow +\infty \\ C_i &\rightarrow \bar{C}_i + \frac{\Delta C_i}{2} & y &\rightarrow -\infty \end{aligned} \quad (\text{II-9})$$

The details in solving equations II-8 and II-9 for the concentrations of the components are given by Fujita and Gosting.²² The desired exact solutions which they obtained are

$$\begin{aligned} C_1 &= \bar{C}_1 + K_1^+ \phi(\sqrt{\sigma_+} y) + K_1^- \phi(\sqrt{\sigma_-} y) \\ C_2 &= \bar{C}_2 + K_2^+ \phi(\sqrt{\sigma_+} y) + K_2^- \phi(\sqrt{\sigma_-} y) \end{aligned} \quad (\text{II-10})$$

in which

$$\phi(q) = \frac{2}{\sqrt{\pi}} \int_0^q e^{-q^2} dq \quad (\text{II-11})$$

and where

$$\begin{aligned} \sigma_+ &= \frac{1}{2} \left\{ H + E + \left[(H - E)^2 + 4FG \right]^{\frac{1}{2}} \right\} \\ \sigma_- &= \frac{1}{2} \left\{ H + E - \left[(H - E)^2 + 4FG \right]^{\frac{1}{2}} \right\} \end{aligned} \quad (\text{II-12})$$

$$\begin{aligned} K_1^+ &= \frac{(\sigma_+ - E)\Delta C_1 - F\Delta C_2}{2(\sigma_+ - \sigma_-)} & K_1^- &= \frac{(\sigma_- - E)\Delta C_1 - F\Delta C_2}{2(\sigma_- - \sigma_+)} \\ K_2^+ &= \frac{(\sigma_+ - H)\Delta C_2 - G\Delta C_1}{2(\sigma_+ - \sigma_-)} & K_2^- &= \frac{(\sigma_- - H)\Delta C_2 - G\Delta C_1}{2(\sigma_- - \sigma_+)} \end{aligned} \quad (\text{II-13})$$

and

$$E = \frac{D_{11}}{|D_{ij}|}, \quad G = \frac{D_{21}}{|D_{ij}|}, \quad H = \frac{D_{22}}{|D_{ij}|}, \quad F = \frac{D_{12}}{|D_{ij}|} \quad (\text{II-14})$$

$$|D_{ij}| = D_{11}D_{22} - D_{12}D_{21} \quad (\text{II-15})$$

It should be noted that the equations for each component concentration are a linear combination of two probability integrals plus a constant term, with the characteristic of each term depending on ΔC_1 , ΔC_2 , and the four diffusion coefficients.

Determination of Diffusion Coefficients

In order to derive equations applicable to experimental techniques utilizing optical methods for studying free diffusion, it is assumed that the dependence of refractive index, n , on the two independent concentrations can be represented by the first three terms of a Taylor series. That is,

$$n = \frac{n}{C} + R_1(C - \bar{C}_1) + R_2(C_2 - \bar{C}_2) \quad (\text{II-16})$$

where R_1 and R_2 are the differential refractive index increments defined by

$$R_1 \equiv \left[\frac{\partial n(C_1, C_2)}{\partial C_1} \right]_{T, P, C_2} \bigg|_{C_1 = \bar{C}_1, C_2 = \bar{C}_2} \quad (II-17)$$

$$R_2 \equiv \left[\frac{\partial n(C_1, C_2)}{\partial C_2} \right]_{T, P, C_1} \bigg|_{C_1 = \bar{C}_1, C_2 = \bar{C}_2}$$

and \bar{n} is the refractive index of a solution in which the solute concentrations are \bar{C}_1 and \bar{C}_2 . R_1 and R_2 are assumed to be independent of concentration. Again, selecting small initial concentration differences justified this assumption. It follows from equation II-16 that the total change in refractive index across the boundary may be written as

$$\Delta n = R_1 \Delta C_1 + R_2 \Delta C_2 \quad (II-18)$$

For convenience component fractions on the basis of refractive index are defined by

$$\alpha_i = \frac{R_i \Delta C_i}{\sum_i R_i \Delta C_i} \quad (II-19)$$

It therefore follows from equation II-18 and II-19 that

$$\alpha_1 + \alpha_2 = 1 \quad (II-20)$$

For optical methods, it is desired to obtain the refractive index, n , as a function of x and t . This can be done by substituting

equations II-10 into equation II-16. The desired refractive index distribution expression which results is then

$$n = n_{\frac{c}{c}} + \frac{\Delta n}{2} \left[\Gamma_+ (\phi \sqrt{\sigma_+} y) + \Gamma_- \phi (\sqrt{\sigma_-} y) \right] \quad (\text{II-21})$$

where

$$\Gamma_+ = \frac{2}{\Delta n} (R_1 K_1^+ + R_2 K_2^+) \quad (\text{II-22})$$

$$\Gamma_- = \frac{2}{\Delta n} (R_1 K_1^- + R_2 K_2^-)$$

From the defining equations for Γ_+ and Γ_- , it can be shown that

$$\Gamma_+ + \Gamma_- = 1 \quad (\text{II-23})$$

The reduced height-area ratio is defined by

$$\mathcal{D}_A = \frac{(\Delta n)^2}{4\pi t \left[\left(\frac{\partial n}{\partial x} \right)_t \right]_{\max}^2} \quad (\text{II-24})$$

Substitution of the maximum value of the first derivative of equation II-21 into equation II-24 yields

$$\frac{1}{\sqrt{\mathcal{D}}_A} = \Gamma_+ \sqrt{\sigma_+} + \Gamma_- \sqrt{\sigma_-} \quad (\text{II-25})$$

Substituting equations II-13 into equations II-22 and making use of the relation $\alpha_1 + \alpha_2 = 1$, equation II-13 becomes

$$\frac{1}{\sqrt{\mathcal{D}}_A} = I_A + S_A \alpha_1 \quad (\text{II-26})$$

where

$$S_A = \frac{H + (R_1/R_2)F - E - (R_2/R_1)G}{\sqrt{\sigma_+} + \sqrt{\sigma_-}} \quad (\text{II-27})$$

$$I_A = \frac{\sqrt{\sigma_+ \sigma_-} + E - (R_1/R_2)F}{\sqrt{\sigma_+} + \sqrt{\sigma_-}} \quad (\text{II-28})$$

Thus a plot of $1/\sqrt{D_A}$ versus α_1 should produce a straight line with slope S_A and intercept I_A at $\alpha_1 = 0$. Another useful relation is the intercept at $\alpha_1 = 1$. This intercept, call it L_A , is given by

$$L_A = I_A + S_A = \frac{\sqrt{\sigma_+ \sigma_-} + H - (R_2/R_1)G}{\sqrt{\sigma_+} + \sqrt{\sigma_-}} \quad (\text{II-29})$$

It should be pointed out that equation II-26 gives two equations involving the four unknowns D_{11} , D_{12} , D_{21} , and D_{22} since E , F , G , H , σ_+ , and σ_- are expressions involving only the four diffusion coefficients. R_1 and R_2 can be experimentally determined. Therefore the slope, S_A , and intercept, I_A , are functions of the diffusion coefficients and R_1 and R_2 .

Obviously, two more independent equations involving the diffusion coefficients are necessary. These can be found from the reduced second moment of the refractive index gradient curves.

The r^{th} moment of the refractive index gradient curve, $(\partial n / \partial x)_t$ versus x , is defined by

$$m_r = \frac{1}{\Delta n} \int_{-\infty}^{+\infty} x^r \left(\frac{\partial n}{\partial x} \right)_t dx \quad r = 0, 1, 2, \dots \quad (\text{II-30})$$

and the reduced r^{th} moment, D_{rm} , is defined by

$$D_{rm} \equiv \frac{m_r}{2t} \quad (\text{II-31})$$

Differentiation of equation II-16 with respect to x and substitution of the result into equation II-30 yields

$$m_r = \frac{1}{\Delta n} \sum_{i=1}^2 R_i \int_{-\infty}^{+\infty} x^r \left(\frac{\partial C_i}{\partial x} \right)_t dx \quad (\text{II-32})$$

To facilitate the derivation, an r^{th} moment of each concentration gradient curve is defined as follows:

$$(m_r)_i \equiv \frac{R_i}{\Delta n} \int_{-\infty}^{+\infty} x^r \left(\frac{\partial C_i}{\partial x} \right)_t dx \quad (\text{II-33})$$

so that

$$m_{r1} + m_{r2} = m_r \quad (\text{II-34})$$

It should be emphasized that only m_r is a measurable quantity however.

Now differentiating equation II-33 with respect to time and then inverting the order of differentiation with respect to t and x gives

$$\frac{d(m_r)_i}{dt} = \frac{R_i}{\Delta n} \int_{-\infty}^{+\infty} x^r \left[\frac{\partial}{\partial x} \left(\frac{\partial C_i}{\partial t} \right)_x \right]_t dx \quad (\text{II-35})$$

These operations are permissible whenever the derivatives,

$\left[\frac{\partial (\partial C_i / \partial t)}{\partial x} \right]_t$ and $\left[\frac{\partial (\partial C_i / \partial x)}{\partial t} \right]_x$ are both continuous.^{11,29} By means of the continuity equation for a constant volume system, which says that

$$\left(\frac{\partial C_i}{\partial t} \right)_t = - \left(\frac{\partial J_i}{\partial x} \right)_t \quad (\text{II-36})$$

the fluxes J_i can be introduced. Substituting equation II-36 into equation II-35 and integrating once the right hand side by parts, gives

$$\frac{d(m_r)_i}{dt} = \frac{rR_i}{\Delta n} \int_{-\infty}^{+\infty} x^{r-1} \left(\frac{\partial J_i}{\partial x} \right)_t dx \quad (\text{II-37})$$

since for free diffusion, $(\partial J_i / \partial x)_t$ is zero at the limits $x = \pm\infty$.

Remembering that J_i is also zero at $x = \pm\infty$, another integration by parts gives

$$\frac{d(m_r)_i}{dt} = - \frac{r(r-1)R_i}{\Delta n} \int_{-\infty}^{+\infty} x^{r-2} J_i dx \quad (\text{II-38})$$

Recalling the assumption that the diffusion coefficients are independent of concentration, we now substitute equation II-1 into equation II-38 and integrate the resulting equations to obtain expressions for the moments.

$$\begin{aligned} \frac{d(m_r)_i}{dt} &= \frac{r(r-1)R_i}{\Delta n} \sum_{j=1}^2 D_{ij} \int_{-\infty}^{+\infty} x^{r-2} \left(\frac{\partial C_j}{\partial x} \right)_t dx \\ &= r(r-1) \sum_{j=1}^2 (R_i/R_j) D_{ij} (M_{r-2})_j \end{aligned} \quad (\text{II-39})$$

This equation is seen to be a recursion formula relating the time derivative of any even moment (r) to a sum of the next lower ($r-2$) even moments, and the time derivative of any odd moment to a sum of the next lower odd moments. Obviously its use depends on determining values for $(m_0)_j$ and $(m_1)_j$.

Integration of equation II-33 for $r = 0$ and substitution of equation II-19 gives an expression for $(m_o)_j$.

$$(m_o)_j = \alpha_j \quad (\text{II-40})$$

Remembering that $J_j = 0$ at $x = \pm\infty$, integration of equation II-38 for $r = 1$ gives

$$\frac{d(m_1)_j}{dt} = 0 \quad (\text{II-41})$$

indicating that the first moment of each concentration gradient curve is zero. Since it doesn't change with time, the first moment must correspond with the position of the initially sharp boundary. In our experiments the origin ($x = 0$) is chosen as the position of the initially sharp boundary, therefore

$$(m_1)_j = 0 \quad (\text{II-42})$$

The fact that $(m_1)_j = 0$ means that all the odd moments are zero; hence, as long as the diffusion coefficients, D_{ij} , and the refractive index increments, R_i , are independent of concentration, the refractive index gradient curve should be symmetrical about the position of the sharp initial boundary. This is indicated for a typical run in Figure 15 of Appendix VI.

Expressions for the even moments can be obtained from equation II-39. Substituting equation II-40 and $r = 2$ gives the second moment expression of component j .

$$(m_2)_i = 2t \sum_{j=1}^2 (R_i/R_j) D_{ij} \alpha_j \quad i = 1, 2 \quad (\text{II-43})$$

Expanding equation II-43 and substituting equation II-34 gives the relation

$$m_2 = 2t \left[(D_{11} + \frac{R_2}{R_1} D_{21}) \alpha_1 + (D_{22} + \frac{R_1}{R_2} D_{12}) \alpha_2 \right] \quad (\text{II-44})$$

Utilizing equation II-20 and rearranging, equation II-44 becomes

$$D_{2m} = \frac{m_2}{2t} = S_{2m} \alpha_1 + I_{2m} \quad (\text{II-45})$$

where D_{2m} is by definition the reduced second moment and the slope, S_{2m} , and intercept, I_{2m} , are

$$S_{2m} = D_{11} + \frac{R_2}{R_1} D_{21} - D_{22} - \frac{R_1}{R_2} D_{12} \quad (\text{II-46})$$

$$I_{2m} = D_{22} + \frac{R_1}{R_2} D_{12} \quad (\text{II-47})$$

The intercept at $\alpha_1 = 1$, L_{2m} is given by

$$L_{2m} = I_{2m} + S_{2m} = D_{11} + (R_2/R_1) D_{21} \quad (\text{II-48})$$

Equation II-45 indicates that a plot of D_{2m} versus α_1 should give a straight line with the slope, S_{2m} , and the intercepts at $\alpha_1 = 0$, I_{2m} , and at $\alpha_1 = 1$, L_{2m} , all being functions of the diffusion coefficients. Therefore, if at least two experimental runs are made at the same average concentration but with different initial concentration differences, values of the slopes and intercepts from plots of $1/\sqrt{D_A}$ versus α_1 and D_{2m} versus α_1 would enable determination of the diffusion coefficients.

It is desired to obtain expressions for the diffusion coefficients in closed form in terms of the slopes and intercepts. First of all, from equations II-27 and II-48 we can obtain the relation

$$|D_{ij}| (D_{11} + D_{22} + 2\sqrt{|D_{ij}|}) - (S_{2m}/S_A)^2 = 0 \quad (\text{II-49})$$

where $|D_{ij}| = \det D_{ij} = D_{11}D_{22} - D_{12}D_{21}$

Similarly, combining equations II-27, II-28, II-47, and II-48 gives

$$D_{11} + D_{22} = I_{2m} - I_A(S_{2m}/S_A) - \sqrt{|D_{ij}|} \quad (\text{II-50})$$

Elimination of $(D_{11} + D_{22})$ from equations II-49 and II-50 leads to a cubic equation in $\sqrt{|D_{ij}|}$ from which $|D_{ij}|$ can be determined either numerically or graphically. This cubic equation is

$$(\sqrt{|D_{ij}|})^3 + [I_{2m} - I_A(S_{2m}/S_A)] (\sqrt{|D_{ij}|})^2 - (S_{2m}/S_A)^2 = 0 \quad (\text{II-51})$$

Also combination of equations II-47 and II-48 with the definition of $|D_{ij}|$ gives

$$I_{2m} D_{11} + L_{2m} D_{22} = |D_{ij}| + I_{2m} L_{2m} \quad (\text{II-52})$$

The value of $|D_{ij}|$ is known from equation II-51, therefore D_{11} and D_{22} can be obtained from the linear equations II-50 and II-52 to yield

$$D_{11} = - \frac{|D_{ij}| + L_{2m}\sqrt{|D_{ij}|} + L_{2m}I_A S_{2m}/S_A}{S_{2m}} \quad (\text{II-53})$$

$$D_{22} = \frac{|D_{ij}| + I_{2m} \sqrt{|D_{ij}|} + I_{2m} L_A S_{2m} / S_A}{S_{2m}} \quad (\text{II-54})$$

Substitution of these expressions for D_{11} and D_{22} into equations II-47 and II-48 permit the evaluation of D_{12} and D_{21} respectively.

$$D_{12} = \frac{R_2}{R_1} (I_{2m} - D_{22}) \quad (\text{II-55})$$

$$D_{21} = \frac{R_1}{R_2} (L_{2m} - D_{11}) \quad (\text{II-56})$$

APPENDIX III

Determination of Activity Expressions $\partial\mu_i/\partial C_j$

It was shown previously that for a ternary system there are four terms of the type $\partial\mu_i/\partial C_j$ that are required to determine the diffusion coefficients D_{ij} and to check the Onsager reciprocal relation with Miller's^{33,34} condition. These are

$$\left(\frac{\partial\mu_1}{\partial C_1}\right)_{C_2} = RT \left(\frac{\partial \ln \gamma_1}{\partial C_1}\right)_{C_2} + RT \left[\frac{1}{C_1} - \frac{1}{C_T} \left(1 - \frac{\bar{V}_1}{\bar{V}_3} \right) \right] \quad (\text{III-1})$$

$$\left(\frac{\partial\mu_1}{\partial C_2}\right)_{C_1} = RT \left(\frac{\partial \ln \gamma_1}{\partial C_2}\right)_{C_1} - RT \left[\frac{1}{C_T} \left(1 - \frac{\bar{V}_2}{\bar{V}_3} \right) \right] \quad (\text{III-2})$$

$$\left(\frac{\partial\mu_2}{\partial C_1}\right)_{C_2} = RT \left(\frac{\partial \ln \gamma_2}{\partial C_1}\right)_{C_2} - RT \left[\frac{1}{C_T} \left(1 - \frac{\bar{V}_1}{\bar{V}_3} \right) \right] \quad (\text{III-3})$$

$$\left(\frac{\partial\mu_2}{\partial C_2}\right)_{C_1} = RT \left(\frac{\partial \ln \gamma_2}{\partial C_2}\right)_{C_1} + RT \left[\frac{1}{C_2} - \frac{1}{C_T} \left(1 - \frac{\bar{V}_2}{\bar{V}_3} \right) \right] \quad (\text{III-4})$$

It is obvious that in order to obtain expressions for $\partial\mu_i/\partial C_j$, expressions for $\partial \ln \gamma_i/\partial C_j$ are required. Most activity data can be correlated in terms of $\ln \gamma_i$ so that the latter expressions can be obtained.

Dodecane (1) - Hexadecane (2) - Hexane (3) - This system was fitted to the ternary Van Laar equations using the binary Van Laar constants A_{ij} and B_{ij} . Binary activity data for the systems hexane-dodecane and hexane-hexadecane were available.⁴ To obtain the constants used in the Van Laar equations, only data on two binaries are needed since the following relations between the constants apply.

$$A_{ij} = \frac{1}{A_{ji}} \quad i, j = 1, 2, 3; \quad i \neq j \quad (\text{III-5})$$

$$A_{ii} = 1 \quad (\text{III-6})$$

$$\sqrt{B_{ij}} = -\sqrt{B_{ji}A_{ij}} \quad i, j = 1, 2, 3; \quad i \neq j \quad (\text{III-7})$$

$$-\sqrt{\frac{B_{12}}{A_{12}}} + \sqrt{\frac{B_{23}}{A_{22}}} + \sqrt{\frac{B_{31}}{A_{32}}} = 0 \quad (\text{III-8})$$

$$A_{ij} = \frac{A_{ik}}{A_{jk}} \quad i, j, k = 1, 2, 3; \quad i \neq j \neq k \quad (\text{III-9})$$

From the binaries, values for A and B are obtained. Care must be taken to designate the right subscripts to A and B. As a check, the subscripts can be determined in the correct order if the relative magnitudes of the Van der Waals' constants, a and b, are known. For example, if the relative magnitude of b_i/b_j and A are greater than unity, then the subscripts are ij. The corresponding B value obtained in binary Van Laar fit is then assigned the same subscripts.

The ternary equations used are

$$T \ln \gamma_1 = - \frac{(C_3 C_{13} + C_2 A_{23} C_{12})^2}{(C_1 A_{13} + C_3 + C_2 A_{23})^2} \quad (\text{III-10})$$

$$T \ln \gamma_2 = - \frac{(C_1 A_{13} C_{21} + C_3 C_{23})^2}{(C_1 A_{13} + C_3 + C_2 A_{23})^2} \quad (\text{III-11})$$

where C_i is the concentration of component i , and A_{ij} and C_{ij} are constants. The C_{ij} are defined in terms of the binary B_{ij} as follows

$$C_{ij} = \begin{matrix} + \\ \text{or} \\ - \end{matrix} \sqrt{B_{ij}} \quad (\text{III-12})$$

It was found for this case that all the binary B values were negative which when substituted into the ternary Van Laar equations 164 yielded a factor of i^2 , where i is the imaginary index, in the numerator. This explains the minus sign in equations III-10 and III-11.

In the case of the value of B , it should also be noted that it occurs in the multicomponent equation as a square root, and this immediately raises the question of whether the value is positive or negative. This question can be answered on the basis of the relative magnitudes of $\sqrt{a_i}/b_i$ where a and b are Van der Waals constants. If, for example, $(\sqrt{a_i}/b_i - \sqrt{a_j}/b_j)$ is positive, then $\sqrt{B_{ij}}$ is taken as positive and $\sqrt{B_{ji}}$ as negative. The term $\sqrt{a_i}/b_i$ corresponds to the square root internal pressure of the liquid. Thus polar compounds which have high internal pressures would be expected to have high values of this group, while compounds of low polarity would be expected to have low values. From the tabulation of a_i , b_i and $\sqrt{a_i}/b_i$ listed in Table 18 of Appendix VI for various hydrocarbons, it can be seen that a_i increases, b_i increases, and $\sqrt{a_i}/b_i$ decreases as the carbon number increases. These observations were used in determining

the sign of C_{ij} . The values of A_{ij} and C_{ij} are given in Table 19 also in Appendix VI.

To obtain equations III-1 - III-4, the partial derivatives of equations III-10 and III-11 must be taken with respect to C_1 at constant C_2 and with respect to C_2 at constant C_1 . These, after simplification and use of equation 34, are

$$T \left(\frac{\partial \ln \gamma_1}{\partial C_1} \right)_{C_2} = \frac{2(C_3 C_{13} + C_2 A_{23} C_{12})}{(C_1 A_{13} + C_3 + C_2 A_{23})^2} \left[C_{13} \frac{\bar{V}_1}{\bar{V}_3} + \left(A_{13} - \frac{\bar{V}_1}{\bar{V}_3} \right) \frac{(C_3 C_{13} + C_2 A_{23} C_{12})}{(C_1 A_{13} + C_3 + C_2 A_{23})} \right] \quad (\text{III-13})$$

$$T \left(\frac{\partial \ln \gamma_1}{\partial C_2} \right)_{C_1} = \frac{2(C_3 C_{13} + C_2 A_{23} C_{12})}{(C_1 A_{13} + C_3 + C_2 A_{23})^2} \left[-A_{23} C_{12} + C_{13} \frac{\bar{V}_2}{\bar{V}_3} + \left(A_{23} - \frac{\bar{V}_2}{\bar{V}_3} \right) \frac{(C_3 C_{13} + C_2 A_{23} C_{12})}{(C_1 A_{13} + C_3 + C_2 A_{23})} \right] \quad (\text{III-14})$$

Expressions for $T \left(\frac{\partial \ln \gamma_2}{\partial C_2} \right)_{C_1}$ and $T \left(\frac{\partial \ln \gamma_2}{\partial C_1} \right)_{C_2}$ can be obtained from equations III-12 and III-13 respectively by interchanging subscripts 1 and 2.

Diethyl Ether (1) - Chloroform (2) - Carbon Tetrachloride (3) - For this system, the model of Wirth⁴⁷ and Anderson^{1,2} which assumes that ether and chloroform form a 1:1 complex was used. The model says that only four species exist in solution: the monomers (unassociated species) of ether and chloroform, the inert species CCl_4 , and the

ether-chloroform dimer. These four form an ideal mixture; thus, according to the model, any non-ideality of this system is attributed to the association of ether and chloroform with each other.

It was shown previously that

$$\begin{aligned}
 a_A &= X_1 \\
 a_B &= X_2 \\
 a_C &= X_3 \\
 a_{12} &= X_{12}
 \end{aligned}
 \tag{92}$$

where the subscripts A, B, C refer to the stoichiometric quantities of ether, chloroform, and carbon tetrachloride respectively and the subscripts 1, 2, 3, and 12 refer to the actual species present. Therefore it is desired to obtain expressions for the mole fractions of the actual species in terms of the stoichiometric concentrations. This would enable the determination of the $\partial \ln a_i / \partial C_j$ expressions.

The equilibrium constant for the association reaction is given by

$$K = \frac{X_{12}}{X_1 X_2} \tag{III-15}$$

Wirth⁴⁷ found $K = 2.73$.

Because of stoichiometry, the following relations exist,

$$\begin{aligned}
 C_A &= C_1 + C_{12} \\
 C_B &= C_2 + C_{12} \\
 C_C &= C_3
 \end{aligned}
 \tag{III-16}$$



and from these, the mole fractions of the actual species can be found in terms of the stoichiometric quantities. We have

$$\begin{aligned}
 x_1 &= \frac{c_1}{c_1 + c_2 + c_3 + c_{12}} = \frac{c_A - c_{12}}{c_A + c_B + c_C - c_{12}} \\
 x_2 &= \frac{c_2}{c_1 + c_2 + c_3 + c_{12}} = \frac{c_B - c_{12}}{c_A + c_B + c_C - c_{12}} \\
 x_3 &= \frac{c_3}{c_1 + c_2 + c_3 + c_{12}} = \frac{c_C}{c_A + c_B + c_C - c_{12}} \\
 x_{12} &= \frac{c_{12}}{c_A + c_B + c_C - c_{12}}
 \end{aligned}
 \tag{III-17}$$

Defining x_{12}^o as follows

$$x_{12}^o = \frac{c_{12}}{c_A + c_B + c_C}
 \tag{III-18}$$

Equations III-17 become

$$\begin{aligned}
 x_1 &= \frac{x_A - x_{12}^o}{1 - x_{12}^o} \\
 x_2 &= \frac{x_B - x_{12}^o}{1 - x_{12}^o} \\
 x_3 &= \frac{x_C}{1 - x_{12}^o} \\
 x_{12} &= \frac{x_{12}^o}{1 - x_{12}^o}
 \end{aligned}
 \tag{III-19}$$

With these substitutions, equation III-15 becomes

$$K = \frac{X_{12}^0(1 - X_{12}^0)}{(X_A - X_{12}^0)(X_B - X_{12}^0)} \quad (\text{III-20})$$

which can be used to eliminate X_{12}^0 in equations III-19 to give

$$\begin{aligned} X_1 &= \frac{(2X_A - 1) + K(2X_A + X_C - 1) + \phi}{1 + K(X_C + 1) + \phi} \\ X_2 &= \frac{(2X_B - 1) + K(2X_B + X_C - 1) + \phi}{1 + K(X_C + 1) + \phi} \\ X_3 &= \frac{2X_C(K + 1)}{1 + K(X_C + 1) + \phi} \\ X_{12} &= \frac{1 + K(1 - X_C) - \phi}{1 + K(X_C + 1) + \phi} \end{aligned} \quad (\text{III-21})$$

where

$$\phi = \left[\left(K(1 - X_C) + 1 \right)^2 - 4X_A X_B K(K + 1) \right]^{\frac{1}{2}} \quad (\text{III-22})$$

Notice that if $K = 0$ (i.e., no association), $\phi = 1$ and equations III-21 reduce to $X_1 = X_A$, $X_2 = X_B$, $X_3 = X_C$, and $X_{12} = 0$.

In terms of stoichiometric concentrations, X_1 and X_2 become

$$\begin{aligned} X_1 &= \frac{(2C_A - C_T) + K(C_A - C_B) + \psi}{C_T + K(C_T + C_C) + \psi} \\ X_2 &= \frac{(2C_B - C_T) + K(C_B - C_A) + \psi}{C_T + K(C_T + C_C) + \psi} \end{aligned} \quad (\text{III-23})$$

where $\Psi = \left[\left(K(C_T - C_C) + C_T \right)^2 - 4C_A C_B K(K+1) \right]^{\frac{1}{2}}$

Therefore

$$\left(\frac{\partial \ln a_A}{\partial C_B} \right)_{C_B} = \frac{1}{X_1} \left(\frac{\partial X_1}{\partial C_A} \right)_{C_B} = \left[\left(1 + \frac{\bar{V}_A}{\bar{V}_C} + K + \Psi'_A \right) \lambda \right. \quad (\text{III-24})$$

$$\left. - \left(2C_A - C_T + K(C_A - C_B) + \Psi \right) \left(1 - \frac{\bar{V}_A}{\bar{V}_C} + K - 2 \frac{\bar{V}_A}{\bar{V}_C} + \Psi'_A \right) \right] / (X_1 \lambda^2)$$

$$\left(\frac{\partial \ln a_A}{\partial C_B} \right)_{C_A} = \frac{1}{X_1} \left(\frac{\partial X_1}{\partial C_B} \right)_{C_A} = \left[\left(-1 + \frac{\bar{V}_B}{\bar{V}_C} - K + \Psi'_B \right) \lambda \right. \quad (\text{III-25})$$

$$\left. - \left(2C_A - C_T + K(C_A - C_B) + \Psi \right) \left(1 - \frac{\bar{V}_B}{\bar{V}_C} + K - 2 \frac{\bar{V}_B}{\bar{V}_C} + \Psi'_B \right) \right] / (X_1 \lambda^2)$$

where

$$\lambda = C_T + K(C_T + C_C) + \Psi \quad (\text{III-26})$$

$$\Psi'_A = \left(\frac{\partial \Psi}{\partial C_A} \right)_{C_B} = \frac{1}{2\Psi} \left(2 \left[K(C_T - C_C) + C_T \right] \times \left[K + 1 - \frac{\bar{V}_A}{\bar{V}_C} \right] - 4C_B K(1 + K) \right) \quad (\text{III-27})$$

$$\Psi'_B = \left(\frac{\partial \Psi}{\partial C_B} \right)_{C_A} = \frac{1}{2\Psi} \left(2 \left[K(C_T - C_C) + C_T \right] \times \left[K + 1 - \frac{\bar{V}_B}{\bar{V}_C} \right] - 4C_A K(1 + K) \right) \quad (\text{III-28})$$

The $\left(\frac{\partial \ln a_B}{\partial C_B} \right)_{C_A}$ and $\left(\frac{\partial \ln a_B}{\partial C_A} \right)_{C_B}$ are the same as equations III-24 and

III-25 respectively except that every A is replaced by B and vice versa.

Acetone (1) - Benzene (2) - Carbon Tetrachloride (3) - This system was fitted to Wohl's ternary equations using binary constants A_{ij} and a ternary constant C_{ijk} obtained from the binaries.⁵⁰ The ternary expressions for $\ln \gamma_1$ and $\ln \gamma_2$ are given by equations 165 and 166. The respective partial derivatives of $\ln \gamma_1$ are

$$\begin{aligned} \left(\frac{\partial \ln \gamma_1}{\partial C_1} \right)_{C_2} &= \left(\frac{1}{C_T^3} \right) \left[C_2^2 \left[A_{12} \left(1 - \frac{\bar{V}_1}{\bar{V}_3} \right) + 2(A_{21} - A_{12}) \right] - 2 \frac{C_3 \bar{V}_1}{\bar{V}_3} \left[A_{13} C_T + \right. \right. \\ &+ 2C_1(A_{31} - A_{13}) \left. \right] + C_3^2 \left[A_{13} \left(1 - \frac{\bar{V}_1}{\bar{V}_3} \right) + 2(A_{31} - A_{13}) \right] \\ &+ C_2 C_3 \left[(A_{21} + A_{13} - A_{32}) \left(1 - \frac{\bar{V}_1}{\bar{V}_3} \right) + 2(A_{31} - A_{13}) \right. \\ &- 2 \left(\frac{\bar{V}_1}{\bar{V}_3} \right) (A_{32} - A_{23}) + C_{123} \left(1 + \frac{\bar{V}_1}{\bar{V}_3} \right) \left. \right] - \frac{C_2 \bar{V}_1}{\bar{V}_3} \left[C_T (A_{21} + A_{13} - A_{32}) \right. \\ &+ 2C_1(A_{31} - A_{13}) + 2C_3(A_{32} - A_{23}) - C_{123}(C_T - 2C_1) \left. \right] - \frac{3 \ln \gamma_1}{C_T^4} \left(1 - \frac{\bar{V}_1}{\bar{V}_3} \right) \end{aligned} \quad (\text{III-29})$$

$$\begin{aligned} \left(\frac{\partial \ln \gamma_1}{\partial C_2} \right)_{C_1} &= \left(\frac{1}{C_T^3} \right) \left[2C_2 \left[A_{12} C_T + 2C_1(A_{21} - A_{12}) \right] + C_2^2 A_{12} \left(1 - \frac{\bar{V}_2}{\bar{V}_3} \right) \right. \\ &+ C_3^2 A_{13} \left(1 - \frac{\bar{V}_2}{\bar{V}_3} \right) - \frac{2C_3 \bar{V}_2}{\bar{V}_3} \left[A_{13} C_T + 2C_1(A_{31} - A_{13}) \right] \end{aligned} \quad (\text{III-30})$$

$$\begin{aligned}
& + c_2 c_3 \left[(A_{21} + A_{13} - A_{32}) \left(1 - \frac{\bar{v}_2}{\bar{v}_3} \right) - 2 \frac{\bar{v}_2}{\bar{v}_3} (A_{32} - A_{23}) - c_{123} \left(1 - \frac{\bar{v}_2}{\bar{v}_3} \right) \right] \\
& + \left[c_3 - c_2 \frac{\bar{v}_2}{\bar{v}_3} \right] \left[c_T (A_{21} + A_{13} - A_{32}) + 2c_1 (A_{31} - A_{13}) \right. \\
& \left. + 2c_3 (A_{32} - A_{23}) - c_{123} (c_T - 2c_1) \right] \left. \right] - \frac{3 \ln \gamma_1}{c_T^4} \left(1 - \frac{\bar{v}_2}{\bar{v}_3} \right)
\end{aligned} \tag{III-30}$$

Similar expressions can be obtained for $\left(\frac{\partial \ln \gamma_2}{\partial c_2} \right)_{c_1}$ and $\left(\frac{\partial \ln \gamma_2}{\partial c_1} \right)_{c_2}$

by taking the appropriate partial derivatives of equation 165.

APPENDIX IV

Fortran Program to Calculate the Reduced Second Moment, D_{2m}

This program obtains the refractive index gradient curve for each exposure and from this calculates the number of fringes, J , the centroid, $x_{c,m}$, and the second moment, m_2 . Using these values of m_2 and the measured time for each exposure, the reduced second moment, D_{2m} , and time correction, $t_{corr.}$, are calculated. The tangent method is used at the ends of each exposure to obtain the refractive index gradients while the difference between fringes is employed in the center regions.

The gradients in the center regions are fitted to a quadratic, $AX^2 + BX + C$, in an attempt to obtain the best maximum. By obtaining a smooth curve by the least squares technique, it is thought that a more reliable maximum can be obtained. It was found that extensive scatter would give unreliable maxima by this technique but would not affect the values of x calculated at which the maxima actually occur.

Areas under curves were obtained by summing the areas calculated under various regions of the curves. At each end of the curve, the points were fitted to a quadratic and the area obtained by integrating the resulting quadratic equation. In the center

region, the area was obtained by using the trapezoidal rule between each adjacent point. This latter technique was very reasonable since the points were so close together in this region. Calculated areas agreed very well with those obtained graphically.

Loading, fortran evaluation, and set-up on the Control Data Corporation's 3600 computer require approximately 45 seconds for this program. Execution time for one run with an average of 5 exposures per run is approximately 3 seconds. Thus in one minute, the computer is capable of calculating 5 runs.

Fortran Program for CDC 3600

```

PROGRAM CALCD2M
  DIMENSION RUN(20),DN(100),X(100),Y(100),T(15),SECMOM(15),D2M(15),
1XR(100),XL(100),THETA(100),RAD(100),BETA(100),XN2(100),XM(100)
C  CONST = THE MAGNIFICATION FACTOR. FOR THIS CASE IT IS = 1.923
C  NRUNS = THE NUMBER OF PLATES EVALUATED
C  J = THE NUMBER OF EXPOSURES EVALUATED
C  T = THE EXPERIMENTALLY MEASURED TIME IN SECONDS WHICH HAS PASSED
C  UP TO THE PARTICULAR EXPOSURE BEING EVALUATED
C  M = THE NUMBER OF DATA POINTS FOR THE PARTICULAR EXPOSURE EVALUATED
C  DN = THE DERIVATIVE OF THE REFRACTIVE INDEX WITH RESPECT TO THE
C  MEASURED DISTANCE.
C  DELN = THE TOTAL REFRACTIVE INDEX CHANGE, CALCULATED NUMERICALLY,
C  ACROSS THE BOUNDARY
C  XCENT = THE CENTROID OF THE REFRACTIVE INDEX GRADIENT CURVE. IT
C  IS = THE FIRST MOMENT OF THE CURVE
C  SECMOM = THE SECOND MOMENT OF THE REFRACTIVE INDEX GRADIENT CURVE
1  FORMAT (8F10.5)
2  FORMAT (I3)
3  FORMAT (*-*,*THE NUMERICALLY INTEGRATED VALUE FOR THE TOTAL REFRAC
1TIVE INDEX CHANGE ACROSS THE BOUNDARY IS -*)
4  FORMAT (*0*,30X, E13.7)
5  FORMAT (F10.4)
6  FORMAT (*0*,*THE CALCULATED CENTROID OF THE GRADIENT OF THE REFRAC
1TIVE INDEX CURVE IS -*)
9  FORMAT (*0*, *SECOND MOMENT*, 5X, *TIME IN SECONDS*,10X,*D2M*)
10  FORMAT (*0*, E13.7, 6X, F10.4, 10X, E13.7)
11  FORMAT (*0*,*THE RESULTS OF THE LEAST SQUARES ANALYSIS ARE -*)
12  FORMAT (*0*,5X,*D2M*,17X,*INTERCEPT*,10X,*ACTUAL INITIAL TIME*)

```



```

13  FORMAT (*0*,E16.9,5X,E16.9,15X,F10.4)
14  FORMAT (*1*,*HERE ARE THE RESULTS FOR RUN NO.      *I 4)
15  FORMAT (10F5.3)
16  FORMAT (* *,E13.6,2X,E13.6,8X,E13.6)
17  FORMAT (* *,5X,*X*,14X,*DN/DX*,6X,*((X - XCENT)XX2 X DN/DX)*)
18  FORMAT (*0*,5X, *XMAX*, 9X, *MAX DN/DX*)
19  FORMAT (*0*,2X, E13.6, 2X, E13.6)
101 FORMAT (16I5)
102 FORMAT (3I4)
103 FORMAT (2F10.7)
1000 FORMAT (*0*,5X,* A *,10X,* B *,10X,* C *)
1001 FORMAT (*0*,1X,E13.6,2X,E13.6,2X,E13.6)
      READ 5, CONST
      READ 2, NRUNS
      READ 101, (RUN(I), I = 1,NRUNS)
      DO 40 NO = 1, NRUNS
      PRINT 14, RUN(NO)
      READ 2, J
      READ 2, NSQ
      READ 103, CONV1, CONV2
      DO 20 L = 1,J
      READ 5, T(L)
      READ 102, N1, N2, N3
      M = N1 + N2 + N3 - 1
      M1 = M - 1
      READ 1, (X(I), I = 1,N1)
      READ 1, (THETA(I), I = 1,N1)
      READ 1, (XN2(I), I = 1,N2)
      READ 1, (BETA(I), I = 1,N2)
      READ 1, (XM(I), I = 1,N3)
      DO 35 II = 1,N2
      III = N1 + N3 - 1 + II
      THETA(III) = BETA(II)
      RAD(III) = THETA(III) * 3.1416/180
      DN(III) = TANF(RAD(III))/CONV2
35  X(III) = XN2(II)
      DO 36 I6 = 2,N3
      N = N1 + I6 - 1
      DN(N) = 1.0/(XM(I6) - XM(I6 - 1))
36  X(N) = (XM(I6) + XM(I6 - 1))/2.0
      DO 37 II1 = 1,N1
      RAD(III) = THETA(III) * 3.1416/180
37  DN(II1) = TANF(RAD(II1))/CONV1
      DO 70 I7 = 1,M
70  Y(I7) = DN(I7)
      M2 = M - 2 * (NSQ - 1)
      NSQ2 = 2 * (NSQ - 1)
      NSQ3 = M - 4 * (NSQ - 1) + 1
      SX = 0.0
      SY = 0.0
      SXY = 0.0

```

```

      SX2 = 0.0
      SX3 = 0.0
      SX4 = 0.0
      SYX2 = 0.0
      DO 80 J4 = NSQ2, M2
      SX = SX + X(J4)
      SY = SY + Y(J4)
      SXY = SXY + X(J4) * Y(J4)
      SX2 = SX2 + X(J4)**2
      SX3 = SX3 + X(J4)**3
      SX4 = SX4 + X(J4)**4
80    SYX2 = SYX2 + Y(J4) * X(J4)**2
      DET = NSQ3*SX2*SX4 - SX**2*SX4 - NSQ3*SX3**2 - SX2**3 + 2.0*SX3*SX2*
1SX
      A = (SYX2*(NSQ3*SX2- SX**2) - SX3*(NSQ3*SXY- SX*SY) + SX2*(SXY*SX
1-SX2*SY))/DET
      B = (SX4*(NSQ3*SXY- SX*SY) - SYX2*(NSQ3*SX3- SX2*SX) + SX2*(SY*SX3
1 - SX2*SXY))/DET
      C = (SX4*(SX2*SY - SX*SXY) - SX3*(SX3*SY- SXY*SX2) + SYX2*(SX3*SX
1 - SX2**2))/DET
      XMAX = -B/(2 * A)
      YMAX = A * XMAX**2 + B * XMAX + C
      PRINT 1000
      PRINT 1001, A, B, C
      PRINT 18
      PRINT 19, XMAX, YMAX
      CALL AREANUM (X,XR,XL,Y,AREA,NSQ,M,M6,A,SX,SY,SX2,SX3,SX4,
1SYX2,DET,B,C,J1,M1,J3,NSQ1)
      DELN = AREA
      PRINT 3
      PRINT 4, DELN
      DO 31 I2 = 1,M
31    Y(I2) = X(I2) * DN(I2)
      CALL AREANUM (X,XR,XL,Y,AREA,NSQ,M,M6,A,SX,SY,SX2,SX3,SX4,
1SYX2,DET,B,C,J1,M1,J3,NSQ1)
      XCENT = AREA/DELN
      PRINT 6
      PRINT 4, XCENT
      DO 32 I3 = 1,M
32    Y(I3) = (X(I3) - XCENT)**2 * DN(I3)
      PRINT 17
      DO 60 I9 = 1,M
60    PRINT 16, X(I9), DN(I9), Y(I9)
      CALL AREANUM (X,XR,XL,Y,AREA,NSQ,M,M6,A,SX,SY,SX2,SX3,SX4,
1SYX2,DET,B,C,J1,M1,J3,NSQ1)
      SECMOM(L) = AREA/(CONST**2 * DELN)
      D2M(L) = SECMOM(L)/(2.0 * T(L))
20    CONTINUE
      PRINT 9
      DO 33 14 = 1,J

```

```

33  PRINT 10, SECMOM(I4), T(I4), D2M(I4)
    SX = 0.0
    SY = 0.0
    SZ = 0.0
    SXY = 0.0
    DO 34 I5 = 1,J
    SX = SX + T(I5)
    SY = SY + SECMOM(I5)/2.0
    SZ = SZ + T(I5)**2
34  SXY = SXY + T(I5) * SECMOM(I5)/2.0
    SLOPE = (SX *SY - J *SXY)/(SX**2 - J * SZ)
    CEPT = (SY - SLOPE * SX)/J
    TINIT = -CEPT/SLOPE
    PRINT 11
    PRINT 12
    PRINT 13, SLOPE, CEPT, TINIT
40  CONTINUE
    END
    SUBROUTINE AREANUM (X,XR,XL,Y,AREA,NSQ,M,M6,A,SX,SY,SX2,SX3,SX4,
1SYX2,DET,B,C,J1,M1,J3,NSQ1)
    DIMENSION X(100), XR(100), XL(100), Y(100)
    AREA = 0.0
    NSQ1 = NSQ - 1
    DO 100 I = 1,NSQ
100  XL(I) = X(I) - X(1)
    M6 = M - NSQ
    DO 110 I = M6,M
110  XR(I) = X(M) - X(I)
    A = Y(2)/XL(2)**2
    AREA = AREA + (A/3.0)*XL(2)**3
    A = Y(M-1)/XR(M-1)**2
    AREA = AREA + (A/3.0)*XR(M-1)**3
    SX = 0.0
    SY = 0.0
    SXY = 0.0
    SX2 = 0.0
    SX3 = 0.0
    SX4 = 0.0
    SYX2 = 0.0
    DO 200 J2 = 2,NSQ
    SX = SX + X(J2)
    SY = SY + Y(J2)
    SXY = SXY + X(J2) * Y(J2)
    SX2 = SX2 + X(J2)**2
    SX3 = SX3 + X(J2)**3
    SX4 = SX4 + X(J2)**4
200  SYX2 = SYX2 + Y(J2) * X(J2)**2
    DET = NSQ1*SX2*SX4 - SX**2*SX4 -NSQ1*SX3**2 - SX2**3 + 2.0*SX3*SX2*
1SX

```

```

      A = (SYX2*(NSQ1*SX2- SX**2) - SX3*(NSQ1*SXY- SX*SY) + SX2*(SXY*SX
1-SX2*SY))/DET
      B = (SX4*(NSQ1*SXY- SX*SY) - SYX2*(NSQ1*SX3- SX2*SX) + SX2*(SY*SX3
1 - SX2*SXY))/DET
      C = (SX4*(SX2*SY - SX*SXY) - SX3*(SX3*SY- SXY*SX2) + SYX2*(SX3*SX
1 - SX2**2))/DET
300  AREA = AREA + (A/3.0)*(X(NSQ - 1)**3 - X(2)**3) + (B/2.0)*(X(NSQ -
1 1)**2 - X(2)**2) + C*(X(NSQ - 1) - X(2))
      SX = 0.0
      SY = 0.0
      SXY = 0.0
      SX2 = 0.0
      SX3 = 0.0
      SX4 = 0.0
      SYX2 = 0.0
      DO 700 I2 = 1,NSQ1
      J2 = M - NSQ + I2
      SX = SX + XR(J2)
      SY = SY + Y(J2)
      SXY = SXY + XR(J2) * Y(J2)
      SX2 = SX2 + XR(J2)**2
      SX3 = SX3 + XR(J2)**3
      SX4 = SX4 + XR(J2)**4
700  SYX2 = SYX2 + Y(J2) * XR(J2)**2
      DET =NSQ1*SX2*SX4 - SX**2*SX4 - NSQ1*SX3**2 - SX2**3 + 2.0*SX3*SX2
1*SX
      A = (SYX2*(NSQ1*SX2- SX**2) - SX3*(NSQ1*SXY- SX*SY) + SX2*(SXY*SX
1-SX2*SY))/DET
      B = (SX4*(NSQ1*SXY- SX*SY) - SYX2*(NSQ1*SX3- SX2*SX) + SX2*(SY*SX3
1 - SX2*SXY))/DET
      C = (SX4*(SX2*SY - SX*SXY) - SX3*(SX3*SY- SXY*SX2) + SYX2*(SX3*SX
1 - SX2**2))/DET
      J1 = M - NSQ + 2
      M1 = M - 1
      AREA = AREA + (A/3.0)*(XR(J1)**3-XR(M1)**3) + (B/2.0)*(XR(J1)**2
1 - XR(M1)**2) + C*(XR(J1) - XR(M1))
      J3 = J1 - 1
      DO 500 J = NSQ1,J3
500  AREA = AREA + (1.0/2.0)*(Y(J) + Y(J+1))*(X(J+1) - X(J))
      RETURN
      END
'RUN,1,1200

```

APPENDIX V

FORTRAN PROGRAM TO SOLVE FOR $\sqrt{|D_{ij}|}$

This program utilizes the Newton-Raphson method to obtain a root to a polynomial and then factors this root by synthetic division in a subroutine. A root to the resulting polynomial (which is of one less degree than the previous) is again obtained by the Newton-Raphson method and is factored out by synthetic division. This is repeated until only a linear equation remains.

This program obtains only real roots. If both imaginary and real roots are present, the real roots are determined first and then the computer cycles until the designated time limit is reached.

This program can be generalized to an N^{th} order polynomial by simply reading in all the coefficients of the polynomial rather than calculating them, as was done here for convenience.

Fortran Program for IBM 1800

```
// JOB
// FOR PRTS
*IOCS(CARD, 1443 PRINTER)
*NONPROCESS PROGRAM
    DIMENSION A(50), B(50), C(50)
1   FORMAT (I2)
2   FORMAT (4E13.6)
3   FORMAT (' COEFFICIENTS OF POLYNOMIAL OF DEGREE '12,2X,'(STARTING
1WITH THE HIGHEST POWER OF X) ARE')
```

```

4   FORMAT (5X, E13.6)
5   FORMAT ('0', ' ROOT NUMBER ' I2,1X, ' IS ' E13.6)
6   FORMAT (' NEW COEFFICIENTS AFTER DIVIDING OUT ABOVE ROOT ARE')
   READ (2,1) N
   N1 = N + 1
   READ (2,2) SA, CTA, S2M, CT2M
   A(1) = 1.0
   A(2) = CT2M - CTA * S2M/SA
   A(3) = 0.0
   A(4) = -(S2M/SA)**2
   WRITE (3,3) N
   DO 14 I = 1,N1
14  WRITE (3,4) A(I)
C   N IS DEGREE OF POLYNOMIAL
C   P = POLYNOMIAL EVALUATED AT X
C   DP = DERIVATIVE OF P EVALUATED AT X
   READ (2,1) NRTS
   DO 12 J = 1, NRTS
   X = 0.000001
10  CALL SYND (A,B,C,X,P,DP,N,N1)
   XPRE = X
   X = XPRE - P/DP
   IF (1.0E-11 - ABS (X- XPRE)) 10, 11, 11
11  WRITE (3,5) J,X
   WRITE (3,6)
   DO 13 I = 1,N
   WRITE (3,4) B(I)
13  A(I) = B(I)
   N = N - 1
12  N1 = N + 1
   CALL EXIT
   END
// FOR SYND
*NONPROCESS PROGRAM
   SUBROUTINE SYND (A,B,C,X,P,DP,N,N1)
   DIMENSION A(50), B(50), C(50)
   B(1) = A(1)
   DO 8 I = 2, N1
8   B(I) = A(I) + X * B(I - 1)
   C(1) = B(1)
   DO 9 I = 2, N
9   C(I) = B(I) + X * C(I - 1)
   P = B(N1)
   DP = C(N)
   RETURN
   END
// XEQ PRIS
*CCEND

```

APPENDIX VI

EXPERIMENTAL DATA

Table 9. Physical properties of the pure components.

Component	Molecular Weight	Temperature °C	Measured Viscosity cp	Molar Volume cc/mole	Measured Refractive Index n_D
Hexane	86.17	25	0.296	131.6	1.3727
Dodecane	170.33	25	1.338	228.6	1.4196
Hexadecane	226.44	25	3.031*	294.1	1.4324#
Toluene	92.13	30	0.515*	107.4	1.4940#
Chlorobenzene	112.56	30	0.713*	106.0	1.5221#
Bromobenzene	157.02	30	0.985*	102.8	1.5576#
Diethyl Ether	74.12	25	0.217	104.7	1.3500
Chloroform	119.39	25	0.542	80.7	1.4422
Carbon Tetra- chloride	153.84	25	0.890	97.12	1.4570
Acetone	58.08	25	0.308	73.99	1.3566
Benzene	78.11	25	0.597	89.40	1.4981

*Reference 50
#Reference 42

Table 10. Initial concentration differences.

Dodecane (1) - Hexadecane (2) - Hexane (3)

$$T = 25^{\circ}\text{C}$$

$$\bar{C}_1 = 1.615 \quad \bar{C}_2 = 1.464 \quad \bar{C}_3 = 1.533 \quad \text{moles/liter}$$

Run No.	α_1	ΔC_1 (moles/l.)	ΔC_2 (moles/l.)
154	-1.134	-0.120	0.134
155	-0.239	-0.018 ₅	0.057 ₁
157	0.176	0.016 ₈	0.046 ₇
158	1.352	0.078 ₈	-0.012 ₂
160	-2.416	0.156	-0.131
161	3.599	0.128	-0.054 ₈
162	1.257	0.071 ₆	-0.008 ₇

Diethyl Ether (A) - Chloroform (B) - Carbon Tetrachloride (C)

$$T = 25^{\circ}\text{C}$$

$$\bar{C}_A = 2.646 \quad \bar{C}_B = 2.653 \quad \bar{C}_C = 5.309 \quad \text{moles/liter}$$

Run No.	α_1	ΔC_A (moles/l.)	ΔC_B (moles/l.)
175	1.002	-0.086 ₄	0.000 ₆
176	0.623	-0.048 ₁	-0.131 ₅
178	1.317	-0.062 ₉	0.068 ₃
179	1.150	-0.056 ₈	0.033 ₄

Table 11. Binary diffusion data at infinite dilution.

Binary system (i dilute in j)	Temperature °C	$D_{ij}^0 \times 10^5$ cm ² /sec	$D_{ij}^0 \times \eta_j \times 10^7$ dynes
Hexane in Dodecane	25	1.42	1.91
Hexane in Hexadecane	25	0.85	2.58
Dodecane in Hexane	25	2.74	0.81
Dodecane in Hexadecane	25	0.49	1.47
Hexadecane in Hexane	25	2.21	0.66
Hexadecane in Dodecane	25	0.67*	0.90
Chlorobenzene in Bromobenzene	30	1.36*	1.34
Chlorobenzene in Toluene	30	2.36*	1.22
Bromobenzene in Chlorobenzene	30	1.76*	1.26
Bromobenzene in Toluene	30	2.27*	1.17
Toluene in Chlorobenzene	30	1.80*	1.28
Toluene in Bromobenzene	30	1.41#	1.39
Acetone in Carbon Tetrachloride	25	1.70#	1.52
Acetone in Benzene	25	2.75#	1.64
Benzene in Carbon Tetrachloride	25	1.38#	1.24
Benzene in Acetone	25	4.23#	1.30
Carbon Tetrachloride in Benzene	25	1.90#	1.13
Carbon Tetrachloride in Acetone	25	3.57#	1.10

*Reference 7

#Reference 12

Table 12. Self diffusion data.

Component	Temperature °C	$D_{ij}^0 \times 10^5$ cm ² /sec	$D_{ij}^0 \times \eta_i \times 10^7$ dynes
Hexane	25	4.21	1.25
Dodecane	25	0.87 ^a	1.20
Hexadecane	25	0.51 ^a	1.67
Toluene	30	2.60 ^b	1.34
Chlorobenzene	30	1.79	1.28
Bromobenzene	30	1.23 ^b	1.21
Acetone	25	4.77 ^b	1.47
Benzene	25	2.16 ^b	1.29
Carbon Tetrachloride	25	1.32	1.18
Chloroform	25	2.44	1.32
Diethyl Ether	25	8.73	1.96

^a obtained from a plot of self diffusion coefficient versus carbon number for various hydrocarbons (Figure 16, Appendix VI)

^b reference 30



Table 13. Reduced second moment, D_{2m} , and reduced height-area ratio, \mathcal{D}_A , data.

Dodecane (1) - Hexadecane (2) - Hexane (3)

$$T = 25\text{ }^{\circ}\text{C}$$

$$\bar{C}_1 = 1.615 \quad \bar{C}_2 = 1.464 \quad \bar{C}_3 = 1.533 \quad \text{moles/liter}$$

Run No.	α_1	$D_{2m} \times 10^5$	$\mathcal{D}_A \times 10^5$	$1/\sqrt{\mathcal{D}_A}$
154	-1.134	0.984	0.947	324.7
155	-0.239	1.203	1.107	300.6
157	0.176	1.197	1.247	283.2
158	1.352	1.411	1.526	256.0
160	-2.416	0.835	0.815	350.3
161	3.599	1.710	2.335	206.9
162	1.257	1.388	1.467	261.9

Diethyl Ether (A) - Chloroform (B) - Carbon Tetrachloride (C)

$$T = 25\text{ }^{\circ}\text{C}$$

$$\bar{C}_A = 2.646 \quad \bar{C}_B = 2.653 \quad \bar{C}_C = 5.309 \quad \text{moles/liter}$$

Run No.	α_1	$D_{2m} \times 10^5$	$\mathcal{D}_A \times 10^5$	$1/\sqrt{\mathcal{D}_A}$
175	1.002	2.113	2.184	218.8
176	0.623	1.585	1.765	243.3
178	1.317	2.557	2.711	193.9
179	1.150	2.303	2.509	203.4

Table 14. Second moment, m_2 , data.

Dodecane - Hexadecane - Hexane

Second Moment $m_2 \times 10^2$ (cm^2)	Measured Time t_m (secs)
Run No. 154	
0.832	305
1.163	485
1.434	605
1.887	845
Run No. 155	
0.636	125
0.917	245
1.209	365
1.356	425
Run No. 157	
0.955	245
1.388	425
1.959	665
2.536	905
Run No. 158	
0.820	125
1.032	185
1.370	305
1.546	365
1.825	485
2.377	665
Run No. 160	
0.631	125
1.010	365
1.326	545
1.517	665



Table 14. (continued)

Second Moment $m_2 \times 10^2$ (cm^2)	Measured Time t_m (secs)
Run No. 161	
1.350	125
1.776	245
2.198	365
2.571	485
3.414	725
Run No. 162	
1.026	185
1.213	245
1.497	365
1.867	485
2.363	665
Diethyl Ether - Chloroform - Carbon Tetrachloride	
Run No. 175	
0.901	125
1.427	245
1.972	365
2.459	485
2.948	605
3.441	725
Run No. 176	
1.272	305
1.660	425
2.080	545
2.662	725
3.224	905
3.725	1085
Run No. 178	
0.801	65
1.123	125
1.509	185
1.786	245
2.735	425
3.278	545
3.577	605

Table 14. (continued)

Run No. 179

Second Moment	Measured Time
$m_2 \times 10^2$ (cm ²)	t_m (secs)
0.926	125
1.200	185
2.010	365
2.260	425
2.925	545
3.380	665

Table 15. Time correction, Δt_{corr} , data.

Dodecane - Hexadecane - Hexane

Run No.	Δt_{corr} (sec)
154	115.3
155	137.6
157	154.0
158	174.6
160	254.4
161	272.4
162	185.0

Diethyl Ether - Chloroform - Carbon Tetrachloride

Run No.	Δt_{corr} (sec)
175	93.6
176	103.8
178	100.1
179	74.6



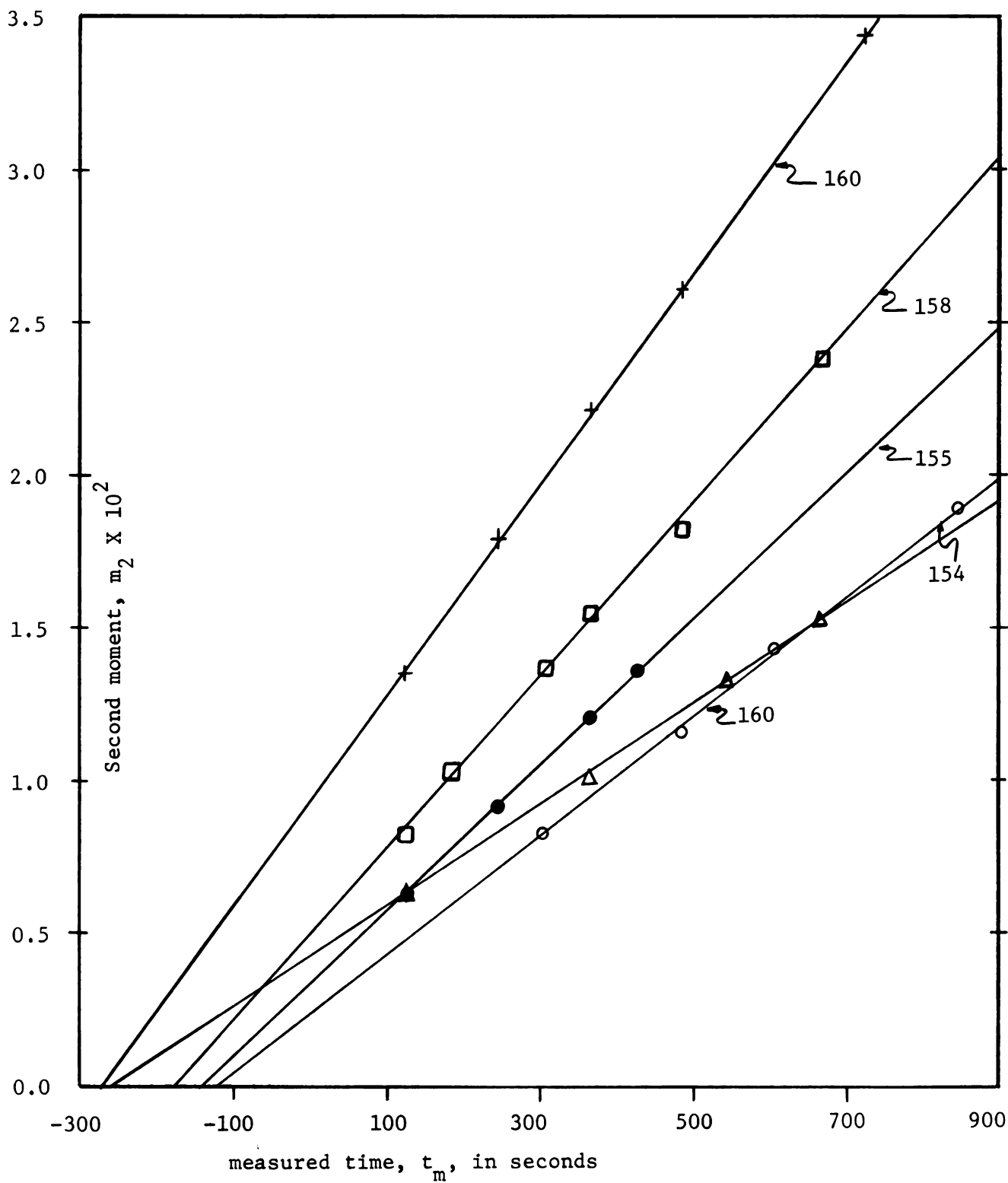


Figure 12. Second moment versus the measured time for the system dodecane (1) - hexadecane (2) - hexane (3).

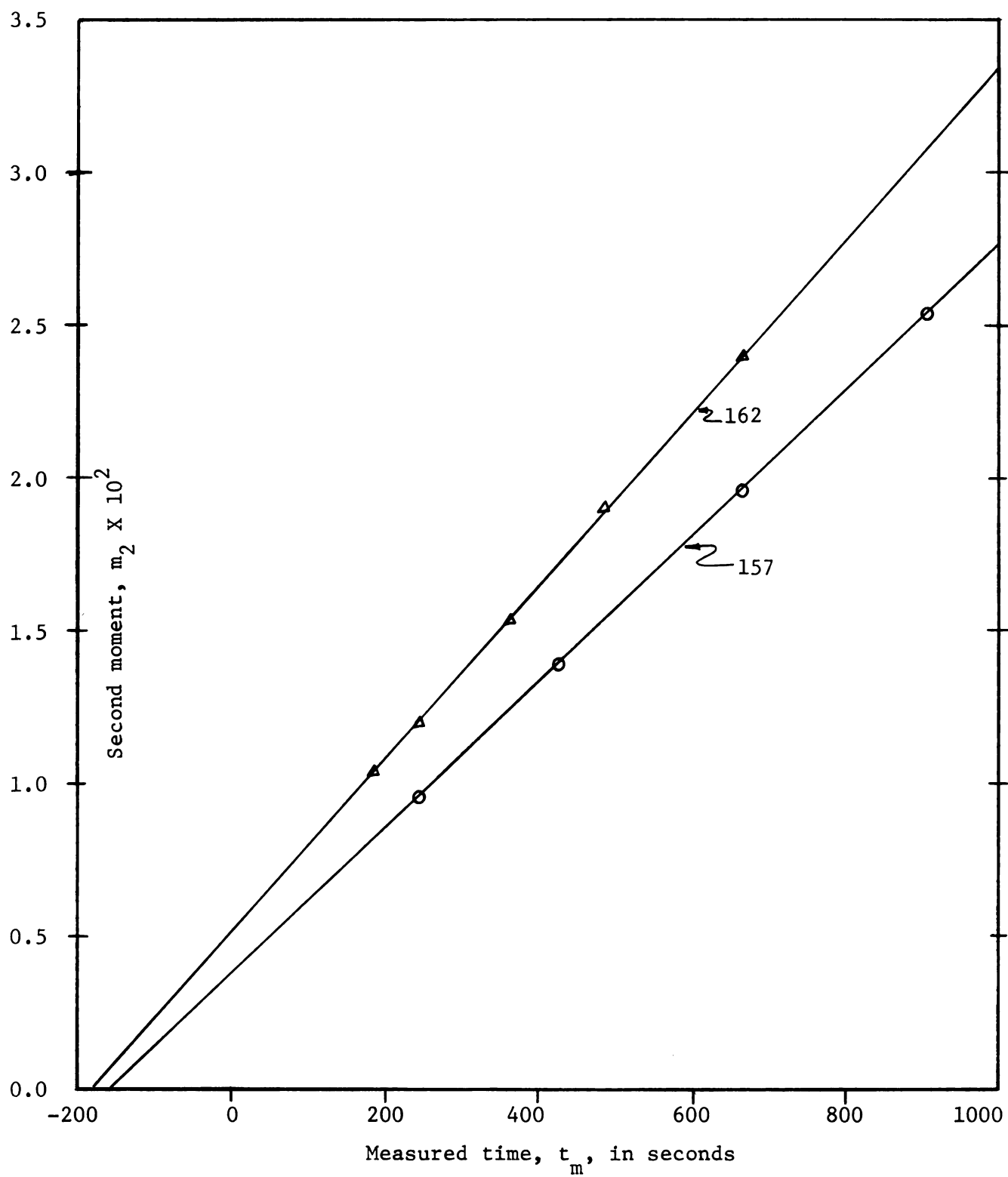


Figure 13. Second moment versus the measured time for the system dodecane (1) - hexadecane (2) - hexane (3).

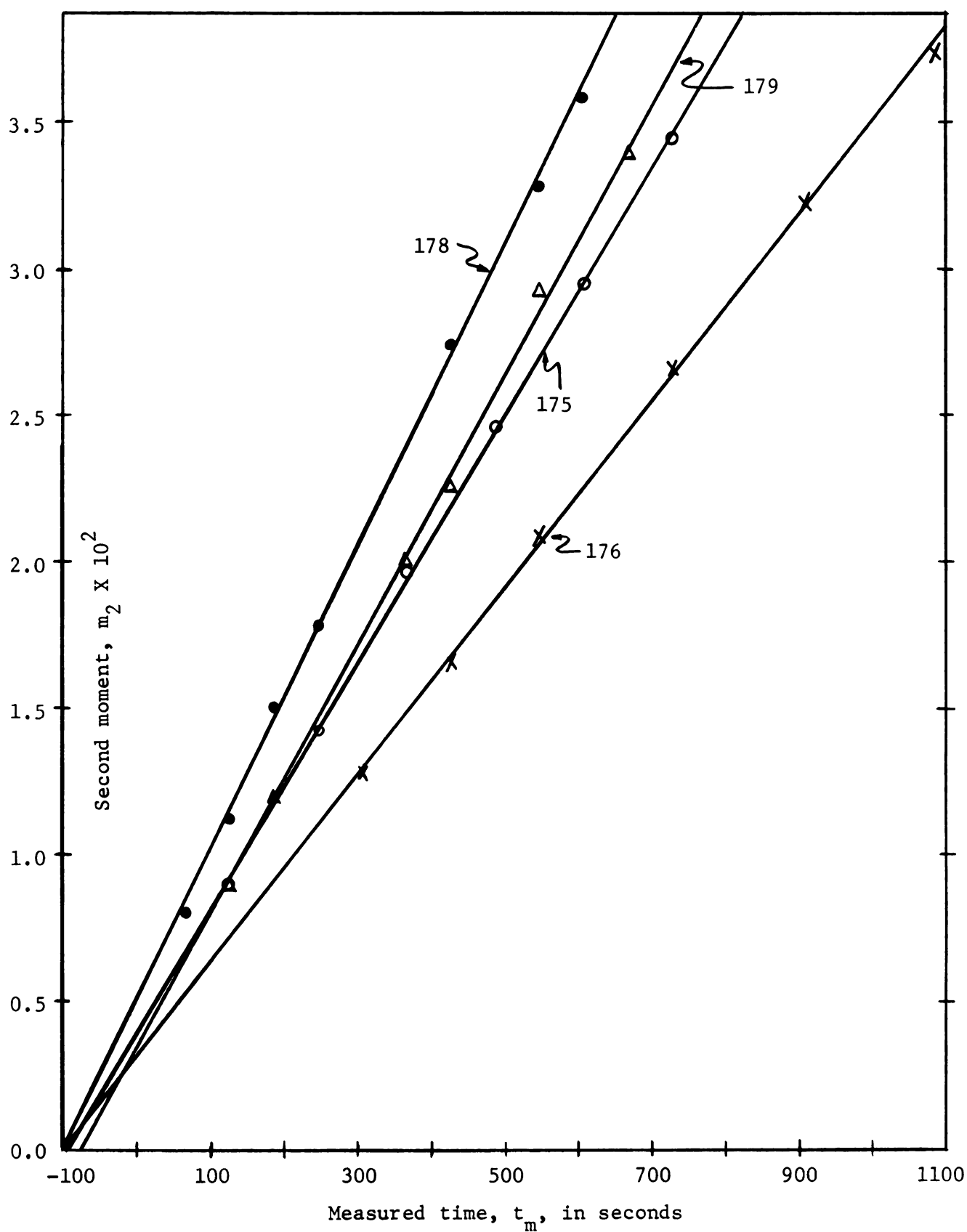


Figure 14. Second moment versus the measured time for the system diethyl ether (1) - chloroform (2) - carbon tetrachloride (3).

Table 16. Data used to calculate the experimental
ternary diffusion coefficients

$$T = 25^{\circ}\text{C}$$

	Dodecane(1)- Hexadecane(2)- Hexane(3)	Diethyl Ether(1)- Chloroform(2)- Carbon Tetrachloride(3)
I_A	292.3 ₀	289.0 ₅
S_A	-24.4 ₅	-72.5 ₃
L_A	267.8 ₅	216.5 ₂
$I_{2m} \times 10^5$	1.192	0.716
$S_{2m} \times 10^5$	0.149	1.391
$L_{2m} \times 10^5$	1.341	2.107
$\text{Det } D_{ij} \times 10^{10}$	0.939	4.401
R_1	0.01091	-0.01143
R_2	0.01803	-0.00253
\bar{C}_1	1.615	2.646
\bar{C}_2	1.464	2.653
\bar{C}_3	1.533	5.309

Table 17. Quantities involved in the calculation of D_{ij} and L_{ij}

Dodecane (1) - Hexadecane (2) - Hexane (3)									
T = 25 °C									
X_1	X_2	(np)	a/RT	b/RT	c/RT	d/RT	$(RT/\sigma_1) \times 10^7$ dynes	$(RT/\sigma_2) \times 10^7$ dynes	$(RT/\sigma_3) \times 10^7$ dynes
0.350	0.317	1.250	2.519	2.415	2.415	3.781	1.089	1.062	1.899
Toluene (1) - Chlorobenzene (2) - Bromobenzene (3)									
T = 30 °C									
0.25	0.50	0.713	0.883	0.455	0.455	0.660	1.323	1.277	1.222
0.26	0.03	0.824	0.560	0.158	0.158	3.626	1.373	1.306	1.199
0.70	0.15	0.596	0.927	0.765	0.765	1.465	1.338	1.243	1.188
0.15	0.70	0.713	1.474	0.759	0.759	0.900	1.307	1.276	1.235
0.45	0.25	0.679	0.619	0.379	0.379	0.797	1.340	1.268	1.202
0.18	0.28	0.801	0.792	0.208	0.208	0.579	1.350	1.300	1.214
Acetone (1) - Benzene (2) - Carbon Tetrachloride (3)									
T = 25 °C									
0.30	0.35	0.564	0.305	0.143	0.143	0.455	1.548	1.275	1.140
0.15	0.15	0.715	0.507	0.040	0.040	0.717	1.533	1.255	1.163
0.15	0.70	0.574	0.790	0.377	0.377	0.606	1.598	1.284	1.136
0.70	0.15	0.399	0.352	0.362	0.362	0.989	1.502	1.290	1.116
0.09	0.90	0.563	5.925	6.154	6.154	7.552	1.624	1.290	1.131
0.24	0.75	0.511	5.175	5.940	5.940	7.308	1.599	1.292	1.126
0.49	0.50	0.433	4.658	5.515	5.515	6.843	1.555	1.295	1.117
0.74	0.25	0.367	4.491	5.365	5.365	6.812	1.511	1.298	1.108
0.895	0.095	0.331	4.525	5.420	5.420	7.360	1.484	1.299	1.102

Table 17 (continued)

Diethyl Ether (A) - Chloroform (B) - Carbon Tetrachloride (C)

T = 25 °C

\bar{C}_A	2.646 moles/liter
\bar{C}_B	2.653 moles/liter
\bar{C}_C	5.309 moles/liter
\bar{C}_{12}	0.880 moles/liter
η	0.573 cp.
a/RT	0.631
b/RT	0.025
c/RT	0.025
d/RT	0.554
$(RT/\sigma_1) \times 10^7$	1.956 dynes
$(RT/\sigma_2) \times 10^7$	1.322 dynes
$(RT/\sigma_3) \times 10^7$	1.174 dynes
$(RT/\sigma_{12}) \times 10^7$	0.896 dynes
K	2.73

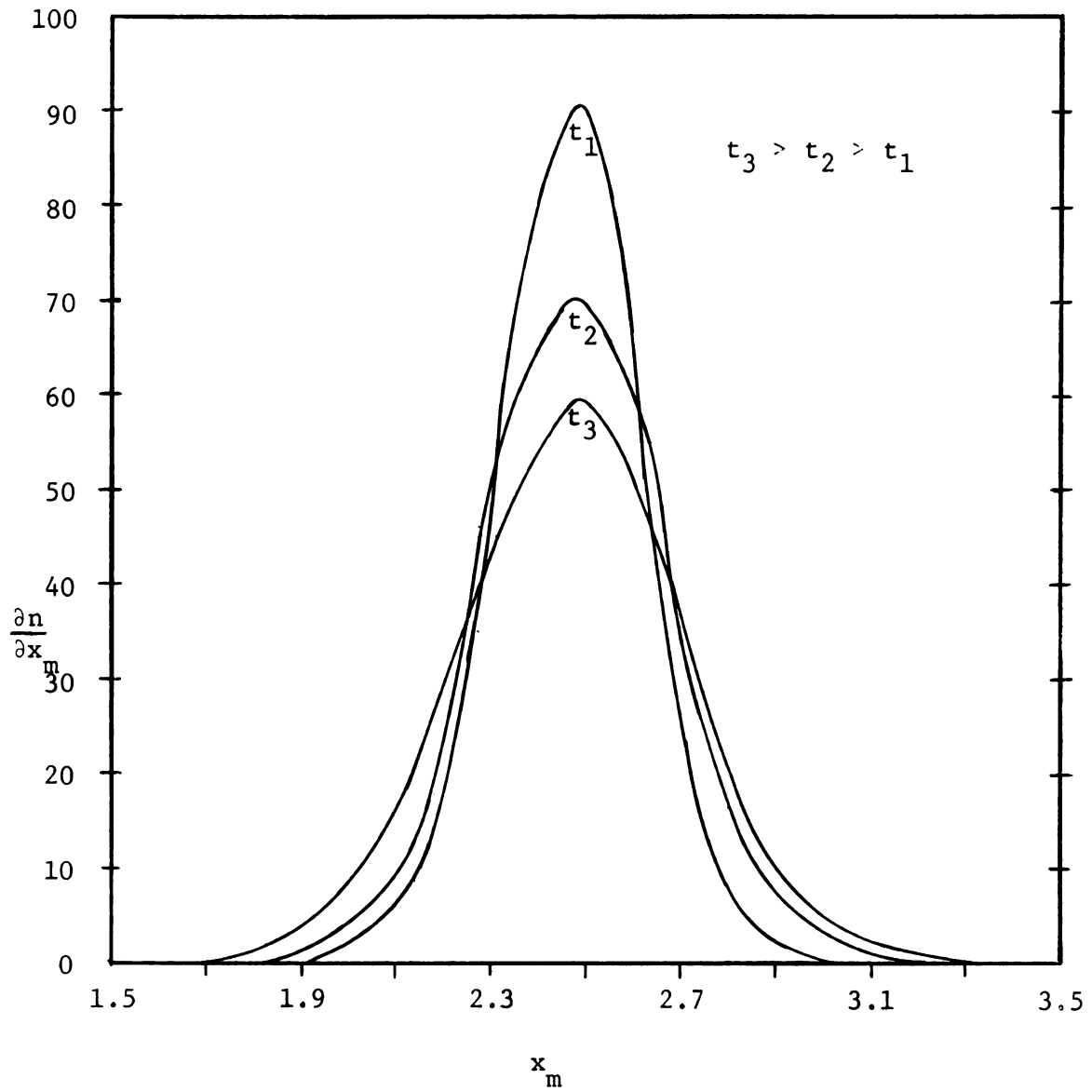


Figure 15. Typical refractive index gradient curve (run no. 160) at various times during diffusion.

Table 18. Van der Waals constants, a and b , for various hydrocarbons

Hydrocarbon	a $\frac{\text{liter}^2 \text{atm}}{\text{mole}^2}$	b liter/mole	a/b $(\text{atm})^{1/2}$
ethane	5.489	0.06380	36.7
propane	8.664	0.08445	35.0
butane	14.47	0.1226	31.0
pentane	19.01	0.1460	29.9
hexane	24.39	0.1735	28.4
heptane	31.51	0.2107	26.6
octane	37.32	0.2368	25.8

Table 19. Activity constants used in the ternary activity equations.

Dodecane (1) - Hexadecane (2) - Hexane (3) $T = 25^{\circ}\text{C}$

ij	A_{ij}	$C_{ij} = \pm\sqrt{B_{ij}}$
12	0.9815	2.0937
21	1.0188	-2.1136
13	1.0521	-3.7004
31	0.9505	3.6066
23	1.0717	-5.8491
32	0.9331	5.6502

Acetone (1) - Benzene (2) - Carbon Tetrachloride (3) $T = 25^{\circ}\text{C}$

ij	A_{ij}
12	0.49
21	0.39
13	0.98
31	0.69
23	0.10
32	0.11

$$C_{123} = 0.10$$

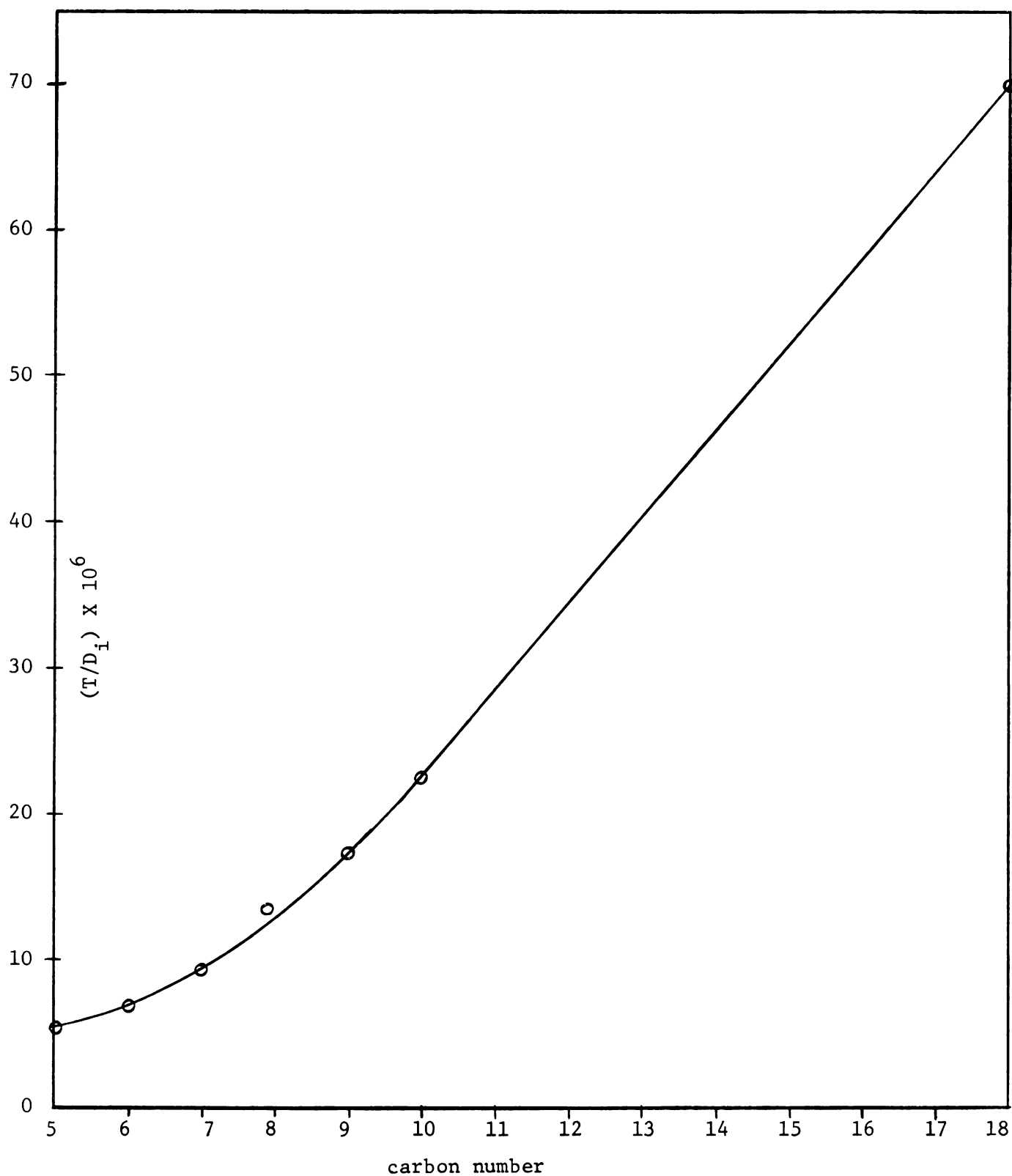


Figure 16. The product of absolute temperature and the reciprocal of the self diffusion coefficient versus carbon number for several hydrocarbons.

NOMENCLATURE

A_{ij}	constant used in Van Laar and Wohl equations
a_i	Van der Waals constant, liter ² atm/mole ²
a_i	activity of component i
B_{ij}	constant used in Van Laar binary equations
b_i	Van der Waals constant, liter/mole
C_i	concentration of component i, moles/cm ³
C_T	total concentration, moles/cm ³
C_{ij}	constant used in Van Laar ternary equation
C_{ijk}	constant used in Wohl ternary equation
\mathcal{D}_A	reduced height-area ratio
D_i	self diffusion coefficient of i, cm ² /sec
D_i^*	tracer diffusion coefficient, cm ² /sec
D_{2m}	reduced second moment
D_{AB}	mutual diffusion coefficient, cm ² /sec
D_{ij}^0	binary diffusion coefficient at infinite dilution, cm ² /sec
D_{ij}	multicomponent diffusion coefficient, cm ² /sec
\mathcal{D}_{ij}	Onsager diffusion coefficient, cm ² /sec
$F_{i,d}$	driving force for diffusion of species i
$F_{i,r}$	frictional resisting force to diffusion of species i
f_i	friction coefficient of species i

I_A	intercept (at $\alpha_1 = 0$) of the reciprocal square root of reduced height-area ratio curve
I_{2m}	intercept (at $\alpha_1 = 0$) of the reduced second moment curve
J	total number of fringes on an exposure
J_i	flux of i relative to the coordinate of the plane across which the net volume flux is zero, moles of $i/\text{cm}^2/\text{sec}$.
J_i^c	flux of i relative to a coordinate-fixed plane
J_i^m	flux of i relative to the medium
J_i^V	flux of i relative to the coordinate of the plane across which the net volume flux is zero
J_i^*	tracer diffusion flux
j	fringe number
K	association equilibrium constant
K_i	viscosity measurement constant
k_1	proportionality constant between refractive index difference and fringe number
k_2	proportionality constant between an increment of measured distance and fringe number
L_A	intercept (at $\alpha_1 = 1$) of the reciprocal square root of the reduced height-area ratio curve
L_{2m}	intercept (at $\alpha_1 = 1$) of the reduced second moment curve
L_{ij}	phenomenological coefficient
M	magnification factor, 1.923
m_r	r^{th} moment of the refractive index gradient curve
$m_{r,i}$	r^{th} moment of component i of the refractive index gradient curve
N	Avogadro's number
n	refractive index

R	gas constant
R_i	differential refractive index constant of component i
R_i'	differential refractive index constant of component i based on total fringes
S_A	slope of the reciprocal square root of reduced height- area ratio curve
S_{2m}	slope of the reduced second moment curve
\dot{s}	rate of internal entropy production per unit volume
$s_e^2(z)$	variance of z
T	absolute temperature
t	actual time
$\Delta t_{\text{corr.}}$	time correction
$u_{i,m}$	velocity of species i relative to the velocity of the medium, cm./sec.
\bar{V}_i	partial molar volume of i , cm. ³ /mole
$v_{m,c}$	velocity of the medium relative to fixed coordinates
$v_{V,c}$	velocity of the plane across which the net volume flux is zero relative to fixed coordinates
X_i	mole fraction of i
x	distance along direction of diffusion
x_c	centroid of the refractive index gradient curve
Y	independent force for diffusion in constant volume system
y	distance perpendicular to the direction of diffusion
y	defined variable = $x/(2\sqrt{t})$
α_i	refractive index fraction of i
γ_i	activity coefficient of i
δ_{ij}	Kronecker delta

η	viscosity
θ	angle formed by the tangent to the refractive index curve, degrees
μ_i	chemical potential of i
μ_{ij}	partial derivative of μ_i with respect to C_j
ν	kinematic viscosity
σ_i	friction coefficient of i ($\sigma_i = Nf_i$)

Subscripts

A	refers to stoichiometric quantity of A
i	refers to arbitrary component or species
m	refers to measured values
1	refers to true quantity of A
2	refers to true quantity of B
11	refers to true quantity of AA complexes
12	refers to true quantity of AB complexes

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