# TRACER AND RUUTUAL DIFFUSOON IN SEVERAL ISOTHERMAL NON • IDEAL LLQUID <br> NON - ELECTROLYTE SYSTEMS 

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## thesis entitled

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# ABSTRACT <br> TKACER AND MUTUAL DIFFUSION IN SEVERAL ISOTHERMAL NON-IDEAL LIQUID NON-ELECTROIYTE SYSTEMS 

By<br>C. Michael Kelly

Hydrodynamic theory is used to develop equations predicting the effect of intermolecular association upon tracer and mutual diffusion. On the basis of simple assumptions about the volume of associated complexes, it is shown that Onsager's Reciprocal Relation should be valid in certain associated systems.

An experimental study is made of tracer and mutual diffusion in several systems. It is found that the association characteristics of a given system may be determined from plots of the tracer diffusivity-viscosity product vs. composition.

It is further shown that several systems which are non-associated, as can be seen from the $D^{*} \eta$ products, fail to obey the Hartley-Crank equation. Possible reasons for this fallure are presented.

A study has been made of the method currently employed for measuring ternary diffusivities. Weaknesses in the current metnod are pointed out, and suggestions are made for improvements. Within experimental precision, however, ternary measurements support both the predictions of hydrodynamic theory, and the Onsager Reciprocal Relations.

# TRACER AND MUTUAL DIFFUSION IN SEVERAL ISOTHERMAL NON-IDEAL LIQUID NON-ELECTROLYME SYSTEMS <br> By <br> ```C. Michael Kelly``` 

## A THESIS

Submitted to<br>Michigan State University<br>in partial fulfillment of the requirements for the degree of<br>DOCTOR OF PHILOSOPHY<br>Department of Chemical Engineering

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Interest in molecular diffusion in liquids has increased considerably in the past few years, from both experimental and theoretical points of view. Several techniques have been developed for measuring ordinary (both binary and multi-component) and tracer diffusive fluxes [22]. A large number of binary solutions, both electrolytic and non-electrolytic, have been studied. In the past few years a number of multi-component systems have also been investigated. Although much work has been done, when one considers the large number of simple systems available it becomes apparent that the surface has barely been scratched. Much more work needs to be done before there can be a precise understanding of molecular diffusion.

Theoretical eiforts have centered on determining the relationship between diffusive fluxes and the physical and chemical properties of the system, such as molecular weight, molecular size and shape, viscosity, state variables and solution thermodynamics. There has also been considerable interest in the relationship of ordinary diffusion to tracer diffusion, both from a predictive and a correlative standpoint. In multicomponent
systems, much emphasis has also been placed lipon verifying the theory of Onsager based upon the prirciples of irreversible thermodynamics, particularly the Onsager reciprocai relationships.

There have been two basic theoretical approaches to the description of diffusion processes. One is based upon modifications of the absolute reaction rate theory of Eyring [16], and tre other upon modifications of the nydrodynamic flow model of Stokes [29]. Tinis work wili follow the hydrodynamic approacn.

According to hydrodynamic theory, transport of a species through a solution in which there is a concentration gradient of that species takes place by means of two processes. The first process is the flow of indiviaual molecules through the surrounding medium as a result of a force acting upon those molecules. This has been termed by Hartley and Crank 'intrinsic diffusion' [20]. The second process is the transport of molecules due to flow of the medium. This flow occurs because of hydrostatic pressure gradients which arise from the differing volumes of the diffusing species. fiartley and Crank termed this process bulk flow.

The first process can be characterized by a combination of chemical and physical properties of the diffusing species which Hartley and Crank called the 'intrinsic diffusivity.' This 'intrinsic diffusivity' is the


#### Abstract

product of two terms, one involving the physical properties of the diffusing species and the surrounding medium, and the other involving solution thermodynamics. The first term will be called here the "intrinsic mobility" of the species, as suggested by Carman [6].


 Equations have been developed relating diffusivities to the intrinsic mobilities of diffusing species and solution thermodynamics. These have been modified by assuming that in some systems molecular interactions can be characterized by a chemical association. In these systems, a given stoichiometric component may undergo intrinsic diffusion not only as monomers, but as dimers, trimers, and other associated complexes as well.In this work ordinary (binary mutual, and ternary) diffusion has been studied by means of a Mach-Zehnder interferometer [5], and tracer diffusion has been studied by a capillary technique, for several systems of interest. It is shown that the degree of associative behavior in a given system can be determined from the tracer diffusivities of the components. Equations are developed relating association (as determined from tracer diffusivities) to the intrinsic diffusion process, and to solution thermodynamics, upon which ordinary diffusion is highly dependent. These equations will be tested by the diffusivity data previously mentioned.

It will be shown that hydrodynamic theory predicts that the Onsager reciprocal relations are valid for nonassociated systems, and several specific types of associated system. Experimental measurements made in the ternary system acetone - benzene - chloroform agree with Onsager's reciprocal relation within experimental accuracy.

Unfortunately, precise experimental verification by this method is quite difficult, for reasons which will be discussed later. An analysis has been made of the probable causes of low experimental precision in the measurement of ternary diffusivities by this method. Possible avenues of investigation will be suggested which might lead to an improvement in the method. It is hoped that future work along these lines will lead to a precise experimental verification of Onsager's reciprocal relation.

## BACKGROUND

## Hydrociynamic Flow Equations

Hydrodynamic theory states that a diffusing molecule behaves like a particle undergoing viscous flow through a continuous medium. The driving force for diffusion which causes this flow is generally agreed to be the gradient of the chemical potential of the diffusing species, acting in the direction opposite to the gradient of the chemical potential:

$$
\begin{equation*}
F_{i d}=-\nabla j_{i} \tag{1}
\end{equation*}
$$

Since there is assumed to be no acceleration, this must be balanced by a drag force upon the molecule, due to the viscosity of the medium.

Sutherland [29] and Einstein [10] independently showed that the viscous drag force for a sphere flowing through a continuous medium is given by

$$
\begin{equation*}
F_{s r}=-6 \pi r_{s} \eta v_{s m} \tag{2}
\end{equation*}
$$

where $r_{s}$ is the radius of the sphere, $\eta$ is the viscosity of the medium, and $v_{s m}$ is the velocity of the sphere with respect to the medium, and the negative
sign is becalise the drag force is in the direction opposite to the flow.

If the molecule were truly a sphere diffusing through a continuous medium, equations (1) and (2) could be combined to obtain

$$
\begin{equation*}
-\frac{d \mu_{i}}{d z}=6 \pi r_{i} n v_{i m} \tag{3}
\end{equation*}
$$

where $\nabla \mu_{i}$ has been replaced by $\frac{d \mu_{i}}{d z}$, denoting onedimensional diffusion. Multiplying by the concentration of the diffusing species, and solving for the flux of that species gives

$$
\begin{equation*}
J_{i}^{m}=v_{i m} C_{i}=-\frac{C_{i}}{\delta \pi r_{i} \eta} \frac{d \mu_{i}}{d z} \tag{4}
\end{equation*}
$$

where $J_{i}{ }^{m}$ is the flux of species $i$ with respect to the medium. However, most molecules are essentially nonspherical, and unless the diffusing molecules are much larger than the surrounding molecules the medium cannot be considered continuous. Therefore, the radius of the diffusing molecule $r_{s}$ will be replaced by an empirical constant $\frac{\sigma_{1}}{6 \pi}$, which will be called the ifriction coefficient' of species i. This yields

$$
\begin{equation*}
J_{i}^{m}=-\frac{C_{i}}{\sigma_{i}^{n}} \frac{d \mu_{i}}{d z} \tag{5}
\end{equation*}
$$

The defining equation for the chemical potential of species 1 is given by

$$
\begin{equation*}
\mu_{i}=\mu_{i}^{\circ}+R T \operatorname{Ln} a_{i} \tag{6}
\end{equation*}
$$

Substituting into equation (5) gives, at constant $T$ and $P$,

$$
\begin{equation*}
J_{i}^{m}=-\frac{C_{i}}{\sigma_{i}^{n}}\left[\frac{\partial \operatorname{Ln} a_{i}}{\partial C_{i}}\right]_{T, P}\left[\frac{\partial C_{i}}{\partial z}\right]_{T, P} \tag{7}
\end{equation*}
$$

This is the expression for the flux of species i due solely to the random molecular motion of 1 molecules, with respect to a coorainate system fixed in the surrounding medium. However, this is not a directly measurable quantity (although experiments can be conceived which could measure this flux, they are beyond the capabilities of current technicues). Tine flux which is measured in most experiments is the flux of component 1 with respect to a coordinate plane across which the total volume flux is zero.

This flux may be obtained from equation (7) by the following argument. First, the flux of component i with respect to a coordinate system fixed in the laboratory in an $N$-component system is given by the expression

$$
\begin{equation*}
\sum_{i=1}^{N} \bar{v}_{i} J_{i}^{m}+v_{m c}=v_{V c} \tag{8}
\end{equation*}
$$

where $v_{m c}$ is the velocity of the medium with respect to laboratory-fixed coordinates, and $v_{V c}$ is the velocity of the volume-fixed coordinate system with respect to laboratory-fixed coordinates. This can be seen by making a balance of volumes of diffusing species in the laboratory-fixed coordinate system. The quantity

$$
\sum_{i=1}^{N} \bar{V}_{i} J_{i}^{m}
$$

which has the units of velocity, represents the flux of volume due to random molecular motion, relative to the medium. To relieve hydrostatic pressure gradients, the medium itself must flow, relative to fixed coordinates, and this velocity is $v_{m c}$.

Unless the partial molar volumes of the diffusing species are constant, the total volume changes as diffusion proceeds. As a result, the volume-fixed coordinate system acquires a velocity relative to fixed coordinates, $\mathrm{V}_{\mathrm{Vc}}$. The total volume flux (which is a velocity, and is represented by the lef't side of equation (8)) with respect to fixed coordinates must
equal the velocity of the volume-fixed coordinate system with respect to fixed coordinates. Equation (8) can then be solved for the velocity of the medium:

$$
\begin{equation*}
v_{m c}=-\sum_{i=1}^{N} \bar{v}_{i} J_{i}^{m}+v_{V c} \tag{9}
\end{equation*}
$$

Wirth [34] gives a detailed derivation of this expression.

The measurable flux $J_{i}{ }^{V}$ is given by

$$
\begin{equation*}
J_{i}^{v}=J_{i}^{m}+c_{i}\left(v_{m c}-v_{v c}\right) \tag{10}
\end{equation*}
$$

Combining equations (7), (8) and (10) gives the basic hydrodynamic flow equation:

$$
\begin{equation*}
J_{i}^{v}=-\frac{c_{i}}{\sigma_{i} \eta} \frac{\partial \mu_{i}}{\partial z}+\frac{c_{i}}{n} \sum_{j=1} \frac{c_{j} \bar{v}_{j}}{\sigma_{j}} \frac{\partial \mu_{j}}{\partial z} \tag{I1}
\end{equation*}
$$

Solution Thermodynamics
Historically, there have been two approaches to describing non-ideal liquid solutions. It is agreed that intermolecular forces lead to deviations from Raoult's law. The differences between the two approaches arise from different interpretations of these intermolecular interactions.

The more widely accepted approach, as originally developed by van Laar [32] and van der Waals and their
followers, considers all intermolecular forces to be general in character. They arise from such phenomena as coulombic attraction and repulsion, dipole interaction (both permanent and induced dipoles), and van der Waals forces. This approach is called the "physical approach," and is readily applicable to most types of solutions.

The second approach, originally set forth by Dolezalek [9], considers all deviations from Raoult's law to arise from specific intermolecular forces which lead to chemical bonds between molecules. According to this theory, a solution of components $A$ and $B$ consists of $A$ monomers, $B$ monomers, plus various associated complexes such as $A_{2}, A_{3}, A_{4}, \ldots, B_{2}, B_{3}$, $B_{4}, \ldots, A B, A_{2} B, A B_{2}$, and so forth, depending upor. the specific interactions present. These individual species are then assumed to obey Raoult's Law. The proportions of the species present in solution are determined by an equilibrium characterized by an equilibrium constart, such as $A+B \underset{K_{A B}}{\rightarrow} A B$. Because of this equilibrium assumption, this is known as the "chemical model" of solution non-ideality.

Dolezalek originally proposed this model before the nature of chemical bonding was well understood. He was led by his model into some rather improbable hypotheses. For example, he tried to describe the
vapor-liquid equilibrium in the system nitrogen-argon by postulating the dimerization of argon, a most unlikely occurrence.

These two approaches are not mutually exclusive, though for years there was rather heated debate between the two schools. As our knowledge of chemical bonding increased, it became apparent that some systems really do associate in liquid solution. This is especially true of molecules which are capable of hydrogen bonding, such as water, alcohols, amines, etc., and of molecules which form charge-transfer complexes. On the other hand, there are many non-ideal solutions in which the formation of associated complexes is rather unlikely. Further, there is no good reason to conclude a priori that the various species present in an associated solution should obey Raoult's Law, as Dolezalek assumed. It would seem logical to try to combine the two approaches.

Non-associated Solutions
Before considering associated solutions, it would be well to look at non-associated solutions. Perhaps the simplest method of describing activity data in non-associated systems is to assume that the natural logarithm of the activity coefficients can be expressed as a power series expansion of the mole fractions of the stoichiometric components. This is the approach
taken by Margules in deriving the equations which bear his name. The constants in the power series expansion are restricted by the Gibbs-Duhem equation. Within these restrictions, the values of the constants are determined by fitting the series to experimental thermodynamic data, generally vapor-liquid equilibria, by means of least-squares analysis. The equation can be made to fit experimental data to whatever degree of accuracy desired by simply taking more and more terms into the series expansion, though at the expense of introducing more arbitrary constants. It can be extended quite easily to multicomponent systems, and is not restricted in its range of application except by the number of terms in the series that ore wishes to use [35]. Though this procedure is mathematically rigorous, and useful for describing experimental data for use in design calculations, it sheds very little light on the true nature of interactions in liquid solutions. Van Laar [32] proposed a far more restricted equation, based upon theoretical considerations, for binary systems. This equation, and modifications of it, have been very successful in describing binary systems, especially those for which the activity data are rather symmetrical, and for which the molecular sizes and shapes are not too different. It has several disadvantages, though. It is not easily extended to multicomponent
systems, without introducing further assumptions and more arbitrary constants, which tend to decrease the physical meaning of the equation. Also, it cannot be used reliably for those systems in which there is considerable bonding-type molecular interaction, nor for such systems as high-polymer solutions. Both the Margules and van Laar equations, as well as several modifications, are discussed in considerable detail by Wohl [35].

Another approach which is based upon theoretical thermodynamic considerations is that of Hildebrand and Scott for regular solutions [25]. Since it forms the basis for some later conclusions, it will be described in a little more detail.

If a solution contains enough thermal energy, the different intermolecular forces of the various components will not be sufficient to cause any one molecule to tend to aggregate with any particular type of molecule, either like or unlike. The entropy of mixing will then be the same as for an ideal solution. Such a solution is termed 'regular', even though it is nonideal, and the partial molar entropy of mixing is given by

$$
\begin{equation*}
\Delta \bar{S}_{i}=-R \operatorname{Ln} X_{i} \tag{12}
\end{equation*}
$$

By making three assumptions, Hildebrand and Scott show that the heat of mixing in the binary regular system of components $i$ and $j$ is

$$
\begin{equation*}
\Delta \bar{H}_{i}=\overline{\mathrm{V}}_{i} \phi_{j}^{2}\left(\delta_{j}-\delta_{i}\right)^{2} \tag{13}
\end{equation*}
$$

where $\phi_{i}$ is the volume fraction of component $i$ (neglecting expansion on mixing) and $\delta_{i}$ is defined by

$$
\delta_{i}=\left[\frac{E_{i}}{\bar{v}_{i}}\right]^{\frac{1}{2}}
$$

where $E_{i} V$ is the internal energy of vaporization. The assumptions leading to this relationship are: (a) the energy of interaction between two molecules depends only upon the distance between them and their orientation, (b) the volume change of mixing at constant pressure is zero, and (c) the mixing of molecules is random. The third assumption is essentially the definition of a regular solution. The first, although not rigorously correct, has been the basis for most successful attempts at modeling the liquid state. The second can be eliminated by extensive modification, as shown by Hildebrand and Scott [21], but will not be done here.

For regular solutions, where the entropy of mixing is ideal, the activity coefficients are given by

$$
\begin{equation*}
\operatorname{Ln} \gamma_{i}=\frac{\Delta \bar{H}_{i}}{R T}=\bar{v}_{i} \phi_{j}^{2}\left(\delta_{j}-\delta_{i}\right)^{2} \tag{14}
\end{equation*}
$$

This can be extended to multicomponent systems quite easily. Under the same assumptions as before, for a ternary system we find that

$$
\begin{equation*}
\operatorname{Ln} \gamma_{i}=\frac{\bar{V}_{i}}{R T}\left(\delta_{i}-\bar{\delta}\right)^{2} \quad i=1, \ldots 3 \tag{15}
\end{equation*}
$$

where

$$
\bar{\delta}=\sum_{i=1}^{3} \delta_{i} \phi_{i}
$$

with $\delta_{i}$ and $\phi_{i}$ as defined before. Detailed derivations of equations (12) through (15) are given by Hildebrand and Scott [21].

Associated Solutions
The intermolecular forces which define an associated solution would seem to be precisely those forces which disqualify that solution from being considered a regular solution. In a regular solution, the molecules mix as though they had no preference as to the nature of their nearest neighbors. In associated solution, on the other hand, any given molecule has a distinct preference for another molecule as its nearest neighbor, as expressed by the polymerization equilibrium. For example, a molecule with a hydroxyl group will prefer
to have another molecule with a hydroxyl group as nearest neighbor (rather than a saturated hydrocarbon, say) due to its ability to form the hydrogen bond.

It might then be a good assumption that all those forces which lead to a solution not being regular are due to complex formation by chemical bonding. Certainly chemical bonding would be the major contributor to nonregularity in associated solutions. It would seem logical then that the true species present mix to form a regular solution.

The mole fractions of the true species are determined by the equiliorium equation and the stoichiometric mole fractions. Consider for example a binary system in which one component dimerizes as a regular ternary system, consisting of monomers of each component plus dimers. Equations (15) can then be used to predict the activity data from knowledge of the equilibrium constant $K$. Alternatively, the equilibrium constant can be determined from activity data by adjusting it until equations (15) give the best fi̇t.

This procedure requires knowledge of the partial molar volume and the molar energy of vaporization of the dimer. This can be handled in either of two ways. These quantities may be treated as adjustable parameters, in which case equations (15) will be a three-parameter set of equations for the binary system [13]. Otherwise,

assumptions can be made about the values of these parameters, or their relation to those parameters for the monomers. Equations (15) will then be a one-parameter set of equations for the activity coefficients in the binary system. The latter method will be used later for fitting activity data in both binary and ternary associated systems.

Solution Thermociynamics--
Nonassociated Solutions
The Gibbs free energy of a system of N components is given by

$$
\begin{equation*}
G=\sum_{i=1}^{N} n_{i} G_{i}^{0}+\sum_{i=1}^{N} r_{i} R T \operatorname{Ln} X_{i}+\Delta G \sum_{i=1}^{N} n_{i} \tag{16}
\end{equation*}
$$

where $n_{i}$ is the number of moles of $i, G_{i}{ }^{0}$ is the molar free energy of pure component $i, X_{i}$ the mole fraction of $i$, and $\Delta G$ represents the difference in free energy between one mole of real solution and one mole of an ideal solution with the same composition.

The partial molar free energy of component $i$, the chemical potential of $i$, is given by

$$
\begin{equation*}
\mu_{i}=\frac{\partial G}{\partial n_{i}}=\mu_{i}^{0}+R T \operatorname{Ln} \gamma_{i} X_{i} \tag{17}
\end{equation*}
$$

where $\mu_{i}{ }^{\circ}$ is a function of $T$ and $P$ only. Carrying out the indicated differentiation on equation (16), and equating to equation (17) gives

$$
\begin{equation*}
\operatorname{Ln} \gamma_{i}=\frac{1}{R T} \frac{\partial}{\partial n_{i}}\left[\Delta G \sum_{i=1}^{N} n_{i}\right] \tag{18}
\end{equation*}
$$

If a power series expansion is written for $\Delta G$, and the coefficients constrained by the Gibbs-Duhem equation, after dropping terms of higher order than $X^{3}$ there results

$$
\begin{align*}
\frac{\Delta G}{R T} & =x_{1} x_{2}^{2} a_{12}+x_{1} x_{3} a_{13}+x_{2} x_{3} 2 a_{23} \\
& +x_{1}^{2} x_{2} 3 a_{112}+x_{1} x_{2}^{2} 3 a_{122}+x_{1}^{2} x_{3} 3 a_{113}  \tag{19}\\
& +x_{1} x_{3}^{2} 3 a_{113}+x_{2}^{2} x_{3} 3 a_{223}+x_{2} x_{3}^{2} 3 a_{233} \\
& +x_{1} x_{2} x_{3}{ }^{6 a_{123}}
\end{align*}
$$

This is the three-suffix Margules Equation for a ternary system [35]. Binary systems may be treated as special cases, and the corresponding Margules Equation obtained from equation (19) by simply setting $X_{3}$ equal to zero. Carrying out the differentiations in equation (18) gives the activity coefficients:

$$
\begin{align*}
\text { In } \gamma_{1} & =2 x_{1} x_{2}\left[A_{21}-x_{1} A_{21}-x_{2} A_{12}\right]+x_{2}^{2} A_{12} \\
& +2 x_{1} x_{3}\left[A_{31}-x_{1} A_{31}-x_{3} A_{13}\right]+x_{3}^{2} A_{13}  \tag{20}\\
& +\left(x_{2} x_{3}-2 x_{1} x_{2} x_{3}\right)\left[A_{21}+A_{13}+A_{32}-C\right]
\end{align*}
$$

$$
\begin{align*}
\text { in } r_{2} & =2 x_{2} x_{1}\left[A_{12}-x_{2} A_{12}-x_{1} A_{21}\right]+x_{1}^{2} A_{21} \\
& +2 x_{2} x_{3}\left[A_{32}-x_{2} A_{32}-x_{3} A_{23}\right]+x_{3}^{2} A_{23}  \tag{21}\\
& +\left(x_{1} x_{3}-2 x_{1} x_{2} x_{3}\right)\left[A_{21}+A_{13}+A_{32}-C\right] \\
\text { Ln } r_{3} & =2 x_{3} x_{1}\left[A_{13}-x_{3} A_{13}-x_{1} A_{31}\right]+x_{1}^{2} A_{31} \\
& +2 x_{2} x_{3}\left[A_{13}-x_{3} A_{13}-x_{1} A_{31}\right]+x_{1}^{2} A_{31}  \tag{22}\\
& +\left(x_{1} x_{2}-2 x_{1} x_{2} x_{3}\right)\left[A_{21}+A_{13}+A_{32}-C\right]
\end{align*}
$$

where the constants are defined by

$$
\begin{array}{ll}
2 a_{12}+3 a_{122} & =A_{12} \\
2 a_{12}+3 a_{112} & =A_{21} \\
2 a_{13}+3 a_{133} & =A_{13}  \tag{23}\\
2 a_{13}+3 a_{113} & =A_{31} \\
2 a_{23}+3 a_{233} & =A_{23} \\
2 a_{23}+3 a_{223} & =A_{32} \\
3 a_{112}+3 a_{133}+3 a_{223}-6 a_{123}=C
\end{array}
$$

The binary analogues to equations (20), (21) and
(22) are

$$
\begin{align*}
& \operatorname{Ln} \gamma_{1}=2 x_{1} x_{2}\left[A_{21}-x_{1} A_{21}-x_{2} A_{12}\right]+x_{2}^{2} A_{12}  \tag{24}\\
& \operatorname{Ln} \gamma_{2}=2 x_{2} x_{1}\left[A_{12}-x_{2} A_{12}-x_{1} A_{21}\right]+x_{1}^{2} A_{21} \tag{25}
\end{align*}
$$

wonl [35] gives cetailed derivations of equations formally similar, and algebraically identical to equations (20) througn (25).

If isothermal ternary activity data are available equations (20), (21) and (22) can be fit to tre data by a least-squares technique, with seven adjustable jarameters. This is an unreasonably large number, but some may be specified by otner means. If the ternary data are available, then binary data for each of the three pairs of comporents are almost sure to be available. The binary data may be fit by a least-squares tecinique, thus fixing six of the seven constants in equations (20) through (23). The constant $C$ may then be determined from the ternary data.

In most cases of interest, ternary isotrermal data is not available, but these equations are still useful. Wohl interprets the various constants in equation (19) in terms of physical interactions between molecules. Thus $a_{12}$ represents the energy of interaction of molecules 1 and $2, a_{113}$ the interaction between two molecules of type 1 and one of type 3, etc. From equation (23) we see that under this interpretation $C$ is a ternary interaction parameter. Since in non-electrolyte solutions threemolecule interactions are not so strong as two-molecule interactions, $C$ can probably be taken as zero. As long as this holds, ternary activity data can be predicted
from data for the subsidiary binaries. This has been done for the system acetone-benzene-chloroform. Data for the system acetone-chloroform have been taken from Hildebrand and Scott [21], for benzene-chloroform and acetone-benzene from Timmermans [30]. These data, and their approximations by equations (24) and (25), as well as the least-squares parameters $A_{12}, A_{21}, \ldots$ are given in Tables $F-1$ through $F-4$ of Appendix $F$.

## Solution Thermodynamics-- <br> Associated Solutions

As discussed previously, an associated solution may be thought of as a regular solution of the true species present. By making approximations as to the values of $\overline{\mathrm{V}}$ and $\delta$ fur the associated complexes, the equilibrium constants may be treated as adjustable parameters in fitting the activity data. This will be done here for a specific case, a binary system of components $A$ and $B$, where the association reaction

$$
A+B \leftrightarrow A B
$$

occurs. To avoid later confusion, let us refer to the stoichiometric components by letters $A$ and $B$, and the true species present by numbers 1,2 , and 12 , where 1 refers to the monomer of component $A, 2$ to the monomer of $B$ and 12 to the dimer. The true equilibrium constant
for this reaction is given by $K_{a}$, the ratio of activities of species:

$$
\begin{equation*}
K_{a}=\frac{a_{12}}{a_{1} a_{2}} \tag{27}
\end{equation*}
$$

Defining $K$ and $K_{\gamma}$ by

$$
\begin{align*}
K & =\frac{x_{12}}{X_{1} X_{2}}  \tag{28}\\
K_{\gamma} & =\frac{\gamma_{12}}{\gamma_{1} \gamma_{2}} \tag{29}
\end{align*}
$$

we see that

$$
\begin{equation*}
K_{a}=K_{\gamma} \tag{30}
\end{equation*}
$$

Nikol'skii [27] has shown that the chemical potential of a component in solution is equal to the chemical potential of its monomer:

$$
\begin{equation*}
X_{A} \gamma_{A}=X_{I} \gamma_{I} \tag{31}
\end{equation*}
$$

Hence, the activity coefficient of component $A$ is given by

$$
\begin{equation*}
\gamma_{A}=\frac{x_{1}}{X_{A}} \gamma_{1} \tag{32}
\end{equation*}
$$

The activity coefficient $\gamma_{A}$ is a directly measurable quantity, but $\gamma_{1}$ is not.

For a regular solution, equation (15) holds:

$$
\begin{equation*}
\operatorname{Ln} \gamma_{1}=\frac{\overline{\mathrm{V}}_{1}}{\mathrm{RT}}\left(\delta_{1}-\bar{\delta}\right)^{2} \tag{15}
\end{equation*}
$$

where $\delta_{1}$ and $\bar{\delta}$ are defined by

$$
\begin{align*}
& \delta_{i}=\left[\frac{E_{1}}{\bar{V}_{i}}\right]^{\frac{1}{2}}  \tag{33}\\
& \bar{\delta}=\sum_{i=1}^{3} \phi_{i} \delta_{i}  \tag{34}\\
& \phi_{i}=\frac{x_{i} \bar{V}_{i}}{X_{1} \bar{V}_{1}+x_{2} \overline{\bar{V}}_{2}+X_{12} \overline{\bar{V}}_{12}} \tag{35}
\end{align*}
$$

Similar equations give the vaiues of $\operatorname{Ln} \gamma_{2}$ and $\operatorname{In} \gamma_{12}$.
Now, for a given $X_{A}$ and $X_{B}$, the mole fractions of the true species depend only upon the value of $K$, and can be determined from equations (28) and the stoichiometric relationships

$$
\begin{align*}
& c_{1}=c_{A}-c_{12} \\
& c_{2}=c_{B}-c_{12} \tag{36}
\end{align*}
$$

Let us make the following approximations:
a) $\bar{v}_{12}=\bar{v}_{1}+\bar{v}_{2}$
b) $E_{12}^{V}=E_{1}^{v}+E_{2}^{V}$

Assumption a) is required for consistency of constant molar volumes which will be assumed later, and which Kett [23] determined to be a good assumption for the associated system ether-chloroform-carbon tetrachloride. Assumption b) is reasonable if the energy of the dimerization bond is approximately the same in the vapor state as in the liquid state, that is, if $\Delta E$ for the equilibrium reaction is the same in both states. Note that $\Delta H$ will probably be different, as there is a change in PV in the vapor state.

Now equations (15) and (32) through (39) can be combined to give in $\gamma_{A}$ in terms of measurable quantities ( $\bar{V}$ 's, $E^{\mathrm{V}}$ 's, stoichiometric mole fractions, temperature) and one adjustable parameter K .

It is now possible to determine the value of K from experimental isothermal activity data, by a least-squares technique. This has been done for the system etherchloroform from total-pressure data at $25^{\circ} \mathrm{C}$ from Kohnstamm and van Dalfson [24]. The results agree reasonably well with the data of Guglielmo [30] at an apparently higher unreported temperature for the vapor-liquid equilibrium.

This procedure can be easily extended to a ternary system of $A, B$, and $C$ where $A$ and $B$ dimerize as before, and $C$ is inert. The value of $K$ found for the binary dimerization equilibrium should not change in the ternary solution, provided the solvent $C$ does not change the mechanism of the reaction but merely dilutes the reactive components. By making this reasonable assumption, it is possible to predict the ternary activity data for such an associating system from physical properties and activity data for the associating binary pair of components.

These principles are easily carried over to other forms of association.

## Tracer Diffusivities-Norassociated Systems

The tracer diffusivity is defined by a modified version of Fick's Law:

$$
\begin{equation*}
J_{i} V_{*}=-D_{i}^{*} \frac{\dot{\alpha} C_{i}^{*}}{\alpha z} \tag{39}
\end{equation*}
$$

where the superscript * designates the tagged molecules. Since the tagged molecules are considered to be identical to the untagged molecules physically and chemically, if there are no external pressure gradients there will be no bulk flow. For every molecule diffusing in one direction, there will be another molecule diffusing back in the other direction. Since these molecules have
the same volume, there will be no hydrostatic pressure gradients, and therefore no bulk flow. In this case, the velocity of the medium-fixed coordinate system and the volume-fixed coordinate system will be zero (relative to laboratory-fixed coordinates).

This means that for tracer diffusion equation (11)
becomes

$$
\begin{equation*}
J_{i} V_{*}=J_{i} m_{*}=-\frac{C_{i}^{*}}{\sigma_{i}^{n}} \frac{d \mu_{i}^{*}}{d z} \tag{40}
\end{equation*}
$$

For tracer diffusion equation (17) becomes

$$
\begin{equation*}
\mu_{i}^{*}=\mu_{i}^{O^{*}}+R T \operatorname{Ln} \gamma_{i}^{*} X_{i}^{*} \tag{41}
\end{equation*}
$$

Applying the chain rule gives the derivative of $\mu_{i}{ }^{*}$ :

$$
\begin{equation*}
\frac{d \mu_{i}^{*}}{d z}=\frac{d \mu_{i}^{*}}{d C_{i}^{*}} \frac{d C_{i}^{*}}{d z}=R T\left[\frac{d \operatorname{Ln}{ }_{i}^{*}}{d C_{i}^{*}}+\frac{d \operatorname{Ln} X_{i}^{*}}{d C_{i}^{*}}\right] \frac{d C_{i}^{*}}{d z} \tag{42}
\end{equation*}
$$

Since the solution is chemically uniform, it can be shown that

$$
\begin{align*}
& \frac{d \operatorname{Ln} \gamma_{i}^{*}}{d C_{i}^{*}}=0 \\
& \frac{d \operatorname{Ln} X_{i}^{*}}{d \operatorname{Ln} C_{i}^{*}}=1 \tag{43}
\end{align*}
$$

Combining equations (40), (42) and (43) gives

$$
\begin{equation*}
J_{i} V_{*}=-\frac{R T}{\sigma_{i}{ }^{n}} \frac{\mathrm{~d} C_{i}{ }^{*}}{\mathrm{~d} z} \tag{44}
\end{equation*}
$$

Comparing equations (39) and (44) we see that

$$
\begin{equation*}
D_{i}^{*}=\frac{R T}{\sigma_{i} \eta} \tag{45}
\end{equation*}
$$

Carman [5] suggested that the combination of physical properties on the rigint nand side of this equation be termed the 'intrinsic mobility' of species i. This designation will be adopted here. The important result is that the tracer diffusivity of a non-associated component is equal to the intrinsic mobility of that component.

## Tracer Diffusion--Associated

## Systems

The most easily analyzed case of tracer diffusion in an associated system is the binary system of $A$ and $B$ where there is an association to form an $A B$ dimer. Denoting the species present as 1,2 and 12 , the total concentration of tagged component $A$ is given by

$$
\begin{equation*}
C_{A}^{*}=C_{1}^{*}+C_{12}^{*} \tag{46}
\end{equation*}
$$

The flux of $A$ molecules in tracer diffusion is

$$
\begin{equation*}
J_{A} V_{*}=-D_{A}^{*} \frac{d C_{A}^{*}}{\dot{\alpha} z}=J_{1} V_{*}+J_{12} V_{*} \tag{47}
\end{equation*}
$$

Substituting equation (40) for the fluxes gives

$$
\begin{equation*}
J_{A} V_{*}=-\frac{R T}{\eta}\left[\frac{1}{\sigma_{1}} \frac{\mathrm{dC}_{1}{ }^{*}}{\dot{\alpha} z}+\frac{1}{\sigma_{12}} \frac{\mathrm{dC}_{12}}{\dot{\alpha} z}\right] \tag{48}
\end{equation*}
$$

Differentiating equation (46) with respect to $C_{A}{ }^{*}$ gives

$$
\begin{equation*}
\frac{\partial C_{1}^{*}}{\partial C_{A}^{*}}+\frac{\partial C_{12}^{*}}{\partial C_{A}^{*}}=1 \tag{49}
\end{equation*}
$$

Substituting into equation (48) gives

$$
\begin{equation*}
J_{A} V_{*}=-\frac{R T}{\sigma_{1} \eta}\left[1-\frac{\partial C_{2}^{*}}{\partial C_{A}^{*}} \frac{d C_{A}^{*}}{d z}-\frac{R T}{\sigma_{12}{ }^{\eta}} \frac{\partial C_{12}^{*}}{\partial C_{A}^{*}} \frac{d C_{A}^{*}}{d z}\right. \tag{50}
\end{equation*}
$$

If the physical and chemical properties of the tagged molecules are the same as the untagged molecules, we may assume that the distribution of tagged molecules is the same in the two species as in the component:

$$
\begin{equation*}
\frac{c_{12}^{*}}{c_{12}}=\frac{c_{1}^{*}}{c_{1}}=\frac{c_{A}^{*}}{c_{A}} \tag{51}
\end{equation*}
$$

This ratio is a constant, since it depends only upon the proportion of $C_{A}$ and $C_{A}^{*}$ when the solution was made up. Therefore,

$$
\begin{equation*}
\frac{\partial C_{12}^{*}}{\partial C_{A}^{*}}=\frac{c_{12}}{C_{A}} \tag{52}
\end{equation*}
$$

Now for convenience, define the pseudo-mole fraction of component 12 by

$$
\begin{equation*}
x_{12}^{0}=\frac{c_{12}}{c_{A}+c_{B}} \tag{53}
\end{equation*}
$$

Combining this with equation (52) and substituting into equation (50) gives, after rearrangement of terms

$$
\begin{equation*}
J_{A} V_{*}=-\frac{R T}{n}\left[\frac{1}{\sigma_{1}}+\left(\frac{1}{\sigma_{12}}-\frac{1}{\sigma_{1}}\right) \frac{X_{12}}{X_{A}}\right] \frac{\partial C_{A}^{*}}{\partial z} \tag{54}
\end{equation*}
$$

Comparing this with the defining equation, Fick's Law, leads to the desired result:

$$
\begin{equation*}
D_{A}^{*}=\frac{\mathrm{RT}}{\eta}\left[\frac{1}{\sigma_{2}}+\left(\frac{1}{\sigma_{12}}-\frac{1}{\sigma_{1}}\right) \frac{\mathrm{X}_{12}}{\mathrm{X}_{\mathrm{A}}}\right] \tag{55}
\end{equation*}
$$

The derivation for component $B$ only requires renumbering the species and components in the previous equation, so that A becomes B, 1 becomes 2, and vice versa. Equation (55) then becomes

$$
\begin{equation*}
D_{B}^{*}=\frac{R T}{n}\left[\frac{1}{\sigma_{2}}+\left(\frac{1}{\sigma_{12}}-\frac{1}{\sigma_{2}}\right) \frac{X_{12}{ }^{\circ}}{X_{B}}\right] \tag{56}
\end{equation*}
$$

Wirth [34] derived equivalent equations, and carried the derivations out for two other simple systems, a binary system where one component is inert and the other forms a self-dimer, and a ternary system where two components form a cross-dimer and the third component is inert. These equations, along with those to be derived in this work are given in Table l, on page .

Theoretically, equations corresponding to (54) and (55) can be developed for any associating system, provided an equation can be written for each association equilibrium. Practically, such equations become very difficult to handle if there are more than 2 or 3 such equilibria. Furthermore, since a considerable part of the value of these equations lies in their ability to model the measured tracer diffusivity data, the number of associations must be small, or there will be a large number of adjustable parameters available to fit the data. Also, whenever the equations become too complex, they lose much of their physical meaning in the algebra.

We will now consider another simple system, and develop equations predicting the tracer diffusivities. Let components $A, B$ and $C$ be ternary system in which there are two competing equilibria

$$
\begin{aligned}
& A+B \leftrightarrow A B \\
& A+C \leftrightarrow A C
\end{aligned}
$$

Let the true species present be designated 1, 2, 3, 12 and 13 representing $A, B, C$ monomers, $A B$ and $A C$ dimers respectively. The relative concentrations at any composition can be determined from the equilibrium constants $K_{1}$ and $K_{2}$. The fluxes and concentrations are given by the following:

$$
\begin{gather*}
J_{A} V_{*}=-D_{A}^{*} \frac{\partial C_{A}^{*}}{\partial z}=J_{1} V_{*}+J_{12} V_{*}+J_{13} V_{*}  \tag{57}\\
J_{B} V_{*}=-D_{S}^{*} \frac{\partial C_{B}^{*}}{\partial z}=J_{2} V_{*}+J_{12} V_{*}  \tag{58}\\
J_{C} V_{*}=-D_{C}^{*} \frac{\partial C_{C}}{\partial Z}=J_{B}^{*} V_{*}+J_{13} V_{*}  \tag{59}\\
C_{A}^{*}-C_{1}^{*}+C_{12}^{*}+C_{13}^{*}  \tag{60}\\
C_{D}^{*}=C_{2}^{*}+C_{12}^{*}  \tag{61}\\
C_{C}^{*}=C_{3}^{*}+C_{13}^{*} \tag{62}
\end{gather*}
$$

Equations (58), (59), (61), and (62) are equivalent to those for the binary system just considered. The tracer diffusivities are analogous to those in equations (54) and (55):

$$
\begin{equation*}
D_{B}^{*}=\frac{R T}{n}\left[\frac{1}{\sigma_{2}}+\left(\frac{1}{\sigma_{12}}-\frac{1}{\sigma_{2}}\right) \frac{X_{12}}{X_{B}}\right] \tag{63}
\end{equation*}
$$

$$
\begin{equation*}
D_{C}^{*}=\frac{R T}{n}\left[\frac{1}{\sigma_{3}}+\left(\frac{1}{\sigma_{13}}-\frac{1}{\sigma_{3}}\right) \frac{X_{13}}{X_{C}}\right] \tag{64}
\end{equation*}
$$

The equations for component A are slightly more complex. From equation (57):

$$
\begin{equation*}
J_{A} V_{*}=-\left[\frac{R T}{\sigma_{1} n} \frac{\partial C_{1}^{*}}{\partial z}+\frac{R T}{\sigma_{12^{n}}^{n}} \frac{\partial C_{12}}{\partial z}+\frac{R T}{\sigma_{13}{ }^{n}} \frac{\partial C_{13}}{\partial z}\right] \tag{65}
\end{equation*}
$$

Differentiating equation (60) with respect to $C_{A}^{*}$ and substituting into equation (65) gives
$J_{A} V_{*}=-\frac{R T}{n}\left[\frac{1}{\sigma_{1}}\left(1-\frac{\partial C_{12}^{*}}{\partial C_{A}^{*}}-\frac{\partial C_{13}^{*}}{\partial C_{A}{ }^{*}}\right)+\frac{1}{\sigma_{12}} \frac{\partial C_{12}^{*}}{\partial C_{A}^{*}}+\frac{1}{\sigma_{13}} \frac{\partial C_{13}{ }^{*}}{\partial C_{A}^{*}}\right] \frac{C_{A}^{*}}{z}$

As before, the derivatives $\frac{\partial C_{12}{ }^{*}}{\partial C_{A}{ }^{*}}$ and $\frac{\partial C_{13} 3^{*}}{\partial C_{A}{ }^{*}}$ can be written
in terms of pseudo-mole fractions $X_{12}{ }^{\circ}=\frac{C_{12}}{C_{A}+C_{B}+C_{C}}$ and

$$
\mathrm{X}_{13}^{\circ}=\frac{\mathrm{C}_{13}}{\mathrm{C}_{\mathrm{A}}+\mathrm{C}_{\mathrm{B}}+\mathrm{C}_{\mathrm{C}}} \text { to give }
$$

$$
\begin{equation*}
J_{A} V_{*}=-\frac{R T}{n}\left[\frac{1}{\sigma_{1}}+\left(\frac{1}{\sigma_{12}}-\frac{1}{\sigma_{1}}\right) \frac{X_{12}{ }^{\circ}}{X_{A}}+\left(\frac{1}{\sigma_{13}}-\frac{1}{\sigma_{1}}\right) \frac{X_{13}}{X_{A}}\right] \frac{o C_{A}^{*}}{\partial z} \tag{67}
\end{equation*}
$$

From this it can easily be seen that

$$
\begin{equation*}
\mathrm{D}_{\mathrm{A}}^{*}=\frac{\mathrm{RT}}{n}\left[\frac{1}{\sigma_{1}}+\left(\frac{1}{\sigma_{12}}-\frac{1}{\sigma_{1}}\right) \frac{\mathrm{X}_{12}{ }^{\circ}}{\mathrm{X}_{\mathrm{A}}}+\left(\frac{1}{\sigma_{13}} \frac{1}{\sigma_{1}}\right) \frac{\mathrm{X}_{13}{ }^{\circ}}{\mathrm{X}_{\mathrm{A}}}\right] \tag{68}
\end{equation*}
$$

which is the desired result. The generalization to a larger number of competing equiiibria is obvious. If component A dimerizes with N other components, the tracer diffusivity of $A$ will be given by

$$
\begin{equation*}
D_{A}^{*}=\frac{R T}{n}\left[\frac{1}{\sigma_{1}}+\sum_{i=2}^{N+1}\left(\frac{1}{\sigma_{1 i}}-\frac{1}{\sigma_{1}}\right) \frac{X_{1 i}^{0}}{X_{A}}\right] \tag{69}
\end{equation*}
$$

This equation is general, and though it provides physical insight into the effect of several association reactions on tracer diffusion, it is probably not too useful in fitting experimental cata, since it allows $N$ adjustable parameters (the friction factors $\sigma_{11}$ ) if the equilibrium constants can be determined independently, or $N^{2}$ if they are aiso considered free. The physical meaning of this equation is that the tracer diffusivity of an associating component is equal to the intrinsic mobility of that species, decreased by the difference between the mobilities of the monomer and the associated complex (corrected for the amount of association) for each of the association reactions.

This same type of result can be obtained for the slightly more complicated case in which one component associates with itself. Consicier the binary system in which component A reacts to form a dimer, according to

$$
A+A \leftrightarrow A_{2}
$$

and component $B$ is inert. In this case, the flux of $A^{*}$ is given by

$$
\begin{equation*}
\bar{J}_{A} V_{*}=-\left[\frac{R T}{\sigma_{1} \eta} \frac{\partial C_{1}^{*}}{\partial Z}+\frac{R T}{\sigma_{11}{ }^{\eta}} \frac{\partial C_{11}^{*}}{\partial z}+2 \frac{R T}{\sigma_{11}{ }^{n}} \frac{\partial C_{11}{ }^{* *}}{\partial z}\right] \tag{70}
\end{equation*}
$$

where the dimer can carry either one or two tags, as denoted by the number of asterisks. Stoichiometry shows

$$
\begin{equation*}
C_{A}^{*}=C_{1}^{*}+C_{11}^{*}+2 C_{11}^{* *} \tag{71}
\end{equation*}
$$

Proceeding as before, we write

$$
J_{A} V_{*}+\left\{\frac{R T}{n \sigma I} \frac{\partial C_{1}^{*}}{\partial C_{A}^{*}}+\frac{R T}{n \sigma_{11}}\left[\frac{\partial C_{11}^{*}}{\partial C_{A}^{*}}+2 \frac{\partial C_{11}^{* *}}{\partial C_{A}^{*}}\right]\right\} \frac{\partial C_{A}^{*}}{\partial z}(72)
$$

Differentiating (71) gives

$$
\begin{equation*}
\frac{\partial C_{1}^{*}}{\partial C_{A}^{*}}=1-\frac{\partial C_{11}^{*}}{\partial C_{A}^{*}}-2 \frac{\partial C_{11}^{* *}}{\partial C_{A}^{*}} \tag{73}
\end{equation*}
$$

which, when substituted into (72) yields, after rearrangement,
$J_{A} V_{*}+-\frac{R T}{n}\left[\frac{1}{\sigma_{1}}+\left(\frac{1}{\sigma_{11}}-\frac{1}{\sigma_{1}}\right) \frac{\partial C_{11}^{*}}{\partial C_{A}^{*}}+2\left(\frac{1}{\sigma_{11}}-\frac{1}{\sigma_{1}} \frac{\partial C_{11}{ }^{*}}{\partial C_{A}^{*}}\right] \frac{\partial C_{A}^{*}}{\partial Z^{*}}\right.$

Equation (74) can be written

$$
\begin{equation*}
J_{A} V_{*}=-\frac{R T}{n}\left[\frac{1}{\sigma_{1}}+\left(\frac{1}{\sigma_{11}}-\frac{1}{\sigma_{1}}\right)\left(\frac{\partial C_{11}^{*}}{\partial C_{A}^{*}}+2 \frac{\partial C_{11}^{* *}}{\partial C_{A}^{*}}\right)\right] \tag{75}
\end{equation*}
$$

The derivatives again depend only upon the equilibrium constant $K$, although calculation of their values is somewhat involved. The tracer diffusivity, from equation (77) is then

$$
\begin{equation*}
\mathrm{D}_{\mathrm{A}}^{*}=\frac{\mathrm{RT}}{n}\left[\frac{1}{\sigma_{1}}+\left(\frac{1}{\sigma_{11}}-\frac{1}{\sigma_{1}}\right)\left(\frac{\partial C_{11}^{*}}{\partial C_{A}^{*}}+2 \frac{\partial C_{11}^{*}}{\partial C_{A}^{*}}\right)\right] \tag{76}
\end{equation*}
$$

Wirth [34] gives a slightly different derivation,
which leads to a formula which is less difficult to evaluate:

$$
\begin{equation*}
\mathrm{D}_{\mathrm{A}}^{*}=\frac{\mathrm{RT}}{n}\left[\frac{1}{\sigma_{11}}+\left(\frac{1}{\sigma_{1}}-\frac{1}{\sigma_{11}}\right) \frac{\mathrm{X}_{1}^{0}}{\mathrm{X}_{\mathrm{A}}}\right] \tag{77}
\end{equation*}
$$

The form given by wirth is more useful for trying to fit data for which there is only one dimerization equilibrium. It is diffucult to generalize, however, while the derivation of generalized forms of equation (78) is rather simple.

Consider the system where there are two components, one of which undergoes two self-polymerization reactions,

$$
\begin{aligned}
& A+A \leftrightarrow A_{2} \\
& A_{2}+A \leftrightarrow A_{3}
\end{aligned}
$$

and the second component $B$ is inert. The flux of tagged A molecules is

$$
\begin{align*}
J_{A} V_{*} & =-\frac{R T}{n}\left[\frac{1}{\sigma_{1}} \frac{\partial C_{1}^{*}}{\partial z}+\frac{1}{\sigma_{11}}\left[\frac{\partial C_{11}}{\partial z}+2 \frac{\partial C_{11}^{* *}}{\partial z}\right]\right. \\
& \left.+\frac{1}{\sigma_{111}}\left(\frac{\partial C_{111}{ }^{*}}{\partial z}+2 \frac{\partial C_{111}{ }^{* *}}{\partial z}+3 \frac{\partial C_{111}{ }^{* *}}{\partial z}\right)\right] \tag{78}
\end{align*}
$$

and the stoichiometric formula is

$$
\begin{align*}
\mathrm{c}_{\mathrm{A}}^{*} & =\mathrm{c}_{1}^{*}+\mathrm{c}_{11}^{*}+2 \mathrm{c}_{11}{ }^{* *}+\mathrm{c}_{111}{ }^{*}+2 \mathrm{c}_{111}{ }^{* *} \\
& +3 \mathrm{c}_{111}^{* * *} \tag{79}
\end{align*}
$$

By the same process as before, this time leaving out the intermediate steps,

$$
\begin{align*}
D_{A}^{*} & =\frac{R T}{n}\left[\frac{1}{\sigma_{1}}+\left(\frac{1}{\sigma_{11}}-\frac{1}{\sigma_{1}}\right)\left(\frac{\partial C_{11}^{*}}{\partial C_{A}^{*}}+2 \frac{\partial C_{11}^{* *}}{\partial C_{A}^{*}}\right)\right. \\
& \left.+\left(\frac{1}{\sigma_{111}}-\frac{1}{\sigma_{1}}\right)\left(\frac{\partial C_{111}^{*}}{\partial C_{A}^{*}}+2 \frac{\partial C_{111}^{* *}}{\partial C_{A}^{*}}+\frac{\partial C_{111}^{* * *}}{\partial C_{A}^{*}}\right)\right] \tag{80}
\end{align*}
$$

The generalization of this equation by this method to a system where one molecule undergoes repeated simple selfpolymerization reactions is straight-forward, but notationally very difficult.

The effect of repeated polymerization on tracer diffusivity is easily seen from equation (80), however. The tracer diffusivity in this case is given by the intrinsic mobility of the monomer, decreased by a correction factor for each polymer. These correction factors involve the intrinsic mcbilities of each polymer, the number of tags carried by each polymer, and the amount of each polymer present (determined by the equilibrium constants).

Once again this model is not too useful in fitting tracer diffusion data unless the number of polymerizations is small, and there is some information indicating that there is no further polymerization beyond a certain point. Of course, assumptions could be made to reduce the number of adjustable parameters. For instance, it would seem reasonable that for hydrogen bonding molecules, after the

TABLE 1.--Summary of Hydrodynamic Theory Predictions of Tracer Diffusivities.

| System and <br> Association | Predicted Tracer Diffusivities |
| :--- | :--- |
| $A, B, C, \ldots . i N$ |  |
| no association |  |$\quad D_{1}{ }^{*}=\frac{F T}{n \sigma_{i}} \quad 1=A, B, C, \ldots N N$.

$\dot{A}, \dot{E}, \quad D_{A}^{*}=\frac{E=}{\eta}\left[\frac{1}{\sigma_{1}}+\left(\frac{1}{\sigma_{11}}-\frac{1}{\sigma_{1}}\right) \frac{\partial \sum_{11}^{*}}{\partial \partial_{A}^{*}}+2\left(\frac{1}{\sigma_{1}}-\frac{1}{\sigma_{11}}\right) \frac{\partial C_{11}^{* *}}{\partial C_{A}^{*}}\right]$
B inert

$$
D_{E}^{*}=\frac{\kappa T}{n \sigma_{2}}
$$

$$
A+A \leftrightarrow A_{2} \quad D_{A}^{*}=\frac{R T}{n}\left[\frac{1}{\sigma_{1}}+\left(\frac{1}{\sigma_{11}}-\frac{1}{\sigma_{1}}\right)\left(\frac{\partial C_{1}}{\partial C_{A}^{*}}+<\frac{\partial C_{1}}{\partial C_{A}^{*}} \frac{1}{*}^{*}\right)\right.
$$

$A+A_{2} \rightarrow A_{3}$

B inert

$$
\left.+\left(\frac{1}{\sigma_{111}}-\frac{1}{\sigma_{1}}\right)\left(\frac{\partial C_{111}^{*}}{\partial C_{A}^{*}}+2-\frac{\partial C_{111}^{* *}}{\partial C_{A}^{*}}+3 \frac{\partial C_{111}^{* * *}}{\partial C_{A}^{*}}\right)\right]
$$

$$
D_{B}^{*}=\frac{\mathrm{RT}}{\eta \sigma_{2}}
$$

$$
\begin{aligned}
& A, B \quad D_{A}^{*}=\frac{\mathrm{KM}_{1}}{\eta}\left[\frac{1}{\sigma_{1}}+\left(\frac{1}{\sigma_{12}}-\frac{1}{\sigma_{1}}\right) \frac{X_{12}^{0}}{X_{A}}\right] \\
& A+B \leftrightarrow A B
\end{aligned}
$$

first one or two polymerizations, all the equilibrium constants might be assumed equal. It might also reasonably be assumed that no polymer carries more than a certain number of tags, say three or four at most. This would make computation much easier. The physical insight of equations of this type is consideraole, as will be seen in later aiscussion.

## Binary Mutual Diffusion-- <br> Nonassociated Systems

For a binary nonassociated system with components
$A$ and $B$, equation (ll) gives the flux of component $A$ :

$$
\begin{equation*}
J_{A}=-\frac{C_{A}}{\sigma_{A}^{n}} \frac{\partial \mu_{A}}{\partial z}+\frac{C_{A}}{n}\left[\frac{C_{A} \bar{V}_{A}}{\sigma_{A}} \frac{\partial \mu_{A}}{\partial z}+\frac{C_{B} \nabla_{B}}{\sigma_{B}} \frac{\partial \mu_{B}}{\partial z}\right] \tag{81}
\end{equation*}
$$

Substituting the definition of chemical potential gives

$$
\begin{align*}
J_{A} & =\frac{R T}{n}\left[-\frac{C_{A}}{\sigma_{A}} \frac{\partial \operatorname{Ln} a_{A}}{\partial z}+C_{A}\left(\frac{C_{A} \bar{V}_{A}}{\sigma_{A}} \frac{\partial \operatorname{Ln} a_{A}}{\partial z}+\right.\right. \\
& \left.\left.+\frac{C_{B} V_{B}}{\sigma_{B}} \frac{\partial \operatorname{Ln} a_{B}}{\partial z}\right)\right] \tag{82}
\end{align*}
$$

By the chain rule

$$
\begin{align*}
& \frac{\partial \operatorname{Ln} a_{A}}{\partial z}=\frac{1}{C_{A}} \frac{\partial \operatorname{Ln} a_{A}}{\partial \operatorname{Ln} C_{A}} \frac{\partial C_{A}}{\partial z}  \tag{83}\\
& \frac{\partial \operatorname{Ln} a_{B}}{\partial z}=\frac{1}{C_{B}} \frac{\partial \operatorname{Ln} a_{B}}{\partial \operatorname{Ln} C_{B}} \frac{\partial C_{B}}{\partial z} \tag{84}
\end{align*}
$$

Substituting (85) and (86) into (84) gives

$$
\begin{align*}
J_{A} & =-D_{A B} \frac{\partial C_{A}}{\partial z}=\frac{R T}{n}\left[-\frac{1}{\sigma_{A}} \frac{\partial \operatorname{Ln} a_{A}}{\partial \operatorname{Ln} C_{A}}+\frac{C_{A} \bar{V}_{A}}{\sigma_{B}} \frac{\partial \operatorname{Ln} a_{B}}{\partial \operatorname{Ln} C_{B}}\right. \\
& \left.+\frac{C_{A} \nabla_{A}}{\sigma_{A}} \frac{\partial \operatorname{Ln} a_{A}}{\partial \operatorname{Ln} C_{A}}\right] \tag{85}
\end{align*}
$$

From the definition of mole fraction and partial molar volume the following hold:

$$
\begin{align*}
& \frac{\partial \operatorname{Ln} X_{A}}{\partial \operatorname{Ln} C_{A}}=\frac{X_{B}}{C_{B} \nabla_{B}}  \tag{8б}\\
& \frac{\partial \operatorname{Ln} X_{B}}{\partial \operatorname{L}_{n} C_{B}}=\frac{X_{A}}{C_{A} \nabla_{A}} \tag{87}
\end{align*}
$$

Substituting (86) and (87) into equation (85) and making use of the fact that $C_{A} \bar{V}_{A}+C_{B} \bar{V}_{B}=1$ one obtains the well known Hartley-Crank Equation [20]:

$$
\begin{equation*}
D_{A B}=\frac{R T}{\eta}\left[\frac{X_{B}}{\sigma_{A}}+\frac{X_{A}}{\sigma_{B}}\right] \frac{\partial \operatorname{In} a_{A}}{\partial \operatorname{Ln} X_{A}} \tag{88}
\end{equation*}
$$

This equation has been used with some success in predicting mutual diffusivities in non-associating solutions. It was originally derived under the assumption that the molar volumes were constant, but this is not a necessary condition.

Taking the limits as $X_{A} \rightarrow 0$ and as $X_{B} \rightarrow 0$, and comparing to equation (45) we see that

$$
\begin{align*}
& \operatorname{Lim}_{X_{A} \rightarrow 0} D_{A B}=\frac{R T}{n \sigma_{A}}=D_{A}^{*}  \tag{89}\\
& \operatorname{Lim}_{X_{B} \rightarrow 0} D_{A B}=\frac{R T}{n \sigma_{B}}=D_{B}^{*} \tag{90}
\end{align*}
$$

## Binary Mutual Diffusion-Associated Systems

Consider a system of two components $A$ and $B$, in which component A undergoes the simple dimerization

$$
A+A \leftrightarrow A_{2}
$$

and the second component $B$ is inert. The flux of $A$ is

$$
\begin{align*}
J_{A}^{V}= & -\frac{C_{1}}{\sigma_{1} n} \frac{\partial \mu_{1}}{\partial z}-2 \frac{C_{11}}{\sigma_{11}} \frac{\partial \mu_{11}}{\partial z}+C_{A}\left(\frac{C_{1} \nabla_{1}}{\sigma_{1}} \frac{\partial \mu_{1}}{\partial z}\right. \\
& \left.+\frac{C_{11} \bar{V}_{11}}{\sigma_{11}} \frac{\partial \mu_{11}}{\partial z}+\frac{C_{2} \bar{V}_{2}}{\sigma_{2}} \frac{\partial \mu_{2}}{\partial z}\right) \tag{91}
\end{align*}
$$

where the true species have been numbered as previously. Proceeding as in the derivation of the Hartley-Crank Equation, using the definition of the chemical potential, the chain rule, the relation $C_{A} \bar{V}_{A}+C_{B} \bar{V}_{B}=1$, and the assumption $\bar{V}_{11}=2 \bar{V}_{A}$, the mutual diffusivity is found to be

$$
\begin{equation*}
D_{A B}=\frac{R T}{n}\left[\frac{X_{A}}{\sigma_{2}}+X_{B}\left(\frac{X_{1}^{\circ}}{X_{A}} \frac{1}{\sigma_{1}}+\frac{X_{11} 0}{X_{A}} \frac{1}{\sigma_{11}}\right)\right] \frac{\partial \operatorname{Ln~} a}{\partial \operatorname{Ln} X} \tag{92}
\end{equation*}
$$

Detailed derivation of this result is given by Anderson, or Wirth [34], and will not be reproduced here.

Consider a syster of two components $A$ and $B$, in
which the dimerization reaction

$$
A+B \leftrightarrow A B
$$

occurs. The flux of $A$ is given here by

$$
\begin{align*}
J_{A}^{V}= & -\frac{C_{1}}{\sigma_{1} \eta} \frac{\partial \mu_{1}}{\partial z}-\frac{C_{12}}{\sigma_{12}{ }^{\eta}} \frac{\partial \mu_{12}}{\partial z}+C_{A}\left(\frac{C_{1} \bar{v}_{1}}{\sigma_{1}} \frac{\partial \mu_{1}}{\partial z}\right. \\
& \left.+\frac{C_{12} \bar{V}_{12}}{\sigma_{12}} \frac{\partial \mu_{12}}{\partial z}+\frac{C_{2} \bar{V}_{2}}{\sigma_{2}} \frac{\partial \mu_{2}}{\partial z}\right) \tag{93}
\end{align*}
$$

By the same process, with the assumption that $\overline{\mathrm{V}}_{12}=\overline{\mathrm{V}}_{\mathrm{A}}+\overline{\mathrm{V}}_{\mathrm{B}}$ this leads to the diffusivity:

$$
\begin{align*}
D_{A B} & =\frac{R T}{n}\left[\frac{1}{\sigma_{1}} \frac{X_{1}}{X_{A}} X_{B}+\frac{1}{\sigma_{2}} \frac{X_{2}^{0}}{X_{B}} X_{A}\right. \\
& \left.+\frac{1}{\sigma_{12}} \frac{X_{12}{ }^{\circ}\left(X_{A}-X_{B}\right)^{2}}{X_{A} X_{B}}\right] \frac{\partial \operatorname{Ln} a}{\partial \operatorname{Ln} X} \tag{94}
\end{align*}
$$

Detailed derivation is again given by Anderson [l] or Wirth [34].

Note that equations (92) and (94) differ from the Hartley-Crank equation only in the addition of an extra term. In the case of self-association, this term is positive, and predicts that the mutual diffusivity is more than that predicted by the Hartley-Crank equation. In the case of cross-association, this term predicts a smaller diffusivity.

It is generally true that the activity term in the Hartley-Crank Equation over-corrects. That is, when the system shows positive deviations from Raoult's Law, the thermodynamic correction predicts the diffusivity to be less than it would be if the solution were ideal. In many of these cases, the experimentally measured diffusivities are greater than those predicted by the HartleyCrank Equation, though still less than for an ideal solution. When the system shows negative deviations from Raoult's Law, the thermodynamic correction predicts diffusivities higher than for an ideal solution. In these cases, the measured mutual diffusivities are found to be less than those predicted by the Hartley-Crank Equation, but still larger than for an ideal solution.

Equations (94) and (96) reduce the magnitude of the deviation of the Hartley-Crank Equation from ideality. In a system where association takes place, they should be better predictors of diffusivity than the Hartley-Crank Equation. This has been found to be so for several
systems. However, in some cases there is strong evidence that the components do not associate significantly, and the Hartley-Crank Equation still tends to over-correct. Two such systems will be presented here. Some tneoretical explanation must still be found for this discrepancy.

## Ternary Mutual Diffusivities--

Nonassociated Systems
There have been two major approaches to multicomponent diffusion. Onsager [28] proposed a set of equations for an $N$-component system relating the flux of each component to the concentration gradients of all the components, thereoy defiring $N^{2}$ diffusion coefficients:

$$
\begin{equation*}
J_{i}^{V}=\sum_{j=1}^{N} D_{i j} \frac{\partial C_{j}}{\partial z} \quad i=1,2, \ldots N \tag{95}
\end{equation*}
$$

Then, based upon the theories of irreversible thermodynamics, he showed that only $(N-1)^{2}$ of these diffusion coefficients were independent. These diffusion coefficients, however, are not easily measured.

Baldwin, Dunlop and Gosting [3] therefore proposed a different description, involving only $N-1$ independent fluxes, and $(N-1)^{2}$ diffusivities:

$$
\begin{equation*}
J_{i}^{V}=\sum_{j=1}^{N-1} \quad D_{i j} \frac{\partial C_{j}}{\partial z} \quad 1=1,2, \ldots N-1 \tag{96}
\end{equation*}
$$

These diffusivities are not the same as the Onsager diffusivities, but are related by the expressions

$$
\begin{equation*}
D_{i j}=D_{i j}-\frac{\bar{V}_{j}}{\nabla_{N}} D_{i N} \quad i, j=1,2, \ldots N-1 \tag{97}
\end{equation*}
$$

Since then, Gostirg and coworkers have presented several methods for experimentally determining the $D_{i j}$ 's [13, 14]. It is preferred, therefore, to relate hydrodynamic theory to the Gosting diffusivities. This will be done for a nonassociated ternary system to demonstrate the method. It is aiso useful to develop equations predicting the phenomenological coefficients of the Onsager theory, to show that hydrodynamic theory predicts the validity of the Onsager Reciprocal Relations.

From equation (11), the fluxes are
$J_{1} V=-\frac{C_{1}}{\sigma_{1} \eta} \frac{\partial \mu_{1}}{\partial z}+C_{1}\left(\frac{C_{1} \bar{V}_{1}}{\sigma_{1}} \frac{\partial \mu_{1}}{\partial z}+\frac{C_{2} \nabla_{2}}{\sigma_{2}} \frac{\partial \mu_{2}}{\partial z}+\frac{C_{3} \bar{V}_{3}}{\sigma_{3}} \frac{\partial \mu_{3}}{\partial z}\right)$

$$
\begin{equation*}
J_{2} V=-\frac{C_{2}}{\sigma_{2}{ }^{n}} \frac{\partial \mu_{1}}{\partial z}+C_{2}\left(\frac{C_{1} \bar{V}_{1}}{\sigma_{1}} \frac{\partial \mu_{1}}{\partial z}+\frac{C_{2} \bar{V}_{2}}{\sigma_{2}} \frac{\partial \mu_{2}}{\partial z}+\frac{C_{3} \bar{V}_{3}}{\sigma_{3}} \frac{\partial \mu_{3}}{\partial z}\right) \tag{98}
\end{equation*}
$$

From the Gibbs-Duhem relationship,

$$
\begin{equation*}
\frac{\partial \mu_{3}}{\partial z}=-\frac{C_{1}}{C_{3}} \frac{\partial \mu_{1}}{\partial z}-\frac{C_{2}}{C_{3}} \frac{\partial \mu_{2}}{\partial z} \tag{100}
\end{equation*}
$$

Combining equations (98), (99) and (100) to eliminate the gradient of chemical potential of component 3 gives
$J_{1}{ }^{V}=-\frac{C_{1}}{n}\left[\frac{\left(1-\bar{V}_{1} C_{1}\right)}{\sigma_{1}}+\frac{\bar{V}_{3} C_{1}}{\sigma_{3}}\right] \frac{\partial \mu_{1}}{\partial z}-\frac{C_{1} C_{2}}{n}\left[\frac{\bar{V}_{3}}{\sigma_{3}}-\frac{\bar{V}_{2}}{\sigma_{2}}\right] \frac{\partial \mu_{2}}{\partial z}$
$J_{2}{ }^{V}=-\frac{C_{1} C_{2}}{n}\left[\frac{V_{3}}{\sigma_{3}}-\frac{\bar{V}_{1}}{\sigma_{1}}\right] \frac{\partial \mu_{1}}{\partial z}-\frac{C_{2}}{n}\left[\frac{\left(1-C_{2} \bar{V}_{2}\right)}{\sigma_{2}}+\frac{\bar{V}_{3} C_{2}}{\sigma_{3}}\right] \frac{\partial \mu_{2}}{\partial z}$

Mathematicaliy, the total derivative of the chemicai potential can be given in terms of the partials of all the independent variables. For a ternary system at constant temperature and pressure, there are only two independent variables, which may be taken as $C_{1}$ and $C_{2}$. Therefore,

$$
\begin{align*}
& \frac{\partial \mu_{1}}{\partial z}=\frac{\partial \mu_{1}}{\partial C_{1}} \frac{\partial C_{1}}{\partial z}+\frac{\partial \mu_{1}}{\partial C_{2}} \frac{\partial C_{2}}{\partial z}  \tag{103}\\
& \frac{\partial \mu_{2}}{\partial z}=\frac{\partial \mu_{2}}{\partial C_{1}} \frac{\partial C_{1}}{\partial z}+\frac{\partial \mu_{2}}{\partial C_{2}} \frac{\partial C_{2}}{\partial z} \tag{104}
\end{align*}
$$

Substituting these into equations (101) and (102) yields

$$
\begin{aligned}
J_{1} V= & -\left\{\frac{C_{1}}{n}\left[\frac{\left(1-C_{1} \bar{V}_{1}\right)}{\sigma_{1}}+\frac{C_{1} \bar{V}_{3}}{\sigma_{3}}\right] \frac{\partial \mu_{1}}{\partial C_{1}}+\left(\frac{\bar{V}_{3}}{\partial 3}-\frac{\bar{V}_{2}}{\partial 2}\right) \frac{C_{1} C_{2}}{n} \frac{\partial \mu_{2}}{\partial C_{1}}\right\} \frac{C_{1}}{\partial z} \\
& -\left\{\frac{C_{1}}{n}\left[\frac{\left(1-C_{1} \bar{V}_{1}\right)}{\sigma_{1}}+\frac{C_{1} \bar{V}_{3}}{\sigma_{3}}\right] \frac{\partial \mu_{1}}{\partial C_{2}}+\frac{C_{1} C_{2}}{n}\left(\frac{\bar{V}_{3}}{\sigma_{3}}-\frac{\bar{V}_{2}}{\sigma_{2}}\right) \frac{\partial \mu_{2}}{\partial C_{2}}\right\} \frac{\partial C_{2}}{\partial z}
\end{aligned}
$$

$J_{2} V=-\left\{\frac{C_{1} C_{2}}{v}\left(\frac{\bar{V}_{3}}{\sigma_{3}}-\frac{\bar{V}_{1}}{\sigma_{1}}\right) \frac{\partial \mu_{1}}{\partial C_{1}}+\frac{C_{2}}{n}\left[\frac{\left(1-C_{2} \bar{V}_{2}\right)}{\sigma_{2}}+\frac{C_{2} \bar{V}_{3}}{\sigma_{3}}\right] \frac{\partial \mu_{2}}{\partial C_{1}}\right\} \frac{\partial C_{1}}{\partial z}$

$$
-\left\{\frac{C_{1} C_{2}}{n}\left(\frac{\bar{V}_{3}}{\sigma_{3}}-\frac{\bar{V}_{1}}{\sigma_{1}}\right) \frac{\partial \mu_{1}}{\partial C_{2}}+\frac{C_{2}}{n}\left[\frac{\left(i-C_{2} \nabla_{2}\right)}{\sigma_{2}}+\frac{C_{2} \nabla_{3}}{\sigma_{3}}\right] \frac{\partial \mu_{2}}{\partial C_{2}}\right\} \frac{\partial C_{2}}{\partial z}
$$

From the definition of chemical potential, these can be written

$$
\begin{align*}
J_{1} V= & -\frac{R T}{n}\left\{C_{1}\left[\frac{\left(1-C_{1} \bar{V}_{1}\right)}{\sigma_{1}}+\frac{C_{1} \bar{V}_{3}}{\sigma_{3}}\right] \frac{\partial \operatorname{Ln} a_{1}}{\partial C_{1}}\right. \\
& \left.+C_{1} C_{2}\left(\frac{\bar{V}_{3}}{\sigma_{3}}-\frac{\bar{V}_{2}}{\sigma_{2}}\right) \frac{\partial \operatorname{Ln} a_{2}}{\partial C_{1}}\right\} \frac{\partial C_{1}}{\partial z} \\
& -\frac{R T}{n}\left\{C_{1}\left[\frac{\left(1-C_{1} \bar{V}_{1}\right)}{\sigma_{1}}+\frac{C_{1} \bar{V}_{3}}{\sigma_{3}}\right] \frac{\partial \operatorname{Ln} a_{1}}{\partial C_{1}}\right. \\
& \left.+C_{1} C_{2}\left(\frac{\bar{V}_{3}}{\sigma_{3}}-\frac{\bar{V}_{2}}{\sigma_{2}}\right) \frac{\partial \operatorname{Ln} a_{2}}{\partial C_{2}}\right\} \frac{\partial C_{2}}{\partial z}  \tag{107}\\
J_{2}= & -\frac{R T}{n}\left\{C_{1} C_{2}\left(\frac{\bar{V}_{3}}{\sigma_{3}}-\frac{\bar{v}_{2}}{\sigma_{2}}\right) \frac{\partial \operatorname{Ln} a_{1}}{\partial C_{1}}+\right. \\
& \left.+C_{2}\left[\frac{\left(1-C_{2} \bar{V}_{2}\right)}{\sigma_{2}}+\frac{C_{2} \bar{V}_{2}}{\sigma_{3}}\right] \frac{\partial C_{1}}{\partial z} \frac{\partial \operatorname{Ln} a_{2}}{\partial C_{1}}\right\} \frac{\partial C_{1}}{\partial z}
\end{align*}
$$

$$
\begin{align*}
& -\frac{R T}{n}\left\{c_{1} c_{2}\left(\frac{\bar{v}_{3}}{\sigma_{3}}-\frac{\bar{v}_{1}}{\sigma_{1}}\right) \frac{\partial \operatorname{Ln} a_{1}}{\partial C_{1}}\right. \\
& \left.+c_{2}\left[\frac{\left.1-c_{2} \bar{v}_{2}\right)}{\sigma_{2}}+\frac{c_{2} \bar{v}_{3}}{\sigma_{3}}\right] \frac{\partial \operatorname{Ln} a_{2}}{\partial C_{2}}\right\} \frac{\partial c_{2}}{\partial z} \tag{108}
\end{align*}
$$

Comparing these to the defining equations (96) gives the diffusivities predicted by hydrodynamic theory:

$$
\begin{align*}
D_{11}=D_{A A} & =\frac{R T}{\eta} C_{1}\left[\frac{\left(1-C_{1} \bar{v}_{1}\right)}{\sigma_{1}}+\frac{C_{1} \bar{v}_{3}}{\sigma_{3}}\right] \frac{\partial \operatorname{Ln} a_{1}}{\partial C_{1}} \\
& \left.+C_{1} C_{2}\left(\frac{\bar{v}_{3}}{\sigma_{3}}-\frac{\bar{v}_{2}}{\sigma_{2}}\right) \frac{\partial \operatorname{Ln} a_{2}}{\partial C_{1}}\right\}  \tag{109}\\
D_{12}=D_{A B} & =\frac{R T}{n}\left\{C_{1}\left[\frac{\left(1-C_{1} \bar{v}_{1}\right)}{\sigma_{1}}+\frac{C_{1} \bar{v}_{3}}{\sigma_{3}}\right] \frac{\partial \operatorname{Ln} a_{1}}{\partial C_{2}}\right. \\
& \left.+C_{1} C_{2}\left(\frac{\bar{v}_{3}}{\sigma_{3}}-\frac{\bar{v}_{2}}{\sigma_{2}}\right) \frac{\partial \operatorname{Ln} a_{2}}{\partial C_{1}}\right\}  \tag{110}\\
D_{21}=D_{B A} & =\frac{R T}{n}\left\{C_{1} C_{2}\left(\frac{\bar{v}_{3}}{\sigma_{3}}-\frac{\bar{v}_{1}}{\sigma_{1}}\right) \frac{\partial \operatorname{Ln} a_{1}}{\partial C_{1}}\right. \\
& \left.+C_{2}\left[\frac{\left(1-C_{2} \bar{v}_{2}\right)}{\sigma_{2}}+\frac{C_{2} \bar{v}_{3}}{\sigma_{3}}\right] \frac{\partial \operatorname{Ln} a_{2}}{\partial C_{1}}\right\} \tag{111}
\end{align*}
$$

$$
\begin{align*}
D_{22}=D_{B B} & =\frac{R^{m}}{n}\left\{C_{1} C_{2}\left(\frac{\bar{V}_{3}}{\sigma_{3}}-\frac{\bar{V}_{1}}{\sigma_{1}}\right) \frac{\partial \operatorname{Ln} a_{1}}{\partial C_{2}}\right. \\
& \left.+c_{2}\left[\frac{\left(1-C_{2} \bar{V}_{2}\right)}{\sigma_{2}}+\frac{c_{2} \bar{V}_{3}}{\sigma_{3}}\right] \frac{\partial \operatorname{Ln} a_{2}}{\partial C_{2}}\right\} \tag{112}
\end{align*}
$$

Kett [23] derived these equations, and generalized them to a system of $N$ components, obtaining

$$
\begin{aligned}
D_{i j} & =\frac{c_{i}}{n}\left[\frac{\left.1-\bar{V}_{i} C_{i}\right)}{\sigma_{i}}+\frac{c_{i} \bar{V}_{N}}{\sigma_{N}}\right] \frac{\partial \mu_{i}}{\partial C_{j}} \\
& +\sum_{\substack{k=1 \\
k \neq i}}^{N-1} \frac{c_{i} c_{k}}{n}\left[\frac{\bar{V}_{N}}{\sigma_{N}}-\frac{\bar{V}_{i k}}{\sigma_{k}}\right] \frac{\partial \mu_{k}}{\partial C_{j}}
\end{aligned}
$$

The theory of irreversible thermodynamics states
that the rate of entropy production in the ternary diffusing system is

$$
T \frac{d S}{d t}=-J_{1} V \frac{\partial \mu_{1}}{\partial z} \quad J_{2} V \frac{\partial \mu_{2}}{\partial z} \quad J_{3} V \frac{\partial \mu_{3}}{\partial z}
$$

However, equation ( 100 ) can be used to eliminate $\mu_{3}$, amd the constant volume relationship $J_{1} \overline{\mathrm{~V}}_{1}+\mathrm{J}_{2} \overline{\mathrm{~V}}_{2}+\mathrm{J}_{3} \overline{\mathrm{~V}}_{3}=0$ can be used to eliminate $J_{3}$ :

$$
\begin{equation*}
T \frac{d S}{d t}=J_{1}{ }^{V} Y_{1}+J_{2}^{V} Y_{2} \tag{114}
\end{equation*}
$$

$$
Y_{i}=-\sum_{j=1}^{2}\left(\delta_{i j}+\frac{C_{i} \bar{V}_{i}}{C_{3} \nabla_{3}}\right) \frac{\partial \mu_{j}}{\partial z} \quad \begin{align*}
& i=1,2  \tag{115}\\
& \delta_{i j}=\left\{_{1}^{0} j \neq i\right. \\
& j=1
\end{align*}
$$

Irreversible thermodynamics also states that

$$
\begin{align*}
& J_{1}{ }^{V}=L_{11} Y_{1}+L_{12} Y_{2}  \tag{116}\\
& J_{2} V=L_{21} Y_{1}+L_{22} Y_{2} \tag{117}
\end{align*}
$$

Substituting the expressions for $Y_{i}$ from (115) into equations (116) and (117) and rearranging yields

$$
\begin{align*}
& J_{1} V=-\left(\alpha L_{11}+\gamma L_{12}\right) \frac{\partial \mu_{1}}{\partial z}-\left(\beta L_{11}+\delta L_{12}\right) \frac{\partial \mu_{2}}{\partial z}  \tag{118}\\
& J_{2} V=-\left(\alpha L_{21}+\gamma L_{22}\right) \frac{\partial \mu_{1}}{\partial z}-\left(\beta L_{21}+\delta L_{22}\right) \frac{\partial \mu_{2}}{\partial z} \tag{119}
\end{align*}
$$

where $\alpha, \beta, \gamma$, and $\delta$ are defined by

$$
\begin{array}{rr}
\alpha=1+\frac{c_{1} \bar{v}_{1}}{c_{3} \bar{v}_{3}} & \beta=\frac{c_{2} \bar{v}_{1}}{c_{3} \nabla_{3}} \\
\gamma=\frac{c_{1} \bar{v}_{2}}{c_{3} \bar{v}_{3}} & \delta=1+\frac{c_{2} \bar{v}_{2}}{c_{3} \nabla_{3}}
\end{array}
$$

Equating coefficients between (118), (119) and (101),
(102) yields four independent equations for the $L_{i j}$ 's:

$$
\begin{align*}
& L_{11} \alpha+L_{12} \gamma=\frac{c_{1}}{n}\left[\frac{\left(1-\bar{v}_{1} c_{1}\right)}{\sigma_{1}}+\frac{\bar{v}_{3} c_{1}}{\sigma_{3}}\right]  \tag{120}\\
& L_{11} \beta+L_{12} \delta=\frac{c_{1} c_{2}}{n}\left[\frac{\bar{v}_{3}}{\sigma_{3}}-\frac{\bar{v}_{2}}{\sigma_{2}}\right]  \tag{121}\\
& L_{21} \alpha+L_{22} \gamma=\frac{c_{1} c_{2}}{n}\left[\frac{\bar{v}_{3}}{\sigma_{3}}-\frac{\bar{v}_{2}}{\sigma_{2}}\right]  \tag{122}\\
& \left.L_{21} \beta+L_{22} \delta=\frac{c_{2}}{n}\left[\frac{\left(1-\bar{v}_{2} c_{2}\right.}{\sigma_{2}}\right)+\frac{\bar{v}_{3} c_{2}}{\sigma_{3}}\right] \tag{123}
\end{align*}
$$

The Onsager Reciprocal Relation states that $I_{12}=L_{21}$. To test this, solve equations (120) through (123) to obtain

$$
\begin{align*}
& L_{12}=\frac{\frac{c_{1} c_{2}}{n}\left[\frac{\bar{v}_{3}}{\sigma_{3}}-\frac{\bar{v}_{2}}{\sigma_{2}}\right] \alpha-\frac{c_{1}}{n}\left[\frac{\left(1-\bar{v}_{1} c_{1}\right)}{\sigma_{1}}+\frac{\bar{v}_{3} c_{1}}{\sigma_{3}}\right] \beta}{\alpha \delta-\beta \gamma}  \tag{124}\\
& L_{21}=\frac{\frac{c_{1} c_{2}}{n}\left[\frac{\bar{v}_{3}}{\sigma_{3}}-\frac{\bar{v}_{1}}{\sigma_{1}}\right] \delta-\frac{c_{2}}{n}\left[\frac{\left(1-\bar{v}_{2} c_{2}\right)}{\sigma_{2}}+\frac{\bar{v}_{3} c_{2}}{\sigma_{3}}\right] \gamma}{\alpha \delta-\beta \gamma} \tag{125}
\end{align*}
$$

Using the relation $C_{1} \bar{V}_{1}+C_{2} \bar{V}_{2}+C_{3} \bar{V}_{3}=1$, and the defining expressions for $\alpha, \beta, \gamma$, and $\delta$ we may obtain from equations (124) and (125) the desired result:

$$
L_{12}=L_{21}=-\frac{c_{1} c_{2} \bar{v}_{1}\left(1-c_{1} \bar{v}_{1}\right)}{\sigma_{1} n}-\frac{c_{1} c_{2} \bar{v}_{2}\left(1-c_{2} \bar{v}_{2}\right)}{\sigma_{2} n}+\frac{c_{1} c_{2} c_{3} \bar{v}_{3}^{2}}{\sigma_{3}{ }^{n}}
$$

Therefore, hydrodynamic theory states that Onsager's Reciprocal Relation is valid for ternary isothermal diffusion in a nonassociating system. The only required assumption is that of constant molar volume, used in obtaining equations (101) and (102).

Miller [26] has developed equations which allow Onsager's Reciprocal Relation to be tested experimentally:

$$
\begin{align*}
& L_{12}=\frac{a D_{12}-c D_{11}}{a d-b c}  \tag{127}\\
& L_{21}=\frac{d D_{21}-b D_{22}}{a d-b c} \tag{128}
\end{align*}
$$

where

$$
\begin{align*}
& a=\left(1+\frac{c_{1} \bar{v}_{1}}{C_{3} \nabla_{3}}\right) \frac{\partial \mu_{1}}{\partial C_{1}}+\frac{c_{2} \bar{v}_{2}}{C_{3} \nabla_{3}} \frac{\partial \mu_{2}}{\partial C_{1}}  \tag{129}\\
& b=\left(1+\frac{c_{2} \nabla_{2}}{C_{3} \nabla_{3}}\right) \frac{\partial \mu_{2}}{\partial C_{1}}+\frac{c_{1} \bar{v}_{2}}{c_{3} \nabla_{3}} \frac{\partial \mu_{1}}{\partial C_{1}}  \tag{130}\\
& c=\left(1+\frac{c_{1} \bar{v}_{1}}{C_{3} \nabla_{3}}\right) \frac{\partial \mu_{1}}{\partial C_{2}}+\frac{c_{2} \bar{v}_{1}}{C_{3} \nabla_{3}} \frac{\partial \mu_{2}}{\partial C_{2}} \tag{131}
\end{align*}
$$

$d=\left(1+\frac{C_{2} \bar{v}_{2}}{C_{3} \nabla_{3}}\right) \frac{\partial \mu_{2}}{\partial C_{2}}+\frac{C_{1} \bar{v}_{2}}{C_{3} \nabla_{3}} \frac{\partial \mu_{1}}{\partial C_{2}}$

Ternary Mutual Diffusion-Associated Systems

Kett [23] has developed equations for the ternary diffusivities in a ternary system of components $A, B$ and $C$ subject to the dimerization equilibrium

$$
A+B \leftrightarrow A B
$$

where component $C$ is inert.
Kett's equations are given here without derivation:

$$
\begin{align*}
& D_{A A}=\left[\frac{C_{1}}{\sigma_{1}{ }^{n}}\left(1-\bar{V}_{1} C_{A}\right)+\frac{C_{12}}{\sigma_{12^{n}}}\left(1-\bar{V}_{12} C_{A}\right)+\frac{\bar{V}_{3} C_{A}}{\sigma_{3}{ }^{n}}\right] \frac{\partial \mu_{1}}{\partial C_{A}} \\
& +\left[-\frac{\bar{v}_{2} C_{2} C_{A}}{\sigma_{2}^{n}}+\frac{C_{12}}{\sigma_{12^{n}}}\left(1-\bar{v}_{12} C_{A}\right)+\frac{\bar{v}_{3} C_{A} C_{B}}{\sigma_{3}^{n}}\right] \frac{\partial \mu_{2}}{\partial C_{A}}  \tag{133}\\
& D_{A B}=\left[\frac{C_{1}}{\sigma_{-}^{n}}\left(1-\bar{V}_{1} C_{A}\right)+\frac{C_{12}}{\sigma_{12^{n}}}\left(1-\bar{V}_{12} C_{A}\right)+\frac{\bar{V}_{3} C_{A}^{2}}{\sigma_{3}^{n}}\right] \frac{\partial \mu_{1}}{\partial C_{B}} \\
& +\left[-\frac{\bar{v}_{2} C_{2} C_{A}}{\sigma_{2}{ }^{n}}+\frac{C_{12}}{\sigma_{12}{ }^{n}}\left(1-\bar{v}_{12} C_{A}\right)+\frac{\bar{v}_{3} C_{A} C_{B}}{\sigma_{3}^{n}}\right] \frac{\partial \mu_{2}}{\partial C_{B}} \tag{134}
\end{align*}
$$

$$
\begin{align*}
D_{B A} & =\left[-\frac{\bar{V}_{1} C_{1} C_{B}}{\sigma_{1} n}+\frac{C_{12}}{\sigma_{12}{ }^{n}}\left(1-\bar{v}_{12} C_{B}\right)+\frac{\bar{V}_{3} C_{A} C_{B}}{\sigma_{3} n}\right] \frac{\partial \mu_{1}}{\partial C_{A}} \\
& +\left[\frac{C_{2}}{\sigma_{2}^{n}}\left(1-\bar{V}_{2} C_{B}\right)+\frac{C_{12}}{\sigma_{12^{n}}}\left(1-\bar{V}_{12} C_{B}\right)+\frac{\bar{V}_{e} C_{B}^{2}}{\sigma_{3}^{n}}\right] \frac{\partial \mu_{2}}{\partial C_{A}}  \tag{135}\\
D_{B B} & =\left[-\frac{\bar{V}_{1} C_{1} C_{B}}{\sigma_{1} n}+\frac{C_{12}}{\sigma_{12}^{n}}\left(1-\bar{v}_{12} C_{B}\right)+\frac{\bar{V}_{3} C_{A} C_{B}}{\sigma_{3}^{n}}\right] \frac{\partial \mu_{1}}{\partial C_{B}} \\
& +\left[\frac{C_{2}}{\sigma_{2}^{n}}\left(1-\bar{V}_{2} C_{B}\right)+\frac{C_{12}}{\sigma_{12}}\left(1-\bar{V}_{12} C_{B}\right)+\frac{\bar{V}_{3} C_{B}{ }^{2}}{\sigma_{3}^{n}}\right] \frac{\partial \mu_{2}}{\partial C_{B}} \tag{136}
\end{align*}
$$

By making the assumption that $\overline{\mathrm{V}}_{12}=\overline{\mathrm{V}}_{\mathrm{A}}+\overline{\mathrm{V}}_{\mathrm{B}}$ he obtained

$$
\begin{align*}
L_{B A} & =L_{A B}=-\frac{C_{1} C_{B} \bar{V}_{1}}{\sigma_{1} n}\left(1-\bar{V}_{1} C_{A}\right)-\frac{c_{2} C_{A} \bar{v}_{2}}{\sigma_{2}^{n}}\left(1-\bar{V}_{2} C_{B}\right) \\
& +\frac{c_{A} C_{B} \bar{V}_{3}}{\sigma_{3}^{n}}\left(1-\bar{V}_{1} C_{A}-\bar{V}_{2} C_{B}\right)+\frac{c_{12}}{\sigma_{12}{ }^{n}}\left(1-\bar{V}_{12} C_{A}\right)\left(1-\bar{v}_{12} C_{B}\right) \tag{137}
\end{align*}
$$

thus verifying Onsager's Reciprocal Relation for this simple associated system. The assumption of constant molar volume leads to the assumption made above, so this verification is exactly as reliable as the previous case. Kett [23] also developed similar equations and verified the Onsager Reciprocal Relation for the selfdimerization system of $A, B$ and $C$, where $A$ is subject to the equilibrium

$$
A+A \leftrightarrow A_{2}
$$

and $B$ and $C$ are inert.
Equations of tinis type now will be derived for a slightly more complex type of associated system. Consider the ternary system with competing equilibria previously discussed under Tracer Diffusion. Using the same nomenclature, the fluxes in ternary diffusion are given by

$$
\begin{align*}
J_{A} V= & -\frac{C_{1}}{\sigma_{1} \eta} \frac{\partial \mu_{1}}{\partial z}-\frac{C_{12}}{\sigma_{12} \eta} \frac{\partial \mu_{12}}{\partial z}-\frac{C_{13}}{\sigma_{13} \eta} \frac{\partial \mu_{13}}{\partial z} \\
& +\frac{C_{A}}{\eta}\left[\frac{C_{1} \bar{V}_{1}}{\sigma_{1}} \frac{\partial \mu_{1}}{\partial z}+\frac{C_{12} \bar{v}_{12}}{\sigma_{12}} \frac{\partial \mu_{12}}{\partial z}+\frac{C_{13} \bar{V}_{13}}{\sigma_{13}} \frac{\partial \mu_{13}}{\partial z}\right. \\
& \left.+\frac{C_{2} \bar{V}_{2}}{\sigma_{2}} \frac{\partial \mu_{2}}{\partial z}+\frac{C_{3} \bar{V}_{3}}{\sigma_{3}} \frac{\partial \mu_{3}}{\partial z}\right] \tag{138}
\end{align*}
$$

$$
\begin{align*}
J_{B} V= & -\frac{C_{2}}{\sigma_{2}{ }^{\eta}} \frac{\partial \mu_{2}}{\partial z}-\frac{C_{12}}{\sigma_{12} \eta} \frac{\partial \mu_{12}}{\partial z} \\
& +\frac{C_{B}}{n}\left[\frac{C_{1} \bar{V}_{1}}{\sigma_{1}} \frac{\partial \mu_{1}}{\partial z}+\frac{C_{12} \bar{\nabla}_{12}}{\sigma_{12}} \frac{\partial \mu_{12}}{\partial z}+\frac{C_{13} \bar{V}_{13}}{\sigma_{13}} \frac{\partial \mu_{13}}{\partial z}\right. \\
& \left.+\frac{C_{2} \bar{V}_{2}}{\sigma_{2}} \frac{\partial \mu_{2}}{\partial z}+\frac{C_{3} \bar{V}_{3}}{\sigma_{3}} \frac{\partial \mu_{3}}{\partial z}\right] \tag{139}
\end{align*}
$$

For this system

$$
\begin{align*}
& \frac{\partial \mu_{12}}{\partial z}=\frac{\partial \mu_{1}}{\partial z}+\frac{\partial \mu_{2}}{\partial z}  \tag{140}\\
& \frac{\partial \mu_{13}}{\partial z}=\frac{\partial \mu_{1}}{\partial z}+\frac{\partial \mu_{3}}{\partial z} \tag{141}
\end{align*}
$$

Therefore, equations (138) and (139) become

$$
\begin{aligned}
n J_{A}= & -\left[\frac{C_{1}}{\sigma_{1}}\left(1-C_{A} \bar{V}_{1}\right)+\frac{C_{12}}{\sigma_{12}}\left(1-C_{A} \bar{v}_{12}\right)+\frac{C_{13}}{\sigma_{13}}\left(1-C_{A} \bar{V}_{13}\right)\right] \frac{\partial \mu_{1}}{\partial z} \\
& -\left[\frac{C_{12}}{\sigma_{12}}\left(1-C_{A} \bar{v}_{12}\right)-\frac{C_{A} C_{2} \bar{v}_{2}}{\sigma_{2}}\right] \frac{\partial \mu_{2}}{\partial z}-\left[C_{B}\left(1-C_{A} \bar{v}_{13}\right)-\frac{C_{A} C_{3} \bar{V}_{3}}{\sigma_{3}}\right] \frac{\partial \mu_{3}}{\partial z}
\end{aligned}
$$

$$
\begin{align*}
\eta J_{B}= & -\left[\frac{C_{12}}{\sigma_{12}}\left(1-C_{B} \bar{V}_{12}\right)-\frac{C_{B} C_{1} \bar{v}_{1}}{\sigma_{1}}-\frac{C_{B} C_{13} \bar{v}_{13}}{\sigma_{13}}\right] \frac{\partial \mu_{1}}{\partial z} \\
& -\left[\frac{C_{12}}{\sigma_{12}}\left(1-C_{B} \bar{V}_{2}\right)+\frac{C_{12}}{\sigma_{12}}\left(1-C_{B} \bar{V}_{12}\right)\right] \frac{\partial \mu_{2}}{\partial z}-\left[\frac{-C_{B} C_{13} \bar{V}_{13}}{\sigma_{13}}\right. \\
& \left.-\frac{C_{B} C_{3} \bar{V}_{3}}{\sigma_{3}}\right] \frac{\partial \mu_{3}}{\partial z} \tag{143}
\end{align*}
$$

By combining the stoichiometric relationships

$$
\begin{align*}
& c_{A}=c_{1}+c_{12}+c_{13} \\
& c_{B}=c_{2}+c_{12}  \tag{144}\\
& c_{C}=c_{3}+c_{13}
\end{align*}
$$

with the Gibos-Dunem equation, we obtain

$$
\begin{equation*}
\frac{\partial \mu_{3}}{\partial z}=-\frac{C_{A}}{C_{C}} \frac{\partial \mu_{1}}{\partial z}-\frac{C_{B}}{C_{C}} \frac{\partial \mu_{2}}{\partial z} \tag{145}
\end{equation*}
$$

Since the chemical potentials are functions of $C_{A}$ and $C_{B}$ only, the expression for the total derivative gives

$$
\begin{align*}
& \frac{\partial \mu_{1}}{\partial z}=\frac{\partial \mu_{1}}{\partial C_{A}} \frac{\partial C_{A}}{\partial z}+\frac{\partial \mu_{1}}{\partial C_{B}} \frac{\partial C_{B}}{\partial z}  \tag{146}\\
& \frac{\partial \mu_{2}}{\partial z}=\frac{\partial \mu_{2}}{\partial C_{A}} \frac{\partial C_{A}}{\partial z}+\frac{\partial \mu_{2}}{\partial C_{B}} \frac{\partial C_{B}}{\partial z} \tag{147}
\end{align*}
$$

Substituting (145), (146) and (147) into equations (142) and (143) yields, after considerable algebraic manipulation

$$
\begin{align*}
n J_{A}= & -\left[\frac { \partial \mu _ { 1 } } { \partial C _ { A } } \left\{\frac{C_{1}}{\sigma_{1}}\left(1-C_{A} \bar{V}_{1}\right)+\frac{C_{12}}{\sigma_{12}}\left(1-C_{A} \bar{v}_{12}\right)+\left(1-\frac{C_{A}}{C_{C}}\right)\left(1-C_{A} \bar{v}_{3}\right) \frac{C_{13}}{\sigma_{13}}\right.\right. \\
& \left.+\frac{C_{A}^{2} C_{3} \bar{V}_{3}}{C_{C} \sigma_{3}}\right\}+\frac{\partial \mu_{2}}{\partial C_{A}}\left\{\frac{C_{12}}{\sigma_{12}}\left(1-C_{A} \bar{v}_{12}\right)-\frac{C_{B}}{C_{C}} \frac{C_{13}}{13}\left(1-C_{A} \bar{V}_{13}\right)\right. \\
& \left.-\frac{C_{A} C_{2} \bar{V}_{2}}{\sigma_{2}}+\frac{C_{A} C_{B} C_{3} \bar{v}_{3}}{C_{C} \sigma_{3}}\right] \frac{\partial C_{A}}{\partial z}-\left[\frac { \partial \mu _ { 1 } } { \partial C _ { B } } \left\{\frac{C_{1}}{\sigma_{1}}\left(1-C_{A} \bar{V}_{1}\right)\right.\right. \\
& \left.+\frac{C_{12}}{\sigma_{12}}\left(1-C_{A} \bar{v}_{12}\right)+\left(1-\frac{C_{A}}{C_{C}}\right)\left(1-C_{A} \bar{v}_{3}\right) \frac{C_{13}}{\sigma_{13}}+\frac{C_{A}{ }^{2} C_{3} \bar{v}_{3}}{C_{C} \sigma_{3}}\right\} \\
& +\frac{\partial \mu_{2}}{\partial C_{B}}\left\{\frac{C_{12}}{\sigma_{12}}\left(1-C_{A} \bar{v}_{12}\right)-\frac{C_{B}}{C_{C}} \frac{C_{13}}{\sigma_{13}}\left(1-C_{A} \bar{v}_{B}\right)-\frac{C_{A} C_{2} \bar{V}_{2}}{\sigma_{2}}\right. \\
& \left.+\frac{C_{A} C_{B} C_{3} \bar{v}_{3}}{C_{C} \sigma_{3}}\right\} \frac{\partial C_{B}}{\partial z} \tag{148}
\end{align*}
$$

$$
\begin{align*}
& n J_{B}=-\left[\frac { \partial \mu _ { 1 } } { \partial C _ { A } } \left\{\frac{C_{12}}{\sigma_{12}}\left(1-C_{B} \bar{v}_{12}\right)-C_{B}\left(\frac{\bar{V}_{1} C_{1}}{\sigma_{1}}+\frac{\bar{v}_{13} C_{13}}{\sigma_{13}}\right)\right.\right. \\
& \left.+\frac{C_{A} C_{B}}{C_{C}}\left(\frac{C_{13} \bar{V}_{13}}{\sigma_{13}}+\frac{C_{3} \bar{V}_{3}}{\sigma_{3}}\right)\right\}+\frac{\partial \mu_{2}}{\partial C_{A}}\left\{\frac{C_{12}}{\sigma_{12}}\left(1-C_{A} \bar{v}_{12}\right)+\frac{C_{2}}{\sigma 2}\left(1-C_{B} \bar{V}_{2}\right)\right. \\
& \left.+\frac{C_{B}^{2}}{C_{C}}\left(\frac{C_{13} \bar{V}_{13}}{\sigma_{13}}+\frac{C_{3} \bar{V}_{3}}{\sigma_{3}} ;\right\}\right] \frac{\partial C_{A}}{\partial z}-\left[\frac { \partial \mu _ { 1 } } { \partial C _ { A } } \left\{\frac{C_{12}}{\sigma_{12}}\left(1-C_{B} \bar{V}_{12}\right)\right.\right. \\
& \left.-C_{B}\left(\frac{\bar{V}_{1} C_{1}}{\sigma_{1}}+\frac{\bar{V}_{13} C_{13}}{\sigma_{13}}\right)+\frac{c_{A} C_{B}}{C_{C}}\left(\frac{c_{13} \bar{V}_{13}}{\sigma_{13}}+\frac{c_{3} \bar{V}_{3}}{\sigma_{3}}\right)\right\} \\
& +\frac{\partial \mu,}{\partial C_{A}}\left\{\frac{C_{12}}{\sigma_{12}}\left(1-C_{A} \bar{v}_{12}\right)+\frac{C_{2}}{\sigma_{2}}\left(1-C_{3} \bar{V}_{2}\right)\right. \\
& \left.+\frac{C_{B}{ }^{2}}{C_{C}}\left(\frac{C_{13} \bar{v}_{13}}{\sigma_{13}}+\frac{c_{3} \bar{v}_{3}}{\sigma_{3}}\right)\right] \frac{\partial C_{B}}{\partial z} \tag{149}
\end{align*}
$$

Comparing this to the defining equations for the diffusivities gives the desired results:

$$
\begin{align*}
D_{A A}= & \frac{1}{n}\left[\frac{C_{1}}{\sigma_{1}}\left(1-C_{A} \bar{V}_{1}\right)+\frac{C_{12}}{\sigma_{12}}\left(1-C_{A} \bar{V}_{12}\right)+\left(1-\frac{C_{A}}{C_{C}}\right) \frac{C_{13}}{\sigma_{13}}\left(1-C_{A} \bar{V}_{13}\right)\right. \\
& \left.+\frac{C_{A}{ }^{2} C_{3} \bar{V}_{3}}{C_{C} \sigma_{3}}\right] \frac{\partial \mu_{1}}{\partial C_{A}}+\frac{1}{n}\left[\frac{C_{12}}{\sigma_{12}}\left(1-C_{A} \bar{V}_{12}\right)-\frac{C_{B} C_{13}}{C_{C} \sigma_{13}}\left(1-C_{A} \bar{V}_{13}\right)\right. \\
& \left.-\frac{C_{A} C_{2} \bar{V}_{2}}{\sigma_{2}}+\frac{C_{A} C_{B} C_{3} \bar{V}_{3}}{C_{C} \sigma_{3}}\right] \frac{\partial \mu_{2}}{\partial C_{A}}  \tag{150}\\
D_{B B}= & \frac{1}{n}\left[_{12}^{\sigma_{12}}\left(1-C_{B} \bar{V}_{12}\right)-C_{C_{B}}\left(\frac{\bar{V}_{1} C_{1}}{\sigma_{1}}+\frac{\bar{V}_{13} C_{13}}{\sigma_{13}}\right)\right. \\
& \left.+\frac{C_{A} C_{B}}{C_{C}}\left(\frac{C_{13} \bar{V}_{13}}{\sigma_{13}}+\frac{C_{3} \bar{V}_{3}}{\sigma_{3}}\right)\right] \frac{\partial \mu_{1}}{\partial C_{B}}+\frac{1}{n}\left[\frac{C_{12}}{\sigma_{12}}\left(1-C_{B} \bar{V}_{12}\right)\right. \\
& \left.\left.+\frac{C_{2}}{\sigma_{2}}\left(1-C_{B} \bar{V}_{2}\right)+\frac{C_{B}{ }^{2}}{C_{C}\left(\frac{C_{13}}{\sigma_{13}} \bar{V}_{13}\right.}+\frac{\bar{V}_{3} C_{3}}{\sigma_{3}}\right)\right] \frac{\partial \mu_{2}}{\partial C_{B}} \tag{15I}
\end{align*}
$$

The cross-coefficients are given by the same expressions, except that the differentiation of the chemical potential is with respect to the other component.

The validity of the Onsager Reciprocal Relation will now be demonstrated for this system. As before, the rate of entropy production is given by

$$
\begin{equation*}
T \frac{d S}{d t}=-J_{1} \frac{\partial \mu_{1}}{\partial z}-j_{2} \frac{\partial \mu_{2}}{\partial z}-J_{3} \frac{\partial \mu_{3}}{\partial z}-J_{12} \frac{\partial \mu_{12}}{\partial z}-J_{13} \frac{\partial \mu_{13}}{\partial z} \tag{152}
\end{equation*}
$$

Applying equations (141) and (142) gives

$$
\begin{align*}
T \frac{\partial S}{d t}= & -\left(J_{1}+J_{12}+J_{13}\right) \frac{\partial \mu_{1}}{\partial z}-\left(J_{2}+J_{12}\right) \frac{\partial \mu_{2}}{\partial z} \\
& -\left(J_{3}+J_{13}\right) \frac{\partial \mu_{3}}{\partial z} \tag{153}
\end{align*}
$$

Equation (146) allows $\frac{\partial \mu_{3}}{\partial z}$ to be eliminated:

$$
\begin{align*}
T \frac{d S}{d t}= & -\left[J_{1}+J_{12}-\frac{C_{A}}{C_{C}} J_{3}+\left(I-\frac{C_{A}}{C_{C}}\right) J_{13}\right] \frac{\partial \mu_{1}}{\partial z} \\
& -\left[J_{2}+J_{12}-\frac{C_{B}}{C_{C}}\left(J_{3}+J_{13}\right)\right] \frac{\partial \mu_{2}}{\partial z} \tag{154}
\end{align*}
$$

The assumption of constant volume

$$
\begin{equation*}
J_{1} \bar{v}_{1}+J_{2} \bar{v}_{2}+J_{3} \overline{\mathrm{v}}_{3}+J_{12} \overline{\mathrm{~V}}_{12}+J_{13} \overline{\mathrm{v}}_{13}=0 \tag{155}
\end{equation*}
$$

allows $J_{3}$ to be eliminated from equation (154):

$$
\begin{equation*}
T \frac{d S}{d t}=-P J_{1}-Q J_{2}-R J_{12}-W J_{13} \tag{156}
\end{equation*}
$$

where the expressions $P, Q, R$, $W$ are defined by

$$
\begin{equation*}
\mathrm{T} \frac{\mathrm{~d} S}{d t}=-J_{1} \frac{\partial \mu_{1}}{\partial z}-\tilde{J}_{2} \frac{\partial \mu_{2}}{\partial z}-J_{3} \frac{\partial \mu_{3}}{\partial z}-J_{12} \frac{\partial \mu_{12}}{\partial z}-J_{13} \frac{\partial \mu_{13}}{\partial z} \tag{152}
\end{equation*}
$$

Applying equations (141) and (I42) gives

$$
\begin{align*}
\mathrm{I} \frac{\mathrm{~d} S}{d t}= & -\left(J_{1}+J_{12}+J_{13}\right) \frac{\partial \mu_{1}}{\partial z}-\left(J_{2}+J_{12}\right) \frac{\partial \mu_{2}}{\partial z} \\
& -\left(J_{3}+J_{13}\right) \frac{\partial \mu_{3}}{\partial z} \tag{153}
\end{align*}
$$

Equation (146) allows $\frac{\partial \mu_{3}}{\partial z}$ to be eliminated:

$$
\begin{align*}
\mathrm{I} \frac{\mathrm{~d} S}{d t}= & -\left[J_{1}+J_{12}-\frac{C_{A}}{C_{C}} J_{3}+\left(i-\frac{C_{A}}{C_{C}}\right) J_{13}\right] \frac{\partial \mu_{1}}{\partial z} \\
& -\left[J_{2}+J_{12}-\frac{C_{B}}{C_{C}}\left(J_{3}+J_{13}\right)\right] \frac{\partial \mu_{2}}{\partial z} \tag{154}
\end{align*}
$$

The assumption of constant volume

$$
\begin{equation*}
J_{1} \bar{V}_{1}+J_{2} \bar{V}_{2}+J_{3} \bar{V}_{3}+J_{12} \bar{V}_{12}+J_{13} \bar{V}_{13}=0 \tag{155}
\end{equation*}
$$

allows $J_{3}$ to be eliminated from equation (154):

$$
\begin{equation*}
T \frac{d S}{d t}=-P J_{1}-Q J_{2}-R J_{12}-W J_{13} \tag{156}
\end{equation*}
$$

where the expressions $P, Q, R, W$ are defined $b y$

$$
\begin{aligned}
P= & \frac{\partial \mu_{1}}{\partial z}+\frac{C_{A} \nabla_{1}}{C_{C} \nabla_{3}} \frac{\partial \mu_{1}}{\partial z}+\frac{C_{B} \nabla_{1}}{C_{C} \nabla_{3}} \frac{\partial \mu_{2}}{\partial z} \\
Q= & \frac{\partial \mu_{2}}{\partial z}+\frac{C_{B} \bar{V}_{2}}{C_{C} \nabla_{3}} \frac{\partial \mu_{2}}{\partial z}+\frac{C_{A} \bar{V}_{2}}{C_{C} \nabla_{3}} \frac{\partial \mu_{1}}{\partial z} . \\
R= & \frac{\partial \mu_{1}}{\partial z}+\frac{\partial \mu_{2}}{\partial z}+\frac{C_{A} \bar{V}_{12}}{C_{C} \nabla_{3}} \frac{\partial \mu_{1}}{\partial z}+\frac{C_{B} \bar{V}_{12}}{C_{C} \nabla_{3}} \frac{\partial \mu_{2}}{\partial z} \\
W= & \frac{\partial \mu_{1}}{\partial z}+\frac{\partial \mu_{2}}{\partial z}+\frac{C_{A} \bar{V}_{12}}{C_{C} \nabla_{3}} \frac{\partial \mu_{1}}{\partial z}+\left(1-\frac{C_{A}}{C_{C}}\right) \frac{\partial \mu_{1}}{\partial z}+\frac{C_{B} \bar{V}_{13}}{C_{C} \nabla_{3}} \frac{\partial \mu_{2}}{\partial z} \\
& -\frac{C_{B}}{C_{C}} \frac{\partial \mu_{z}}{\partial z}
\end{aligned}
$$

Now substituting the stoichiometric relations

$$
\begin{aligned}
& J_{A}=J_{1}+J_{12}+J_{13} \\
& J_{B}=J_{2}+J_{12}
\end{aligned}
$$

yields

$$
\begin{equation*}
T \frac{d S}{d t}=-J_{A} P-J_{B} Q-J_{12}(R-P-Q)-J_{13}(W-P) \tag{157}
\end{equation*}
$$

Now if we assume that $\overline{\mathrm{V}}_{12}=\overline{\mathrm{V}}_{1}+\overline{\mathrm{V}}_{2}$ and $\overline{\mathrm{V}}_{13}=\overline{\mathrm{V}}_{1}+\overline{\mathrm{V}}_{3}$, leaving

$$
\begin{align*}
T \frac{d S}{d t}= & -J_{A}\left(\frac{\partial \mu_{1}}{\partial z}+\frac{C_{A} \nabla_{1}}{C_{C} \nabla_{3}} \frac{\partial \mu_{1}}{\partial z}+\frac{C_{B} \nabla_{1}}{C_{C} \nabla_{3}} \frac{\partial \mu_{2}}{\partial z}\right) \\
& -J_{B}\left(\frac{\partial \mu_{2}}{\partial z}+\frac{C_{A} \nabla_{2}}{C_{C} \nabla_{3}} \frac{\partial \mu_{1}}{\partial z}+\frac{C_{B} \nabla_{2}}{C_{C} \nabla_{3}} \frac{\partial \mu_{2}}{\partial z}\right) \tag{158}
\end{align*}
$$

Irreversible thermodynamics also states that the fluxes are related to the phenomenological coefficients:

$$
\begin{align*}
J_{A}= & -L_{A A}\left(\frac{\partial \mu_{1}}{\partial z}+\frac{C_{A} \bar{V}_{1}}{C_{C} \nabla_{3}} \frac{\partial \mu_{1}}{\partial z}+\frac{C_{B} \bar{v}_{1}}{C_{C} \nabla_{3}} \frac{\partial \mu_{2}}{\partial z}\right) \\
& -L_{A B}\left(\frac{\partial \mu_{2}}{\partial z}+\frac{C_{A} \bar{V}_{2}}{C_{C} \nabla_{3}} \frac{\partial \mu_{1}}{\partial z}+\frac{C_{B} \bar{v}_{2}}{C_{C} \nabla_{3}} \frac{\partial \mu_{2}}{\partial z}\right)  \tag{159}\\
J_{B}= & -L_{B A}\left(\frac{\partial \mu_{1}}{\partial z}+\frac{C_{A} \bar{v}_{1}}{C_{C} \nabla_{3}} \frac{\partial \mu_{1}}{\partial z}+\frac{C_{B} \bar{v}_{1}}{C_{C} \nabla_{3}} \frac{\partial \mu_{2}}{\partial z}\right) \\
& -L_{B B}\left(\frac{\partial \mu_{2}}{\partial z}+\frac{C_{A} \bar{V}_{2}}{C_{C} V_{3}} \frac{\partial \mu_{1}}{\partial z}+\frac{C_{B} \bar{v}_{2}}{C_{C} \nabla_{3}} \frac{\partial \mu_{2}}{\partial z}\right)
\end{align*}
$$

Carrying out the multiplications in equations
and (160), equating coefficients to ecuations (142) and (143) and solving for $L_{A B}$ and $L_{B A}$ gives

$$
\begin{align*}
L_{A B}=L_{B A}= & -\frac{c_{1} C_{B} \bar{v}_{1}}{\sigma_{1} n}\left(1-\bar{v}_{1} C_{A}\right)-\frac{c_{2} c_{A} \bar{v}_{2}}{\sigma_{2} \eta}\left(1-\bar{v}_{2} c_{B}\right) \\
& -\frac{c_{A} C_{B} \bar{v}_{3}}{\sigma_{3}^{n}}\left(\bar{v}_{1} C_{A}+\bar{v}_{2} C_{B}-1\right) \\
& +\frac{c_{12}}{\sigma_{12^{n}}}\left(1-\bar{v}_{12} c_{A}\right)\left(1-\bar{v}_{12} C_{B}\right) \\
& +\frac{c_{13}}{\sigma_{13^{n}}}\left(1-\bar{v}_{13} C_{A}\right)\left(1-\bar{v}_{13} C_{B}\right) \tag{161}
\end{align*}
$$

Whus, hydrodynamic tneory predicts the validity of the Onsager Reciprocal Relation for this associated system, under tine assumptions of constant volume and that the volume of the dimer is equal to the sum of the volumes of the component monomers.

## Tracer Diffusivities

Tracer diffusivities for this work were measured by means of the capillary tecnrique, as modified by Wirth [8]. In the basic capillary technique, a capillary of known length, with one end closed, is filled with a solution containing tagged molecules of one component. This capillary is then immersed in a relatively large volume of a solution with the same chemical composition, but containing no tagged molecules. Diffusion is then allowed to proceed for a period of time, after which the capillary is removed from the bulk solution and emptied. The relative amounts of tagged material before and after the experiment are determined. The boundary value problem for diffusive transfer from the capillary is then solved to give the change in the concentration of tagged molecules as a function of time, capillary dimensions and tracer diffusivity. Since the time and capillary dimensions are known, the tracer diffusivity can then be found from the change in concentration of tagged materiai.

Ordinarily, the molecules are tagged with a radioactive isotope. In this case it is easiest to measure
the total amount of radicactivity present rather than the concentration. This presents no difficulty, however.

There are four main sources of error in this basic technique:
a. Inaccuracies in determining precisely the amount of radioactivity before and after diffusion. This is particulariy important in determining the initial count rate.
b. Proper maintainance of the conditions of the boundary value problem during the experiment. This means that there must be no convective mixing within the capillary during the experiment, and no material may be transferred by any means other than diffusion.
c. Immersion effects. Materia_ must not be washed out the end of the capillary by the turbulence created in the bulk solution when immersing the capillary or removing it at the end of the experiment.
d. Convective transfer during the experiment. Convection near the end of the capillary must be strong enough to maintain the boundary condition of zero concentration at the end of the capillary. Yet it must not be so strong that it washes material from a segment of the capillary, thus effectively shortening the length of the capillary during the experiment.

The two latter problems are due to the open end of the capillary, and are difficult to correct as long as the
end is open. The other two proolems are generally less serious.

To correct for (c) and (d), Wirth covered the open end of the capillary with a very thin (0.007 in.) porous glass disc. This changed the boundary value problem, introducing a resistance term at the end instead of a constant concentration. Since material could diffuse through the disc, but could not flow through, this procedure effectively eliminated convection from the capillary. However, since the resistance of the frit had to be calibrated by measuring a known diffusivity, a new possible source of error was introduced.

The error due to (b) can be largely eliminated by making the bulk solution slightly less dense than that in the capillary. Then, as diffusion proceeds, a density gradient is established, which tends to eliminate convection within the capillary. This unfortunately introduces the possibility of some mutual diffusion occurring along with the tracer diffusion. It has been shown by Van Geet and Adamson [31] that if the concentration difference between bulk and capillary solutions is greater for tracer diffusion than for ordinary diffusion, the tracer flux will be much greater than the ordinary diffusive flux. Since the difference in the concentration gradients was quite large in these experiments, the author feels that any error
introduced from simultaneous mutual diffusion will be covered by the calibration of the resistance of the glass frit.

Inaccuracies introduced by (a) can be decreased only by careful experimental tecnnique. Wirtn's [34] original technique was modified in this study only slightly to improve the accuracy of the initial count.

The procedure for an experimental run is given in some detail in Appendix A.

Calculation of Tracer Diffusivities
Let the closed end of the capillary be designated $z=0$, and the open end be designated $z=L$, the lengtin of the capillary. If transfer of material within the capillary is only due to diffusion, the well-known diffusion equation holds. The initial concentration is constant througnout the capillary. At the closed end, a material balance will show that the concentration gradient must be zero. If, at the open end there is a constant resistance to flow, the following boundary value problem holds:

$$
\begin{equation*}
\frac{\partial C_{i}^{*}}{\partial t}=D_{i}^{*} \frac{\partial^{2} C_{i}^{*}}{\partial z^{2}} \tag{162}
\end{equation*}
$$

B.C. I: $\frac{\partial C_{i}^{*}}{\partial z}=0$ for $z=0, i \geq 0$
B.C. 2: $-D_{1}^{*} \frac{\partial c_{i}^{*}}{\partial z}=\frac{1}{\bar{Z}} c_{i}^{*}$ for $z=-, t \geq 0$

IC. $\quad C_{i}^{*}=C_{i, 0}^{*}$ for $t=0,0 \leq z \leq i$
where $C_{i}{ }^{*}$ is the concentration of tagged component i, $t$ is the time, $z$ is the $\dot{\text { instance coordinate, }} 0_{1,0}^{*}$ is the initial value of $C_{i}^{*}$ and $\bar{R}$ is tire constant resistance to transfer from the open end oi tine capillary. This couraary value problem can be easily solved by separation of variacies, to give tine concentration as


where $\lambda_{n}$ is giver by the solution of

$$
\cot \left(\lambda_{n_{1}}^{2}\right)=F \Sigma_{2}^{*} \lambda_{r}
$$

A detailed solution of tine boundary-value problem is
given in Appendix III of reference [34]
If equation (164) is integrated over the iengtin of the capillary, a very useful raこ̇o results:
$\frac{C_{i, \operatorname{avg}}^{*}}{C_{i, 0}^{*}}=2 \sum_{n=1}^{\infty}\left[\frac{\sin ^{2} \beta_{n}}{\beta_{n}\left(\beta_{n_{1}}+\sin \beta_{n} \cos \beta_{n}\right)} \exp \left(-\beta_{n}^{2} \frac{D_{i}^{*} t}{L^{2}}\right)\right]$
where $\beta_{n}$ is given by the solution of

$$
\cot \beta_{n}=\beta_{n} \frac{R D_{i}^{*}}{L}
$$

where $C_{i,}^{*}$, ave is the average concentration in the capillary, as defined by the expression $\int_{0}^{V} C_{i}^{*} d V=$ $C_{i, a v e}^{*} V$. This ratio is the ratio of the final count to the initial count measured for the capillary in the experiment.

Since transfer through the frit is diffusive, as soon as the process reaches steady-state the resistance of the frit becomes inversely proportional to the diffusivity:

$$
R=\frac{\alpha}{D_{i}^{*}}
$$

The constant of proportionality a depends only upon the pore geometry of the frit. Therefore the group $\frac{R D_{i}^{*}}{L}$ is dependent only upon geometry of the experimental apparatus, and can be determined by some calibration technique.

From equation (165) a plot can be made of
$\frac{C_{i, a v g}^{*}}{C_{i, 0}^{*}}$ vs $\frac{D_{i}^{*} t}{L^{2}}$ for several values of $\frac{R D_{i}^{*}}{L}$. Then
from an experiment witr a chemical whose self-diffusivity is known, the value of $R$ may be determined. Wirth did this, using carbon tetrachioride. He determired that $\frac{R D_{i}}{L_{i}^{*}}$ had a value of 0.012 , with a variation from capillary to capillary which would iead to a $.7 \%$ maximum variation in measured tracer diffusivity. Consequently, the value of $\frac{R D_{i}^{*}}{L}$ was taken as 0.012 .

the tracer diffusivity is determined from the count rates resulting from each experiment. The ratio of final count rate to initial count rate is equal to $\frac{C_{i,}^{*}}{C_{i, 0}^{*}}$. The value of $\frac{C_{i,}^{*} \text { avg }}{C_{i, 0}^{*}}$ fixes the value of $\frac{D_{i}^{*} t}{L^{2}}$. Since $t$ and $L$ are known, the diffusivity $D_{i}^{*}$ is easily calculated.

## Mutual Diffusivities

Mutual diffusivities were measured in this laboratory by means of a Mach-Zehnder [4,5] interferometer. This instrument is shown schematically in Figure B-l of

```
Appendix B. A collimated monocrromatic light beam is
split into two beams by a half-silvered mirror. Ore
beam is passed through a soiution in which diffusion is
occurring. The otner beam is passed througn a reference
solution in wrich trere is no concentration g=adient.
When the two beams are recomoined, if the optical path
lengths are only siightiy differert, interference pro-
duces a fringe pattern.
    Since the optical path lergtin is dependent upon the
refractive incex of tie medium, it can be shown that the
fringe pattern formed by the recombination of the beams
represents a piot of refractive index vs position in the
diffusing system. The refractive index is in turn reiated
to the composition of the system. By photographically
recording the changes in the fringe pattern with time,
the changes ir cornosition iand nence the diffusivities)
can be determined.
    The diffusion cell was corstructed so that a step-
change initial condition could be approximated, and so
that diffusion wouid be one-dimensional along the vertical
axis. The cell was filled from the bottom with the
denser of two solutミons varying slightly in composition.
The less dense solution was slowly introduced down the
wall of the ceil, forming a layer above the denser
solution. When the cell was full, and had reached
equilibrium temperature in tise inverferometer thermostat,
```

solution was removed slowly through slits on opposite sides of the cell, and replaced in the cell from top and bottom. After some time, a steady state was reached, in which the solution above the slit was of one composition, and that below the slit of another. The thiciness of the boundary determined how closely the step-change approximation was obeyed. In practice, the boundary could be made small enough that it closely approximated the concentration distribution after a few seconds of diffusion from a true step-change initial condition.

The flow into and out of the cell was stopped, and free diffusion from this initial condition occurred, which was followed photographically. Details of an experimental run are given in Appendix $B$.

## Analysis of Results of Binary Mutual Diffusion Experiment

The problem of one-dimensional free diffusion in an infinite medium is an old one. It was solved by Wiener [33] in 1893. If the initial position of the boundary is designated as $z=0$, and the initial distribution of concentration gradients is Gaussian, the solution for the gradient in terms of position and time is given by

$$
\begin{equation*}
\frac{d C}{d z}=\frac{\Delta C_{0}}{2 \sqrt{\pi D_{A B} t}} \exp \left(-z^{2} / 4 D_{A B} t\right) \tag{166}
\end{equation*}
$$

provided the diffusivity is constant. If the initial concentration difference is small enough, both these conditions will be met. Furthermore, the refractive index difference may be considered a linear function of the concentration difference for small $\Delta C$. This solution may then be written

$$
\begin{equation*}
\frac{\partial n}{d z}=\frac{\Delta n}{2 \sqrt{\pi D_{A B} t}} \exp \left(-z^{2} / 4 D_{A B} t\right) \tag{167}
\end{equation*}
$$

This may be integrated to give the refractive index difference between the points $z=0$ and $z=z$.

$$
\begin{equation*}
\frac{n_{z}-n_{0}}{\Delta n_{1}}=\frac{1}{2} \operatorname{erf}\left(z / \sqrt{4 D_{A B}^{t}}\right) \tag{168}
\end{equation*}
$$

Solving this for z gives

$$
\begin{equation*}
z=\sqrt{4 D_{A B^{\tau}}} \operatorname{erf}^{-1}\left(2 \frac{n_{z}-n_{0}}{\Delta n}\right) \tag{169}
\end{equation*}
$$

The photograpnic image can be considered a plot of refractive index vs position in the cell. The total refractive index difference between any two points is proportional to the number of fringes crossed by a vertical line between the two points. The fringe number can then be used as a measure of refractive index. Call the fringe number of a reference point in the straight line portion of the photograph fringe number zero. The
$z_{j}$
$Z=0$
$Z_{K}$

total number of fringes crossed by the vertical line is J. The fringe number of the point $z=0$ is $J / 2$, from the choice of coordinates in the boundary vaiue problem. the difference between the refractive indexes of the point $z=z_{j}$ and $z=0$ is given by

$$
\begin{equation*}
\frac{n_{j}-n_{0}}{\Delta n}=\frac{j-\frac{1}{2} J}{j} \tag{170}
\end{equation*}
$$

The distance between any two fringes numbered $j$ and $k$ is

$$
\begin{equation*}
z_{j}-z_{k}=\sqrt{4 D_{A B^{t}}}\left[\operatorname{erf}^{-1}\left(2 \frac{n_{j}-n_{o}}{\Delta n}\right)-\operatorname{erf}^{-1}\left(2 \frac{n_{k}-n_{o}}{\Delta n}\right)\right] \tag{171}
\end{equation*}
$$

The actual distance in the cell is not the same as that measured on the photograph, but differs by the magnification factor of the camera:

$$
\begin{equation*}
z_{j}^{\prime}=M z_{j} \tag{172}
\end{equation*}
$$

where $a_{j}{ }^{\prime}$ is the measured distance, $z_{j}$ the true distance and $M$ the magnification factor of the camera. Combining equations (170), (171) and (172) leads to the desired result:

$$
\begin{equation*}
4 M^{2} D_{A B} t=\left[\frac{z_{j}^{\prime}-z_{k}^{\prime}}{\operatorname{erf}^{-1}\left(\frac{2 j-J}{J}\right)-\operatorname{erf}^{-1}\left(\frac{2 K-J}{J}\right)}\right]^{2} \tag{173}
\end{equation*}
$$

The true time of diffusion is not the measured time, since the initial boundary was not a perfect step-change:

$$
t=t_{m}+t_{0}
$$

where $t_{m}$ is the measured time, $t$ is the true time, and $t_{0}$ the true initial time. If the right side of equation (173) is plotted vs $t_{m}$, the slope of the line will give the diffusivity, and the intercept the true initial time:

$$
\begin{align*}
\text { slope } & =4 \mathrm{M}^{2} \mathrm{D}_{A B}  \tag{174}\\
\text { intercept } & =-4 \mathrm{M}^{2} \mathrm{D}_{A B} t_{0}
\end{align*}
$$

## Calculation of Binary Mutual Diffusivities

The photographic plate was measured by a microscope with a traveling eyepiece, capable of measuring down to 0.0001 cm . The total number of fringes was counted and recorded. Then a set of ten fringe numbers was chosen, five of which were higher than $J / 2$ and five of which were lower. These were chosen so as not to extend into the region of curved fringes near the edge of the diffusion boundary. These were paired, and the right side of equation (173) calculated for each pair.

For each exposure, $z_{j}^{\prime}$ and $z_{k}^{\prime}$ were measured for each pair of fringes. From the measurements and the previous calculations, five values of the right side of equation (173) were calculated and averaged. The average
values were then plotted against $t_{m}$ as described above. A straight line was fit to these points by the method of least-squares. If the correlation coefficient was less than .995 , the run was rejected (althougn generally it was above .999). Otherwise, the value of $D_{A B}$ was calculated from the least-squares slope and intercept.

## Analysis of Results of Ternary Mutual Diffusion Experiment

Fujita and Gosting [13] have shown that the ternary diffusivities defined by equations (98) can be determined experimentally from knowledge $0^{-2}$ the behavior of the refractive index gradient curves as diffusion proceeds. Their method involves measuring the second moment and the height-area ratio of graphs of $\frac{d n}{d z}$ vs $z$ at several times during the experiment, and from these determining the reduced second moment and the reduced height-area ratio. This is done for severai different initial composition differences, and the graphs of reauced second moment and reduced height-area ratio vs refractive index fraction are then used to calculate the diffusivities.

A typical plot of refractive index gradient vs position is shown on the following page. Here $z_{c}$ is the centroid of the curve, and $\left.\frac{d n}{d z}\right|_{\max }$ is the maximum value of $\frac{d n}{d z}$, which is at the centroid for Gaussian curves.


The centroid is defired by

$$
\begin{equation*}
z_{c}=\frac{\int_{-\infty}^{\infty} z\left(\frac{\left(\frac{d n}{d z}\right) d z}{\int_{-\infty}^{\infty}\left(\frac{d n}{d z}\right) d z}, \frac{d}{d}\right.}{} \tag{175}
\end{equation*}
$$

It can easily be seen that tine denominator is equal to the total refractive index change across the boundary, which is proportional to the number of fringes $J$. Therefore

$$
\begin{equation*}
z_{c}=\frac{1}{\lambda \bar{J}} \int_{-\infty}^{\infty} z\left(\frac{\dot{\mathrm{a}},}{\dot{\mathrm{~L}} \mathrm{z}}\right) d \mathrm{~d} \tag{176}
\end{equation*}
$$

where $\lambda$ is the proportionality constant.
The second moment is defined by

$$
m_{2}=\frac{\int_{-\infty}^{\infty}\left(z-z_{c}\right)^{2}\left(\frac{d n}{d z}\right) d z}{\int_{-\infty}^{\infty}\left(\frac{d n}{d z}\right) d z}=\frac{1}{\lambda J} \int_{-\infty}^{\infty}\left(z-z_{c}\right)^{2}\left(\frac{d n}{d z}\right) d z
$$

and the total area under the curve is

$$
\begin{equation*}
\text { area }=\Delta n=\int_{-\infty}^{\infty}\left(\frac{d n}{d z}\right) d z=\lambda J \tag{178}
\end{equation*}
$$

The refractive index gradient can be determined from the photographic plate as follows. Near the center of the boundary, where the fringes are almost straight, $\frac{d n}{d z}$ can be approximated from the distance between two fringes:

$$
\begin{equation*}
\left.\left(\frac{\partial n}{\partial z_{m}}\right)\right|_{z_{m}}=\frac{z_{j+1}+z_{j}}{2}=\frac{\lambda}{z_{j+1}-z_{j}} \tag{179}
\end{equation*}
$$

In the curved portions of the pattern near the edges of the boundary, this approximation does not hold, and the value of $\frac{d n}{d z_{m}}$ must be determined by measuring the tangent to the curve:

$$
\begin{equation*}
\frac{d n}{d z_{m}}=\frac{d n}{d y} \frac{d y}{d z_{m}}=\frac{d n}{d y} \tan \theta \tag{180}
\end{equation*}
$$

The value of $\frac{d n}{d y}$ can be determined by measuring the distance between two fringes in the $y$ direction:

$$
\begin{equation*}
\frac{d n}{d y}=\frac{n_{j+1}-n_{j}}{y_{j+1}-y_{j}}=\frac{\lambda(j+1-j)}{y_{j+1}-y_{j}}=\frac{\lambda}{y_{j+1}-y_{j}} \tag{181}
\end{equation*}
$$

Equation (180) can now be written

$$
\begin{equation*}
\frac{d n}{d z_{m}}=\frac{\lambda}{y_{j+1}-y_{j}} \tan \theta=\frac{\lambda}{\psi} \tan \theta \tag{182}
\end{equation*}
$$

where $\lambda$ and $\psi$ are proportionality constants representing the change in refractive index per fringe in the $z$ direction, and the distance between fringes in the $y$ direction respectively.

The distances measured on the photograph are not true distances, so equations (176) and (177) must be corrected for the magnification factor of the camera:

$$
\begin{align*}
& z_{c, m}=\left.\frac{1}{J M} \int_{-\infty}^{\infty} z_{m}\left(\frac{1}{z_{j+1}-z_{j}}\right)\right|_{z_{m}} d z_{m}  \tag{183}\\
& m_{2}=\left.\frac{1}{J M^{2}} \int_{-\infty}^{\infty}\left(z_{m}-z_{c, m}\right)^{2}\left(\frac{1}{z_{j+1}-z_{j}}\right)\right|_{z_{m}} d z_{m} \tag{184}
\end{align*}
$$

Note that in substituting for $\frac{d n}{d z_{m}}$ the constant $\lambda$ cancels.
The reduced second moment is defined by

$$
\begin{equation*}
D_{2 m}=\frac{m_{2}}{2 t} \tag{185}
\end{equation*}
$$

and the reduced height-area ratio is defined by

$$
\begin{equation*}
D_{A}=\frac{(\Delta n)^{2}}{4 \pi t\left[\left.\frac{\partial n}{\partial x}\right|_{\max }\right]^{2}}=\frac{(\lambda J)^{2}}{4 \pi t M^{2}\left[\left.\frac{\lambda}{z_{j+1}-z_{j}}\right|_{\max }\right]^{2}} \tag{186}
\end{equation*}
$$

The measured time is not the true time, but $t=t_{m}+t_{0}$ so these can be written

$$
\begin{gather*}
\frac{m_{2}}{2}=D_{2 m} t_{m}+D_{2 m} t_{0}  \tag{187}\\
\frac{J^{2}}{4 \pi M^{2}\left[\left.\frac{1}{z_{j+1}-z_{j}}\right|_{\max }\right]^{2}}=D_{A} t_{m}+D_{A} t_{0} \tag{188}
\end{gather*}
$$

$D_{2 m}$ and $D_{A}$ can be calculated by plotting $\frac{m_{2}}{2}$ and the left side of equation (188) vs $t_{m}$. The slopes will be $D_{2 m}$ and $D_{A}$ respectively, and the intercepts will give the true initial time. The left side of equation (188) and $\frac{m_{2}}{2}$ can be calculated from measurements of the photographic plate. This would ordinarily be rather difficult, but a computer program has been written for this. This program, the data deck structure, and the procedure for measuring the plate are given in Appendix C. Sample refractive index gradient curves and plots of $\frac{m_{2}}{2}$ vs $t_{m}$ are given in Appendix $D$, with the experimental results. In a ternary system, the refractive index can be expressed as a function of the concentrations of any two components, for example $n=n\left(C_{A}, C_{B}\right)$. This in turn can be expressed as a Taylor series expansion in terms of $C_{A}$ and $C_{B}$. For small enough concentration differences, the higher order terms of the expansion can be dropped, and

$$
\Delta n=R_{A} \Delta C_{A}+R_{B} \Delta C_{B}
$$

Defining the refractive index fraction of component $A$ by

$$
\begin{equation*}
\alpha_{A}=\frac{R_{A} \Delta C_{A}}{R_{A} \Delta C_{A}+R_{B} \Delta C_{B}} \tag{189}
\end{equation*}
$$

we see that

$$
\begin{equation*}
\alpha_{A}+\alpha_{B}=1 \tag{190}
\end{equation*}
$$

The values of $R_{A}$ and $R_{B}$ can be determined from measurements of $\Delta n$ at several different $\Delta C^{i} s$ by a leastsquares technique. Since accurate direct measurements of $\Delta n$ require relatively large concentration differences, the preferred method is to determine the values of $R_{A}{ }^{\prime}$ and $R_{B}^{\prime}$ defined by the equation

$$
\begin{equation*}
J=R_{A}^{\prime} \Delta C_{A}+R_{B}^{\prime} \Delta C_{B} \tag{191}
\end{equation*}
$$

where $R_{A}^{\prime}=\lambda R_{A}$ and $R_{B}^{\prime}=\lambda R_{B}$.

This will allow smaller composition differences to be used, since $J$ can be measured more precisely than $\Delta n$. By equation (191), we see that if $\frac{-\Delta C_{A}}{J}$ is plotted vs. $\frac{\Delta C_{2}}{J}$, the result should be a straight line, with slope
$\frac{R^{\prime} B}{R_{A}^{\prime}}$ and intercept $\frac{1}{R_{A}^{\prime}}$. As can be seen in figure $D-10$, this is true for the ternary system chloroform acetonebenzene which will be investigated in this work. Note that $\frac{R^{\prime}}{R_{B}^{\prime}}=\frac{R_{A}}{R_{B}}$ and that only this ratio is needed in defining the refractive index fraction.

Fujita and Gosting [l3] have shown that plots of reduced second moments and the reciprocal of the squareroot of the reduced height-area ratio vs. refractive index fraction of one component should be straight lines:

$$
\begin{align*}
& D_{2 m}=S_{2 m} \alpha_{A}+I_{2 m}  \tag{192}\\
& \frac{I}{\sqrt{D_{A}}}=S_{A} \alpha_{A}+I_{A} \tag{193}
\end{align*}
$$

where $S_{2 m}$ and $S_{A}$ are the slopes and $I_{2 m}$ and $I_{A}$ are the intercepts at $\alpha_{A}=0$. Their proof is based on the same assumptions which have been made here, and which hold whenever the concentration differences are small.

For convenience in notation, define the intercepts at $\alpha_{A}=1$ by the expressions

$$
\begin{align*}
& L_{2 m}=I_{2 m}+S_{2 m}  \tag{194}\\
& L_{A}=I_{A}+S_{A} \tag{195}
\end{align*}
$$

Their expressions for the diffusivities are

$$
\begin{gather*}
D_{A A}=-\frac{\left|D_{i j}\right|+L_{2 m}\left|D_{i j}\right|^{\frac{1}{2}}+\frac{L_{2 m} S_{2 m} I_{A}}{S_{A}}}{S_{2 m}}  \tag{196}\\
D_{B B}=-\frac{\left|D_{i j}\right|+I_{2 m}\left|D_{i j}\right|^{\frac{1}{2}}+\frac{I_{2 m} S_{2 m} L_{A}}{S_{A}}}{S_{2 m}}  \tag{197}\\
D_{A B}=\frac{R_{2}}{R_{1}}\left(I_{2 m}-D_{B B}\right)  \tag{198}\\
D_{B A} \quad \frac{R_{1}}{R_{2}}\left(I_{2 m}-D_{A A}\right) \tag{199}
\end{gather*}
$$

where $\left|D_{1 j}\right|^{\frac{1}{2}}$ is the root of the cubic equation

$$
\begin{equation*}
\left|D_{i j}\right|^{3 / 2}+\left(I_{2 m}-I_{A} \frac{S_{2 m}}{S_{A}}\right)\left|D_{1 j}\right|-\left(\frac{S_{2 m}}{S_{A}}\right)^{2}=0 \tag{200}
\end{equation*}
$$

A detailed derivation of these equations is given by Fajita and Gosting, or may be found in Appendix II of reference [23]. A computer program which solves equation (200) for $\left|D_{i j}\right|^{\frac{1}{2}}$ and then calculates the four ternary diffusivities is given in Appendix C. The lInearity of the plots of equations (192) and (193) for the system studied in this work may be seen in Appendix $D$.

## RESULTS AND DISCUSSION

The following systems were studied experimentally in this work:
a. Tracer diffusivity of 2-butanone in the system 2-butanone - carbon tetrachloride
b. Tracer diffusivity of p-benzoquinone in the system p-benzoquinone - benzene
c. Mutual diffusivity in the system p-benzoquinone - benzene
d. Tracer diffusivity of diethyl ehter in the system ether - carbon tetrachloride
e. Mutual diffusivity in the system diethyl ether - carbon tetrachloride
f. Mutual diffusivity in the system carbon tetrachloride - chloroform
g. Mutual diffusivity in the system benzene chloroform
h. Ternary mutual diffusion at equimolar composition in the system acetone - benzene - chloroform Experimental results, and intermediate determinations for the ternary system, are given in Appendixes $D$ through $F$.

The discussion of results will be organized by type of diffusivity studied, rather than by composition of the systems studied.

## Tracer Diffusivities

Equation (82) predicts that for a self-associating component in a binary system, the product of the tracer diffusivity and the viscosity should have its highest value when that component is very dilute. As the concentration increases, the ratio of polymers to monomers present in the system will increase, and the tracer diffusivity will decrease.

In binary system with cross-association the situation is slightly different. As can be seen from the equilibrium constant expression,

$$
K=\frac{X_{12}}{X_{1} x_{2}}
$$

the ratio of dimers to monomers of component $A$ is proportional to the mole fraction of component B. Hence the percentage of $A$ molecules which are tied up in the dimers is highest when component $A$ is very dilute, i.e. when $x_{B} \rightarrow 1$. Therefore, the tracer diffusivityviscosity product of a component is lowest when that component is extremely dilute, and increases as the concentration increases.

Figure 1 shows the variation of the $D_{A}^{*} \eta$ product for associating components in three systems. In the systems ethanol - carbon tetrachloride and acetic acid carbon tetrachloride hydrogen bonding is quite strong


Figure l. $-D_{i}^{*} \eta$ vs Mole Fraction for Associating Components.
between ethanol molecules and acetic acid molecules. Carbon tetrachloride, on the other hand, is probably quite inert. The curves for these two systems have exactly the shape predicted by equation ( 80 ). The $D_{A}^{*} \eta$ product is highest when $\mathrm{x}_{\mathrm{A}} \rightarrow 0$, and decreases as $x_{A} \rightarrow 1$.

In the system ether - chloroform, spectroscopic evidence [15] suggests that hydrogen bonding occurs between ether and chloroform to form dimers with the form


Presumably, steric hindrance prevents the formation of larger ploymers in this system. Ether-chloroform is therefore a cross-associating system. The curves in Figure 1 agree with the predictions of equation (55). The $D_{i}^{*} \eta$ product for each component is lowest when that component is extremely dilute, and increases as the concentration increases.

Equation (45) predicts that for a system where neither component associates appreciably, the tracer diffusivity - viscosity product will be a constant independent of composition. Figure 2 shows the tracer diffusivity - viscosity product for several systems in


Figure 2. $--D_{i}^{*} \eta$ vs Mole Fraction for Nonassociating Components.


Figure 2. $-D_{i}^{*} \eta$ vs Mole Fraction for Nonassociating
Components.
which there is good reason to believe that there is no association. The normal iodides for instance are essentially non-polar, saturated, and contain no groups active enough to form hydrogen bonds. Carbon tetrachloride is also non-polar, and the electron clouds of the chlorines are quite inert to hydrogen bonding, even in an electron-donor capacity.

As predicted by equation (45) the $D_{i}^{*} n$ products for these systems are straight lines. Furthermore, the $D_{i}^{*} \eta$ product for $\mathrm{CCl}_{4}$ is the same for all the systems given here. This can be taken as supporting evidence for the assumption that diffusing species behave like particles flowing through a continuous medium. The diffusion process is influenced by the viscosity of the medium, but not by the character of the molecules which comprise the medium.

Spectroscopic studies have suggested that ketones, being polar molecules, undergo some dipole-dipole interactions which lead to the formation of self-polymers in solution. Anderson [l] successfully applied the selfdimerization model to explain the positive deviation from Raoult's Law in the system 2-butanone - carbon tetrachloride. He then used equation (92) to fit experimentally measured mutual diffusivity data with excellent results. Wirth [34] later measured the tracer
diffusivities of carbon tetrachioride in this system, confirming the fact that carbon tetrachloride did not associate.

In this work, the tracer diffusivities of 2-butanone were measured, hoping to verify the self-association model. Experimental results for this system are given in Appendix $E$, and shown in Figure 3.

The tracer diffusivity - viscosity products for this system are shown in Figure 4. Since the $D_{i}^{*} \eta$ products are constant throughout the entire concentration range, it must be concluded that there is no association in this system, at least with respect to diffusion. The dipole-dipole interactions observed spectroscopically apparently are not strong enough to hold the dimers together against the shear forces they presumably undergo while diffusing. This would indicate that the inability of equation (88) to predict mutual diffusivities in this system is not due to the formation of polymers. A possible cause would be inaccuracies in the vapor-liquid data in the literature. The system clearly warrants further study.

Spectroscopic studies have shown that highly conjugated molecules with electron withdrawing groups adjacent to the conjugation, such as


Figure 3.--Mutual and Tracer Diffusivities for the System 2-Butanone - Carbon Tetrachloride at $25^{\circ} \mathrm{C}$.


[^0]

$1,3,5-$ trinitro
benzene
can undergo charge-transfer interactions with donor molecules, usually aromatics, which stabilize the structure


It has been established that p-benzoquinone will associate to form dimers in solution with aromatics [2, 11] and equilibrium constants have been measured for several of these systems.

In an effort to experimentally verify equations (150) through (151) for a ternary system with competing equilibria, it was decided to study the system p-benzoquinone - benzene - p-xylene. It was expected that the quinone would form dimers with benzene and xylene, and that no other associations would occur.

Mutual and tracer diffusivities were studied for the component binary system quinone-benzene. Since quinone is only slightly soluble in benzene at $25^{\circ} \mathrm{C}$, the results cover only the solubility range. Experimental results are given in Appendix $E$ and shown in Figure 5.


Figure 5.--Mutual and Tracer Diffusivities in the System p-benzoquinone (A) - benzene (B) at $25^{\circ} \mathrm{C}$.

The tracer diffusivity-viscosity product for quinone is also given in Figure 5. The variation of this $D_{A}^{*} \eta$ product siould be that predicted by equation (55), since this system is considered to have only crossassociation. That is, the $D_{A}^{*} \eta$ product should increase as the concentration of quinone increases. As can be seen in the figure, it does not increase, but decreases instead. This was interpreted as some sort of interaction leading to self-association of quinone which masked the effect of the cross-association.

The change in the $D_{i}^{*} \eta$ product for a small change in concentration is much greater for self-association than for cross-association. It is possible that if the concentration of quinone could be increased, the crossassociation effect would again become predominant. In any event, the associations present are too complex to be treated by the equations developed here, and work in the ternary system was not carried further.

Tracer diffusivities were measured for ether in the system diethyl ether - carbon tetrachloride across the entire composition range, and for carbon tetrachloride at the two endpoints. Results for this system are given in Appendix $E$, and shown in Figure 6. There were considerable experimental difficulties in working with this system, due to the high volatility, the low viscosity, and the surface-wetting characteristics of solutions with


Figure 6.--Mutual and Tracer Diffusivities in the System Diethyl Ether - Carbon Tetrachloride at $25^{\circ} \mathrm{C}$.
high ether content. As a result, the uncertainty of this data is higher than for the other systems studied, as indicated by the bars on Figure 6.

It was assumed that the ether - carbon tetrachloride system would be a simple nonassociated system, and tracer diffusivities would be as predicted by equation (45). In fact, the shape of the $D_{A}^{*} n$ product curve for ether is more like what one would expect for a cross-associated system. Since the carbon tetrachloride is non-polar, and its chlorines do not form hydrogen bonds, this phenomenon is rather difficult to explain.

Being somewhat unfamiliar with the mechanics of charge-transfer complexing, the author hesitates to eliminate this possibility, but it does seem unlikely. Furthermore, over a period of time the bulk solution discolored, indicating a reaction of some sort proceeding. It is possible that the reaction (though not extensive and rather slow) indicates that some intermolecular interactions were occuring beyond the usual attractive and repulsive forces. Another alternative is that the assumption of a continuous medium breaks down here. This is supported by the fact that the $D_{B}^{*} n$ product of $\mathrm{CCl}_{4}$ changes only about $10 \%$ over the concentration range, while that for ether changes about $30 \%$. Again, this system warrants further study. Investigation
of other properties besides diffusion might also provide some insight.

## Mutual Diffusivities

As part of a study of the ternary system ether chloroform - carbon tetrachloride, Wirth [34] measured tracer diffusivities for both chloroform and carbon tetrachloride in the component binary chloroform - carbon tetrachloride. These measurements showed that, as expected, both chloroform and carbon tetrachloride are nonassociated in this system.

The Hartley-Crank Equation, equation (88), should describe mutual diffusion in this system. Wirth [34] measured mutual diffusivities in this system to experimentally verify this equation. He encountered some experimental difficulties, and scatter of data cast some doubt on his results. The best data he could obtain from his results, however, showed that the Hartley-Crank Equation is inadequate to describe this system. The shape of the Hartley-Crank curve is wrong when compared to Wirth's data. It was of interest then to attempt to duplicate Wirth's data, to determine whether the discrepency is truly in the equation, or whether it might be in the experimental results.

The author encountered less experimental difficulty in measuring this system. Experimental results are given in Appendix $E$, and shown (along with Wirth's
results) in Figure 7. As can be seen, the author's results agree quite well with the best results obtained by Wirth. The Hartley-Crank Equation is definitely inadequate for describing this system.

The discrepancy in this case is very hard to explain. The assumption of a continuous medium is probably a good one, since otherwise the effects would have shown up in the tracer diffusivities as well. The activity data reported in the literature used in calculating the thermodynamic correction factor appear to be quite good. The system is only slightly non-ideal, so the correction factor is not too large in any case. There is definitely no association, as can be seen from the $D_{i}^{*} \eta$ products. This phenomenon is puzzilng, and will probably require further investigation to provide an explanation.

The Hartley-Crank Equation also fails in another nonassociated system, 2-butanone - carbon tetrachloride. In this case, however, the predicted mutual diffusivity curve has the correct shape, differing only in the magnitude of the correction from ideality (see Figure 3). The author suggests that this may be due to a slight error in the activity data, from the experimental vaporliquid equilibrium measurements of Fowler and Norris [12].


Figure 7.--Mutual and Tracer Diffusivities in the System Chloroform (A) - Carbon Tetrachloride (B) at $25^{\circ} \mathrm{C}$.

The author measured mutual diffusivities in the system benzene - chloroform, to further test the HartleyCrank Equation. Experimental results are given in Appendix E, and shown in Figure 8. It was expected that this would be a simple nonassociated system. Although tracer diffusivities were not measured in this system, the self-diffusivities of both components are available. When the $D_{i}^{*} \eta$ product of the pure component is compared to the $D_{A B}$ n product when that component is extremely dilute, the results indicate that both components are nonassociated.

As can be seen in Figure 8, the Hartley-Crank Equation again fails for this system. The shape of the curve is qualitatively correct, but the correction is again too much. The error in tinis case is probably too large to attribute to inaccurate activity data. Further investigation in this system is warranted, particularly measurement of the tracer diffusivities over the entire concentration range, to make certain there is no association.

The author has also measured mutual diffusivities in the system diethyl ether - carbon tetrachloride. Activity data are not available for this system, therefore it cannot be used to test the Hartley-Crank Equation. Furthermore, experimental difficulties (previously described under Tracer Diffusivities) caused


Figure 8.--Mutual Diffusivities in the System Benzene (A) - Chloroform (B) at $25^{\circ} \mathrm{C}$.
considerable scatter in the data, especially near the center of the concentration range. Experimental results are given in Appendix $E$, and shown in Figure 6. As a measure of the uncertainty, the standard deviation of the data are listed in Table E-3, and are indicated by bars on Figure 6.

Mutual diffusivities were also measured for the system p-benzoquinone - benzene, up to the solubility limit. Results are given in Appendix $E$, and shown in Figure 5. Again, no activity data are available. The complex associations present in this system precluded testing the hydrodynamic equations in any case.

$$
\frac{\text { Error Analysis--Mutual and }}{\text { Tracer Diffusion }}
$$

Bidlack [27] and Kett [16] found that for the instrument used in this study, the experimental precision was $\pm 1 \%$ for volatile liquids such as used here. This was based upon several runs on aquaeous solutions of sucrose. These runs were compared to determinations made by Gosting [17] on the sucrose - water system, with agreement within $\pm 0.5 \%$. They therefore conservatively estimated the precision of the method using this interferometer as $\pm 1 \%$.

This author accepts the figure of $\pm 1 \%$ for the precision of the method and the instrument. Since the experimental procedure was not changed from earlier
procedures, the only remaining source of error would be that introduced by the experimenter. The author takes the agreement between his data and that collected by Wirth for the system chloroform - carbon tetrachloride as evidence that no systematic error has been introduced which would give consistently high or low experimental diffusivities. At several compositions in the systems chloroform carbon tetrachloride and benzene - chloroform mutual diffusivities were measured two or more times. At all these compositions, the values obtained agreed within $\pm 2 \%$, and in most cases within $\pm 1 \%$. The author takes this as evidence that random error introduced by the experimenter is within the precision specified for the method by Bidiack and Kett. The experimental precision for the studies in this work will therefore be taken as $\pm 1 \%$.

This figure does not apply to the system ether carbon tetrachloride, because of experimental difficulties felt to be inherent in this system, which have been discussed previously. In this system four or more. determinations were made at each composition, and averaged. The averages are reported, along with the standard deviation of the data, in Appendix E.

Wirth [34] has shown that the modified capillary technique used in this study has an experimental precision of $\pm 2 \%$. This was shown by comparing tracer diffusivities at extreme dilution with mutual diffusivities extrapolated to zero concentration (which must be
identical according to equations (91) and (92)), and by repeated runs for the same composition and comparing the reproducibility.

The author accepts this as the experimental precision of the method using this experimental apparatus. To determine the amount of error introduced by changing the experimenter, the author reproduced the self diffusivity of carbon tetrachloride (which wirth used for calibrating the cells), with a deviation of about $\pm l \%$. Furtrer evidence is the comparison between mutual and tracer experimental diffusivities at extreme dilution in the systems 2-butanone - carbon tetrachloride, and p-benzoquinone benzene. The author concludes that the experimental error introduced inco the method by changing the experimenter is within the experimental precision reported by Wirth. Tracer diffusivities reported here are therefore assumed to be accurate to within $\pm 2 \%$.

Again, this coes not apply to the system ether carbon tetrachloride. Experimental difficulties here make the results somewhat more uncertain. Determination of precision is rather difficult. The values at extreme dilution are within $\pm 5 \%$ of mutual diffusivities (which are themselves uncertain). The author estimates tracer diffusivities in this system are accurate within $\pm 5 \%$, and are so reported in Appendix E.

## Ternary Diffusivities

Ternary diffusivities were measured in the system acetone - benzene - chloroform, at an average composition of $x_{A}=x_{B}=x_{C}=.333$. Typical curves showing the change of the refractive index gradient throughout the run are given in Figure $D-1$. Values of $D_{2 m}$ and $D_{A}$ and the time correction factors are given in Appendix D. The linearity of equations (187) and (188), which are used to evaluate the reduced quantities, can be seen in Figures $D-2$ and $D-3$.

Plots of $D_{2 m}$ and $\frac{1}{\sqrt{D_{A}}}$ vs refractive index fractions for all three independent choices of components are given in Figures D-4 through D-9. (Ternary Diffusivities can be expressed in three different ways, depending on which components are considered, i.e., $D_{A A}, D_{A B}, D_{B A}, D_{B B}$ or $D_{A A}, D_{A C}, D_{C A}, D_{C C}$ or $D_{B B}, D_{B C}$, $D_{C B}, D_{C C}$. As will be pointed out later one set of diffusivities may be more advantageous in testing the hydrodynamic model and Onsager's Reciprocal Relation than the other two sets.) The slopes and intercepts of these lines were determined by a least-squares analysis, and are given in Appendix D. These slopes and intercepts were then used with the computer program given in Appendix $C$ to determine the diffusivities, which are given in Table 2 for the optimal choice of components for this system.

TABLE 2.--Predicted and Experimertal Ternary Diffusivities in the System Cnloroform (C) - Acetore (A) - Benzene (B) at $25^{\circ} \mathrm{C}$.

|  |  | Predíctec | Experimental | 95\% | Confidence |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\mathrm{D}_{\mathrm{CC}}$ | 3.674 | 3.70 |  | $\pm 1.62$ |
|  | $\mathrm{D}_{\mathrm{CA}}$ | - . 544 | I. 55 |  | $\pm 7.15$ |
|  | $\mathrm{D}_{\text {AC }}$ | -. 942 | -. 80 |  | $\pm .815$ |
|  | $\mathrm{D}_{\text {AA }}$ | 2.515 | 1.74 |  | $\pm 1.52$ |
|  | $\frac{i_{12}}{R_{m}^{m}}$ | -3.582 | 2.337 |  | $\pm 9.88$ |
|  | $\frac{L_{21}}{\bar{K} T}$ | -3.581 | -2.915 |  | $\pm 1.40$ |

From the tracer diffusivities available for this system it was difficuil to determine the association characteristics. As can be seen in Figure 9 and Figure 10, the scatter in the data is large enough jo mask any curvature aue to association. It is probabie that there may be some cross-association in the binary acetone chloroform, but tre otner two binaries are felt to be nonassociated.

In any event, the curvature due to association
is not likely to be extreme, since the end points vary by only $25 \%$ in the binary systems. It was trerefore assumed that the ternary system could be consicered a


Figure 9. $-D_{i}^{*} \eta$ vs Mole Fraction in the System Acetone Chloroform at $25^{\circ} \mathrm{C}$.


Figure 10. $-D_{1}^{*} \eta$ vs Mole Fraction in the System Acetone Benzene at $25^{\circ} \mathrm{C}$.
non-associated system, at least as an approximation. Equations (111) through (114) can then be used to predict the ternary diffusivities. These equations depend on the assumption that the molar volumes are constant. Since the composition differences within the diffusion cell were kept very small, the author feels that this assumption has been met experimentally.

Activity data for the three binaries were fit to Margules equations and then combined to give ternary isothermal activity data (as discussed on pages 18-21). The friction factors were taken to be the weighted averages of the friction factors at the end-points in the various binaries. Viscosity was measured with a Canon-Fenske viscometer. These quantities were then used with the computer program in Appendix $C$ to predict the ternary diffusivities, which are given in Table 2 along with the experimentally measured values.

The $95 \%$ confidence levels of the measured data, which will be determined in the next section are also listed with the experimental data. It can be seen that the predicted values of the diffusivities fall well within the $95 \%$ confidence limits. The author therefore feels that the experimental determinations support hydrodynamic theory. The predicted values of the phenomenological coefficients $L_{12}$ and $L_{21}$ are also within the $95 \%$ confidence limits of the measured values.

Within experimentai precision, this can be taken as empirical verification of the Onsager Reciprocal Relations.

The $95 \%$ conficience levels are quite large for this set of experimental data. This will be discussed in the next section in detail. It will be shown that the values of the cross-coefficients are extremeiy sensitive to the experimentally measurec intercepts, and that a very siight error in determining the intercepts can lead to an extreme error in the cross-coefficients, as well as a significant error in the main coefficient. From this sensitivity anaiysis, and a consideration of the experimental ciata, suggestions will be made for modifying this procedure. The author believes that through a thorough investigation of certain factors leading to experimental uncertainties in the present method, techniques can be deveioped which wili allow this method to give $95 \%$ confidence ievels within $20 \%$ or so for the cross-coefficierts. Tris would then give a rigorous test of the hydrodynamic model and the Onsager Reciprocal Relation.

## Error Araiysis--Terrary Diffusion

Since ternary diffusion has been studied in so few systems, and since the time involved in making a complete determination at any one composition is so long, determination of experimental precision by comparison to
published data is virtually impossible. The number of reference systems is also quite small. In the past, the usual procedure was simply to determine the experimental uncertainties in the measuremert of the various slopes and intercepts used in calculating the experimental ternary diffusivities.

Kett [23], for instance, reported $95 \%$ confidence levels of a percent or so, and concluded (implicitly) that his experimental diffusivities were of the same order of precision, a percent or so. In fact, this confidence level would lead to a much larger confidence level for the cross-diffusivities than he implied. Later evaluation of his data showed that the confidence levels were actually somewhat larger than he reported, which would lead to even more error in the diffusivities. The errors in the cross-coefficient resulting from a $1 \%$ error in the value of the intercepts can be as large as $200 \%$. This is because the calculation of the cross-diffusivities involves subtraction of two rather large numbers to obtain a small one, so that uncertainties in the larger numbers are greatly magnified. Furthermore, errors in the main coefficients as large as $20 \%$ can result from a $1 \%$ error in the intercepts. It would seem quite worthwhile then to look at the sensitivity coefficients of the ternary diffusivities, wich relate the change in a calculated diffusivity to a cnange in a measured parameter.

If a dependent variable is a function of several independent variables, the functional form usually involves several arbitrary parameters. The values of the parameters for a given physical system are usually determined by measuring the dependent variable at several values of the independent variables. The experimental "best" values of the parameters are then assumed to be those which give the least-square error when fitted to the data of the experimental measurements.

If the equation is of the form

$$
\begin{equation*}
y=f\left(a_{1} a_{2} \ldots a_{n} ; x_{1} x_{2} \ldots x_{m}\right) \tag{201}
\end{equation*}
$$

where the $a_{i}$ 's are the parameters and the $X_{i}$ 's are the independent variables, then the sensitivity coefficients are defined by

$$
y_{a_{i}}=\left(\frac{\partial f}{\partial a_{i}}\right)_{a_{j}}, x_{K} \begin{align*}
1, j & =1,2, \ldots n \\
K & =1,2, \ldots m
\end{align*}
$$

The sensitivity coefficients measure the charge in the dependent variable with a change in the parameters, and are themselves functions of the independent variables.

Ternary diffusivities can be treated as dependent variables whose values depend upon independent variables (component mole fractions, temperature and pressure) and the parameter $I_{A}, I_{2 m}, S_{A}$, and $S_{2 m}$. The functional form of this dependence is given by equations (196)
through (200). Since the functionai form is rather complex, anaiytical evaluation of the sensitivity coefficients is rather iifficult. They can easily be determined numerically with the aid of a computer, however. A small change is mace in the value of one of the slopes or intercepts, keeping the others constant, and the change in tie difflusivities is noted. This has been done for the system measured in this study. If the sensitivity coeifizcient is multiplied by the value of tre artitrary parameter, a reduced sensitivity coefficient may be ciefired

$$
\begin{equation*}
s_{a_{i}}^{y} \equiv a_{i} y_{a_{i}}=a_{i}\left(\frac{\partial f}{\hat{o} a_{i}}\right)_{a_{i}}, x_{K} \tag{203}
\end{equation*}
$$

This gives the charge in the diffusivities for a onepercent change in the parameter. This is useful, since if the percentage lincertainty in experimentaily measured parameters is known, the uncertainty in the diffusivities car be cetermined. These same arguments also hold for the prenomerological coefficients used to test the Onsager Reciprocal Reiations.

If tine experimental ciata are to be used to test a proposed model, it wouid be best if the sensitivity coefficients with respect to the measured parameters were as small as possible. In the case of ternary diffusivities, trree indeperdent choices of components may
be made. The sensitivity of the main and crossdiffusivities will not necessarily be the same for each choice. It would be best then to choose trose components for which the sensitivities are icwest. It can be seen from Table 3 that in tre system acetone (A) - benzene (B) - chloroform (C), the sensitivity coefficients are generally lower when the set of diffusivities $D_{C C}, D_{C A}$, $D_{A C}$ and $D_{A A}$ is chosen to describe diffusion. This is the basis for the choice made in preparing Table 2. If the $95 \%$ conficience levels for the parameters are known, then the $95 \%$ confiderce levels for the diffusivities car be approximated from the sensitivity coefficier.us. By assuming that the sensitivity coefficients are constant for different values of the parameters, upper ard lower limits for the diffusivities may be calcuiated by

$$
\begin{equation*}
95 \% \text { iimits of } D_{a, j}= \pm t \sqrt{\sum_{i} y_{a_{i}}^{2} s_{e}^{2}\left(a_{i}\right)} \tag{204}
\end{equation*}
$$

Confidence limits on the parameters $I_{A}, I_{2 m}, S_{A}$ ard $S_{2 m}$ may be determined irom the variances of the parameter (which are determined during the least-squares analyses) by means of a statistical t-test:

$$
\begin{equation*}
95 \% \text {, iimits on } a_{i}= \pm t \sqrt{S_{e}^{2}\left(a_{i}\right)} \tag{205}
\end{equation*}
$$

TABLE 3.--Reduced Sensitivity Coefficients, $S_{a_{i}}^{y}$ in the System Acetone (A) - Benzene (B) - Chloroform (C) for all Choiced of Coordinates.

| $y^{a_{1}}$ | $\mathrm{I}_{2 \mathrm{~m}}$ | $\mathrm{I}_{\mathrm{A}}$ | $S_{2 m}$ | $S_{\text {A }}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{D}_{\text {AA }}$ | +. 12 | +.18 | +. 03 | -. 01 |  |
| $\mathrm{D}_{\text {AB }}$ | -. 09 | -. 10 | +. 03 | +. 03 | $\times 10^{-5}$ |
| $\mathrm{D}_{\text {BA }}$ | +. 12 | +. 24 | 0.0 | 0.0 |  |
| $\mathrm{D}_{\mathrm{BB}}$ | -. 09 | -. 13 | +. 03 | +. 04 |  |
| $\mathrm{D}_{\text {AA }}$ | -. 19 | +. 34 | 0.0 | +. 01 |  |
| $\mathrm{D}_{\text {AC }}$ | -. 08 | +. 12 | -. 02 | +. 02 | $\times 10^{-5}$ |
| $\mathrm{D}_{\mathrm{CA}}$ | +. 38 | -. 78 | 0.0 | -. 02 |  |
| $\mathrm{D}_{\mathrm{CC}}$ | +. 16 | -. 27 | $+.03$ | -. 05 |  |
| $\mathrm{D}_{\mathrm{BB}}$ | -. 21 | -. 36 | +. 03 | -. 04 |  |
| $D_{B C}$ | -. 11 | -. 23 | 0.0 | 0.0 | $x 10^{-5}$ |
| $\mathrm{D}_{\text {CB }}$ | $+.42$ | +. 65 | -. 08 | +. 07 |  |
| $\mathrm{D}_{\mathrm{CC}}$ | +. 24 | +. 42 | 0.0 | 0.0 |  |

where $t$ stands for the statistical parameter from the t-test, and $S_{e}^{2}\left(a_{i}\right)$ is the statistical estimate of variance of the parameter $a_{1}$, as determined from the least-squares analysis. The $95 \%$ confidence limits on
the diffusivities were determined by these formulae, and are given with the values of the diffusivities in Table 2.

To provide a rigorous test of hydrodynamic theory and of the Onsager Reciprocal Relations, it would be necessary to reduce the $95 \%$ confidence levels on the main coefficients to about $10 \%$ or so of the values of those coefficients, and the $95 \%$ confidence levels on the cross-coefficients to at least $50 \%$ or so of the values of the cross-coefficients. Since the sensitivity coefficients for the intercepts are so high, it would be necessary to reduce the variances of those intercepts to within a few tenths of a percent. It would also be necessary to reduce the value of $t$ from the t-test. Since $t$ decreases with the number of degrees of freedom (i.e. experimental measurements made) at a given confidence level, a statistically large number of measurements should be made for every set of diffusivities desired.

Since $t$ approaches a constant value as the number of measurements increases, it becomes apparent that the sample variance must also be reduced. Concisely, this means that more precise measurements must be made, as well as more of them.

This means that the spread in the data seen in the plots of $D_{2 m}$ and $\sqrt{D_{A}}$ vs $\alpha$ must be reduced. The
reasons for tre spread in tre aata are difficult to determine. One probably impontant cause of tinis spread is the quality of the initial boundary. It can be seen from Tabie 4 that the true inさtial time determined from equation (187) and the $D_{2 m}$ vs $t_{m}$ curves is not the same as that determired from equation (188) and tie $\frac{1}{\sqrt{D_{A}}}$ vs $t_{m}$ durves. If tree initial boundary nad been a true step crarge, and tre timer started the instant that fiow from the ceil was stopped, the true initial time would rave ieen $t_{m}=0$. It was assumed that the initial bounciary is suich as would have deen sormed by diffusion from a step-craree for a short period of time. Inis would rave resulted in a true initial boundary in which the reiractive index grai̇ent curve was Gaussian, ard the true initial time would rave been the same whether determined from ecuatior (187) or (188).

It can be seen that the measured reiractive index gradient curves in some rurs are obviously not Gaussian. The curves are slizitiy skewed to one side or the otner. Ternary diffusior from a sten cnange courdary aiways gives skew curves, except at two times during the run when they are true Gaussian curves. However, in order for equations (187) and (188) to apply, the irue initial distributions must be Gaussian. (Note that this is the true initial distribution, not the experimental boundary.) The author believes that tre error introduced by a

TABLE 4.--True Initial Times for Ternary Runs, as Predicted by Equations (187) and (188).

| Run Number | $t_{0}$, sec. <br> eq. (187) | $t_{0,}$, sec. <br> eq. (188) |
| :---: | :---: | :---: |
| 60 | -20 | -43.8 |
| 62 | -23 | -37.1 |
| 63 | -90 | -55.2 |
| 65 | -56 | -49.2 |
| 66 | -13 | -7.8 |
| 68 | -52 | -65.7 |
| 69 | -74 | -72.8 |
| 70 | -58 | -47.9 |

non-step-change boundary can be related mathematically to the difference in the initial times determined from the two curves, and possibly one measurement of the refractive index gradient during the run. He was not able to derive such a relation, however.

It certainly seems reasonable, however, to use the difference between the time corrections for the two curves as a criterion for rejecting a run. If the two initial times varied by more than a certain amount, the run would be rejected. Determination of what difference should lead to rejection will probably take considerable study and experimentation.

It mignt also be wortrwhile to investigate other possible methous of forming tree original boundary. If this boundary couij be improved, tre better approximation to a step-charge would undoubtedly lead to better results, and less spread in the $D_{2 m}$ and $\frac{1}{\sqrt{D_{A}}}$ vs $\alpha$ curves.

In summary, tice experimental results for the system acetone - benzene - chioroform suppor the predictions of nycrociynamic theory, within the experimental precision of tre present metnod. Due to the extreme sensitiviこy oi the cross-coefficients, the metnod presently is not capabie of providing a rigorous test of tine Onsager र̄eciprocal Reiation, altiough it is as valid as many previously published verifications. The autnor beiieves that tiee method can be improved enough, through furtiner irvestigation, to give a rigorous test of the Cnsager Reciprocal Relation.
Hydrodynamic theory has been used to derive equations describing the effects of composition on mutual and tracer diffusion in certain associated and nonassociated liquid systems. These equations have been tested by experimental measurements of binary mutual, ternary mutual and tracer diffusivities.
Tracer diffusivities have generally verified the predictions of hydrodynamic theory quite well (ether carbon tetrachloride being an exception). As the percentage of a component which is associated into complexes increases, the tracer diffusivity - viscosity product decreases, and vice-versa.
Although many systems have been found for which hydrodynamic theory does apply quite well, three nonassociated systems are presented here which seem to be exceptions. In non-associated systems, the HartleyCrank equation should describe mutual diffusion. In benzene - chloroform and 2-butanone - carbon tetrachloride, the Hartley-Crank equation qualtitatively predicts the shape of the mutual diffusivity curve, but fails quantitatively. In chloroform - carbon tetrachloride, it fails qualitatively as well. These fallures may well
be due to inaccurate vapor - liquid equilibrium data, however. In the ternary system acetone - benzene chloroform (which is here considered to be nonassociated) hydrodynamic theory predicts the ternary diffusivities, within experimental precision. Unfortunately, experimental uncertainty is rather large, and this may not be considered a rigorous test of the theory. Within experimental precision, hydrodynamic theory also predicts the validity of the Onsager Reciprocal Relation.

The author feels that this experimental uncertainty is due primarily to the difficulty of forming a good boundary within tree diffusion cell, which is critical in measuring ternary diffusivities. Suggestions are given for future investigations to reduce the experimental error and provide a more rigorous test of hydrodynamic theory.

## FUTURE WORK

The author suggests that future work in liquid non-electrolyte diffusion is needed in four particular areas: (a) improvement of experimental metnods and techniques, so that diffusivities may be measured more precisely, reliably, and hopefully more easily than is now possible; (b) more systems need to be studied to support conclusions which have been previously arrived at on the basis of a smail number of studies; (c) those systems which seem to offer contradictions to hydrodynamic theory need to be studied more carefully; (d) further theoretical work needs to be done, possibly extending the principles usea here to continious association, or simultaneous self-association ana crossassociation for example.

Experimental probiems which lead to low precision in measurements were aiscussed considerably under the Ternary Diffusion error anaiysis. The author feels that a thorough study of the effects oi different boundary conditions, different methods of forming the initial boundary, and possibly a new mathematical treatment for obtaining diffusivities from refractive index gradient curves would be a self-contained and quite worthwhile research program.

Besides this work on ternary diffusivities, however, the author feels that much improvement could still be made in the techniques used for measuring binary mutual and tracer diffusivities. For example, a technique which would totally eliminate convection in the capillary, perhaps by using a porous capillary instead of an open one, would be well worth developing. Or an interferometer which used a laser light source and a better set of lenses, or for which a better boundary could be established, would be worth investigating.

Although the systems so far studied have generally supported hydrodynamic theory, there is not enough evidence to conclusively say that it is correct. This is a general problem in liquid diffusion--there simply has not been enough raw data generated in the past to thoroughly test any new theory proposed except for a comparatively small number of cases. For instance, to the author's knowledge, there has never been published a complete study of any ternary system (mutual and tracer isotherms of all three component binaries, ternary mutual diffusion isotherms, and ternary tracer diffusion, to say nothing of the effect of temperature on all of these).

Systems such as 2-butanone - carbon tetrachloride, and chloroform - carbon tetrachloride, which appear to contradict hydrodynamic theory (or at least present ambiguities to be resolved) should be studied more

```
carefully. It is quite possiole that studies of
phenomena otner than difficion would be very usefui
here. It has been recently proposed that the chlorine
atoms of carbon tetraciioride engage in a limited form
Of nyärogen bonäing with alcohols, and therefore they
might cause some very weak bonding effects in these
systems which lead to tre breakdown of the Hartley-
Crank equation. Tris seems uniikely, but pernaps
spectroscopic stuaies airected at this particular
phenomenon mignt provide some useful information.
    Theoretical work based upon hydrociynamic theory
colila be directed at finaing a simpiification of equation
(80) and its generalization wnich could be applied to
tracer diffusivity in a system with extensive association,
such as ethanol - rexane, or aniline - benzene. Or
equations could be developed for application to systems
like aniline - toluol wrere there is both se=f-
association ard cross-association. Equations for con-
tinuous self-association as applied to tracer difiusion
could be relatec to similar equations for mutual
diffusion. This field is again open for mucr investigation.
```

APPENDICES

APPENDIX A

## APPENDIX A

## PROCEDURE FOR ZミACER DIFRUSION <br> EXPERINENT

```
    Figure A-l is a schematic iiagram of the ciffusion
capiliary. Specific details regaraing dimensions,
materials, etc. are giver by Wirtr [34].
    Tracer solutions of the desired compositions were
prepared gravimetrically to within \pm.O0l mole fraction,
by means of a Christian ana Becker Torbal torsicn
balarce. Builk soiutions were prepared to within 土.005
mole fraction on a large analytical balance. Tre tracer
solutions were degassed just beiore an experiment for 15
minutes at about 400}\textrm{C}\mathrm{ to remove air from the solution.*
Six capillaries were filled by the following procedure:
    1. The foil ci̇sc, consisting of maileable nickei
    0.00l inches thick, was rolled flat to insure
    a good seai to the tefion capillary, and placeu
    in the screw cap. The capillary was inserted
    Air bubbles coming out of solution during the run
and drifting up to the giass disc were one of the principie
experimental difficulties. They would mix the contents of
the capillary as they drifted lipwards, and probably
changed the resistance constant in the boundary
condition at the capillary end.
```



Figure A-I.--Schematic Diagram of the Modified Capillary Cell.
into tine screw cap, and tightened with a pair of pliers to insure a good seal to the foil iisc.
2. The capiiiary was immersed to within one half Erch in the buik solution, and the buik container was piaced in a thermostat to equiliorate at $25^{\circ} \mathrm{C}$ for ore hour.
3. Tine capiiiaries were then filled with degassed tracer solution by a . 50 cc tuberchiin syringe, with a ig ga needie cut to the same lengtin as the capillary. Great care was taken to avoid trappirg air oubbies in the capillary. The syringe was emptied of air bubbies by inverting and ejecting some of tine solution. The syringe was then inserted in the capillary, and witharawn siowiy, discharging solution as it was removed. A puade of tracer solution was left covering the top of the capillary.
4. The giass frit was then filled by dipping it in the bulk solution, and allowing the excess to drain away. The frit was then carefully placed on top of the capillary, in such a way that no air buibles were trapped, and with the puade of tracer solution covering the frit.
5. The frit holder was then placed over the end oi the capillary. By this time the excess tracer mentioned above had generally evaporated. To
prevent the irit from drying out ard trapping air, the cepression in the frit hoider was filled with tracer solution. The entire assembly was tren placed in the bulik solution, washing away the excess tracer solution in the process.

Aiter all six capillaries had been filled, the top was placed on the blilk container, ieavirg the vent open until the vapor pressure coula arive out the excess air. The bulk container was then placed in the thermostat, and the time recorded. The filling process took about half an hour for ail six capillaries.

After three to five ciays, deperding upon the diffusivity, the buik solution was removed from the thermostat. The six capillaries were emptiec into nylon courting vials as foliows:

1. 5 cc of scintillation fluid was placed in the bottom of the counting viai, and a syringe was filled with io cc of scintillation fluid for step number (4) below.
2. The capiliary was removed from the oulk solution, and the frit nolder carefilly removed without disturbing the frit. The excess solution on tine frit was allowed to evaporate.
3. The capillary was inverted into the counting vial, which washed the frit from the end. The
end oi the capillary was kept beneath thesurface to avoid fiash evaporation of tracersolution.4. The conicai depression in the screw cap wasfilled with iluid from the syringe mentionedin step (i). The foil disc was then puncturedby the syringe reedie, and tracer solutionflushed from the capiliary with scintillationfluiaj. When 2 or 3 cc remained in the syringe,the capillary was removed from the vial, andwashed off with the remaining scintillationfluid, so inat ail the tracer solution was inthe vial.5. The counting vial was capped, and Identifiedby the capiilary number. It was shaken gentlyto thoroughly mix the contents, ana the glassfrit was removed. The glass frit was washedin acetone to remove scintillation materiai inpreparation for the next experiment.This procedure was repeated for all six capillaries,and the time recorded. The emptying process took aboutThe capillaries and screw caps were then cleanedwith acetone, dried, and prepared as before. Initialcounts were then prepared as follows:20 minutes.
4. A courting vial was prepared as in step (i) of the emptying procedure.
5. The capiiiary was iilled with tracer solution as in step (3) of the filiing procedure, except that the puciale was kept as small as possible, ideally covering only the opening of the
capiliary.*
6. The excess tracer solution was allowed to evaporate lintil levei with the surface of the capiliary. The capillary was then quickiy inverted into tree counting vial, and flushed as in the previous emptying procedure. The vial was then identified by the capiliary number as an initial count.

* 

This proceaure had to be modified slightly for solutions containing a higr concentration of ether, since these wetted the surface of the capillary extensively. The solutions would not evaporate level with the surface, but would form a cepression into the capillary before ail the solution had evaporated from the surface.

The capillaries were filled with a solution for which wetting was rot a problem, and emptied in tre lisual manner. They were then refilled with the same solution, and allowed to evaporate to the same estimated depth as the probiem solutions. Emptying these and comparing the count rates from the two sets gives an estimate of the ratio of the true initial count to the measured counts for the problem solutions.

Since the depth of the depression could only be estimatea by eye, this procedure introauces some error, but it is at least a random error, due to the estimation, rather than a systematic error due to incorrect initial counts. The diffusivities for these solutions are reported with an uncertainty of $\pm 5 \%$, instead of the usual $\pm 2 \%$.

The equipmert was then cieaned and prepared for the next run.

The initiai and finai counts were then counted using a Packard Tri-Carb scintillation counter. Since some of the chemicals used, notably carbon tetrachloride and p-benzoquinone, acted as quenching agents, the gain of the scintillation counter was reset before every counting session to give optimum count rates.

When the data from the count rates had been analyzed, if the spread of the five closest values of the tracer diffusivity (as calcuiated for the six capillaries) was greater than $5 \%$ i.e. $\pm 2.5 \%$ from the mean value, the experiment was iiscarcied. This was to eliminate those runs in which there may have been convective mixing witnin the capillaries. Since the magnitude of such effects deperds upon when during the experiment they occurred, convection wouid cause a spread in the values of the diffusivity as weil as an increase in the apparent value. It was feit that this screening procedure wouid eliminate those runs in which convection occurred.

APPENDIX 3

## APPENDIX B

## PROCEDUK̃E FOR MUTUAZ DIFGUSION EXPERIMENT

Figure B-i is a scnematic diagram of tre MachZennder interferometer used for measuring the binary and ternary mutual diffusivities. Figure B-2 is a diagram of the diffusion cell. Specific details of construction are given by Eidiack [4], as are instructions for alignment and adiusiment of mirrors to produce the proper fringe pattern.<br>Two solutions witin siigntly different compositions were prepared gravimetrically using a Christian and Becker Torbal torsion balance. The difference in composition of the two solutions was generally .01 mole fraction for binary systems, but could be varied to give tie proper number of fringes, depending upon the refractive inaexes of the two components. The cell was filled according to the following procedure:<br>1. The plunger was placed in the filling syringe, and all vaives were ciosed, except valve 2.<br>2. Approximately 40 cc of the derser solution were placed in reservoir $B$, and the top of the


Figure B-I.--Schematic Diagram of Mach-Zehnder Interferometer.


Figure B-2.--Diagram of Diffusion Cell.
reservoir was covered with aluminum foil to retard evaporation.
3. Valve 5 was opened, and solution allowed to fill the celi to fust beiow the level of the siit. The filiing syringe was ther used to draw fluid back and forth tirough valve 5 to remove air butbies trapped near the valve stem. Solution was then allowed to fill the cell to about one half inch above the slit. Valve 5 was tien ciosed.
4. Valve 4 was then opered. Solution was forced through valve 4 by the filling syringe, until tre soiution ievel ir the cell was just above the slit. Care was taken rot to force any air from the cell into the siphon line. Valve 4 was then closed, ana valve 5 openea. Solution was allowed to fiow into the cell until the level was again one half inch above the slit.
5. Step (4) was repeated until fluid flowed from the siphor Iine, to Ensure that the line was completely filled up to the tee in the line.
6. The process of steps (4) and (5) was then repeated for valve 3 , to fill the other side of the siphon line.
7. Valve 1 was opened, and the plunger removed from the filling syringe. At this point, the siphon was checked by slightly opering valves 3 and 4 consecutively to make sure fluid would flow freely from the cell. Valves 3 and 4 were left closed after checking the siphon.
8. Valve 2 was closed, and the filling syringe filled with the less dense solution. The plunger was then repiaced.
9. Valve 2 was then opened very slightly, and solution was allowed to flow very slowly down the wall of the cell. The flow rate was kept very slow until the level was an inch or so above the slit, to avoid turbulence and mixing at the boundary. After this time, valve 2 was opened a little to allow solution to flow in more freely. To stabilize the boundary, valves 3 and 4 were opened so that solution flowed through the siphon at a rate of one drop every two or tinree seconds.
10. When solution began to appear in reservoir $A$, valves 3 and 4 were again closed. Solution was forced back and forth through valve 1 to remove any air bubbles from the valve stem. With liquid above the bottom of reservoir $A$, valve 2 was then closed.

1i. The less ciense solution was then added to reservoir A lintil the level was even with that in reservoir B. Reservoir A was then covered with aluminum foil to retard evaporation. The diffusion celi was now ready to be placea in the water bath for the experiment.

Before the cell was placed in the water bath, tre fringe pattern was checked to make sure the fringes were straight, vertical and in focus. It was uslially found that they had arifted slightly away from the vertical since the last experiment. This could almost always be corrected by making a fine adjustmert of mirror 3.

The cell was then placed in the water bath. Vaives 1 and 5 were openec several tunns each. Valve three was then opened until the flow rate from the siphon was approximately one arop every six seconds. Valve 4 was then opened until the flow rate was one drop every three secoris. It was important that the flow rate be the same from each side oi the ceil maintain a flat boundary. It was also important that the flow rate into the top and bottom of the cell be the same so that the initial distribution of concentration gradients woliid be symmetric about the boundary.

It usually took about 20 to 30 minutes for the
 boundary to form. Wher the coundary rad formed, valves

3, 4, ará 5 were ciosed̀ anà the timer started. A series of seven pictures, it intervals of 2 minutes were taken. (In the faster aiffusing systems, the intervals were somewhat shorter.) in some cases, valves 3,4 and 5 were again opened, arotier bouiadary formed, and a second set of pictures taken.

The photographic plate, a Kodak Type N plate, was Geveloped by the following procedure:

1. The plaze was deveioped for 5 minuzes in Kodak =-iy Ïigh Contrast Deveioper, with intermittent agitation.
2. Tre deveiopmeri was inen stopped $k$ y a oneminute soak, witin continual agitation, in tap water.
3. The image was tinen fixed by a 5-minute soak, with intermittent agitation, in Koaak Rapiaíix.
4. Tine plate was tinen removed from the fixxer, and washed for about one minute uncier running water, ard tien ailowed to dry for at least 2 hours before measuremert.

The photographic plates were extremely sensivive to light, and had to be nanciled in absolute darkness fo safe lignt) trrougiout the entire procedure, until ine fixing step had been completed.

A new plate was then inserted into the film holder, making sure that the emulsion side of the plate faced outward. This was important because the thickness of the
plate was enoligh to throw the image out of iocus, and perhaps chañe the magnification factor of the camera. The developer anc fixer were replaced after every ten runs, in order to maintain a consistently hión image quality in develoomert.

APPENDIX C

## APPENDIX C

## COMPUTER PROGRAMS FOR DAGA ANALYSIS

The foliowing comouter proeram uses measlired values of the slopes ard irtercepts to calculate experimental values of tre ternary aiffusivities. The program Language is FORRRAN IV, with specific deck structure forl the IBM 1800 computer of the College of Ergineering, Michigan State University. Ore constant, $R^{2} / R^{1}$, must be specified within tre program at the designated point. Other data (tre slopes and intercepts) is read by the computer.

```
// U\notDB
// FDR FDIEF
        *I\varnothingCS (CARD, 1443 PRINDER)
        *EXTENDED PRECISIDN
        *N\notNPRZCESS PR\notOCRAM
        *\mathscr{NE WZRD INMEGEFS}
        *LIST SDURCE DRZUEAAM
```

            REAL I2M, IA, I2M, iA
                CDMMDN X
    $\bar{i} \operatorname{READ}(2,10)$ I2M, IA, S2M, SA
10 FめRMAT (4E 10.5$)$
$\Sigma A=I A+S A$
L2M $=I 2 M+S 2 M$
IF (I2M) 3, 4, 3
3 WRITE (3, 20) I2M, IA, S2M, SA, L2M, IA
20 FØRMAT (IH1, 6 E 15.5)
C
C THE VALUE $\not \subset \mathrm{R}=\mathrm{R} 2 / \mathrm{RI}$ MUST BE SPECIFIED
C AT THIS PDINT
C
e.g. $\quad R=.42999$


```
// FDR SVND
    *EXMENDED PREOZSZZN゙
    *めNE W义ミD INMEOERS
    *NDNPROCESS PRZORAM
    *LIST SXUURCE PEDGFAM
            SUSRDUMINE SVND (A, \Xi, C, X, P, DP,N,NI)
            DIMENS=DN A(4), S(4), C(4)
                B(1) = A(1)
                DZ I I = 2, N
                E(I) = A(I) + X * B (I-こ)
                C(I) = S(I)
                DD 2 I = 2, NI
                C(I) = B(エ) + X * C(こージ
                P = E(NI)
                OP=O(N)
                RENURN
                    END
// XEQ TDIFF
*CC END
```

The Foilowine program preaícts ternary えiffusivities in a ron－associatec system Irom friction coefsicients， molar volumes，viscosities and the Marguies constants of the binary systems．Trese constants misi be read as in data．The program ianguage is fORTRAN IV，with specific deck structure for tre＝EM 1800 computer of tree College of Engineering，Michizan State üniversity．
／／JZ3
／／FDR PRED
＊IDCS（CARD， 1443 PRINTER）
＊IIST SDURCE PEZGRAM
＊NQNPROCESS PRZGRAM
＊EXTENDED PRECISIDR
＊ØNE WØRD INTEGERS
real livgi，ingz，iNA，iNB READ（2，200）A12，A21，A13，A31，A23，A32，C
200 FXEMAT（7F 10．5） READ（2，20I）ETA

```
200 FDRMAG (FIO.5)
    IF (ETA) 1, 2, 1
l
202
BEAD (2, 202)VI, V2, V3
READ (2, 202) SIGl, SIG2, SIG3
FEAD (2, 202) XA, X3, XC
FZFMAT (3FIO.j)
SIGZ REPEESENQS KR/(FRIONZZN CDEFF)
ØF CXMPDNENG I ØR A
```

```
\(V \not Z L D=X A * C 1+X B * V 2+X C * V 3\)
```

$V \not Z L D=X A * C 1+X B * V 2+X C * V 3$
$C A=X A / V E D$
$C A=X A / V E D$
$C 3=X E / V \neq D$
$C 3=X E / V \neq D$
$C C=X C / V Q D$
$C C=X C / V Q D$
ENGI $=2 * X A * X E *\left(A 2 I-X A * A 21-X B^{*} A 12\right)+X E * X B * A 12$
ENGI $=2 * X A * X E *\left(A 2 I-X A * A 21-X B^{*} A 12\right)+X E * X B * A 12$
$+2^{*} X A * X C^{*}\left(A 3 I-X A^{*} A 3 I-X C^{* A I 3}\right)+X C * X C * A I 3$
$+2^{*} X A * X C^{*}\left(A 3 I-X A^{*} A 3 I-X C^{* A I 3}\right)+X C * X C * A I 3$
$+\left(X \Xi^{*} X C-2 * X A * X \Xi^{*} X C\right) *(A 21+A 13+A 32-C)$
$+\left(X \Xi^{*} X C-2 * X A * X \Xi^{*} X C\right) *(A 21+A 13+A 32-C)$
XAP = XA
XZP = XB
XCP = XC
LNG2 = 2.*XB*XA*(AII2-XI*A12-XA*A2I) + XA*XA*A2I
+2.**B*XC*(A32-XB*A32-XC*A23) + XC*XC*A23
+(XA*XC-2.*XA*XE*XC)*(A21 + AI3 + A 32 - C)
LNA = INGI + AL\mathscr{G (XA)}
LNB = LNG2 + ADDG (XB)
VCNEN = VOLD - (XA + .003) * VI - XE * V2
CMZIS = VCNEW/V3
TMZLS = XA + XB + .003 + CNOLS
XA = (XA + .003)/RMXLS
XB = XS/MVDLS
XC=CMZIS/FMDIS
LNGI = 2.*XA*XE*(A21-XA*A2I-XB*A12) + XB*XS*AI2
I
2 + 2.**A*XC*(A31-XA*A31-XC*A13) + XC*XC*A13
+(XB*XC-2.*XA*XB*XC)* (A21 + A13 + A32 - C)
ING2 = 2.**3*XA*(A12-XB*A12-XA*A21) + XA*XA*A21
+2.*XS*XC*(A32-XB*A32-XC*A23) + XC*XC*A23
+(XA*XC - 2.*XA*XB*XC)* (A21 + A13 + A32 - C)
DADCA = (LNGI + ALOG(XA) - LNA) * VOID/.003
DBDCA = (LNG2 + ALOG(XB) - LNB) * VOLD/.003
VCNEW=V\varnothingLD - XAP * V1 - (XBP + .003) * V2
CMOLS = VCNEW/V3
MMDLS = XAP + XBP + CMDLS + .003
XA = XAP/MMDLS
SB}=(X3P+.003)/mMDL
XC = CNZDS/TMDES

```
```

LNGI = 2.*XA*XS* (A21-XA*A21-XS*A12) + XE*XB*A12
+2.*YA*XC*(A3I-XA*A3I-XC*A13) + XC*XC*A13
+(XE*XC-2.*XA*XB*XC)* (A21+A1S+A32-C)
LNG2 = 2.*XS*XA*(AI2-XB*AI2-XA+A2I) + XA*XA*A2I
LNG2 = 2.*XB*XA*(AI2-XJ*AI2-XA+A2I) + XA*XA*A2I
\NG2 = 2.*XS*XA*(AI2-XZ*AI2-XA+A2I) + XA*XA**
\NG2 = 2.*XB*XA*(AI2-XB*AI2-XA+A2I) + XA*XA**
\NG2 = 2.*XB*XA*(AI2-XB*AI2-XA+A2I) + XA*XA**
WRITE (3,100)
WRITE (3,101) DADCA, DBDCA, DADCB, DBDCE (,)
WRITE (3,101) DADCA, DBDCA, DADCB, DBDCE (1, DADCA DEDCA DADCB, DBDCE !)
XA = XAP
XB + XBP
XC + XCP
DAA = DADCA/EFA*CA*(SIGI*(1.-V1*SIGI) + SIG3*V3*CA)
1 + DBDCA/ETA*CA*CE*(V3*SIG3-V2*SIG2)
DAB = DADCS/EMA*CA*(SIGI*(1.-VI*SIGI) + SIG3*V3*CA)
1 + DBDCB/ERA*CA*CE*(V3*SIG3-V2*SIG2)
DBA = DADCA/\XiRA*CA*CB*(V3*SIG3-VI*SIGI)
l + DEDCA/EFA*CE*(S=G2*(1.-V2*CB) + SIG3*V3*CB)
DBB = DEDCB/ETA*CA*CD*(V3*SIG3-VI*SIGI)
I + DBDCB/ETA*CE*(SIG2*(1.-V2*CS) + SIG3*V3*CB)
WRITE (3,105)
WEITE (3,106) DAA
WRITE (3,107) DAB
WRITE (3,100) こЗA
WRITE (3,109) DBB
105
106
107
108
FORMAT (I\# , // 'TGE PREDICMED DIFFUSIVITIES ARE ',/)
FORMAT (IE:, DDAA = , F 25.5)
I
I
l
100
2
1 + DBDCE/ERA*CA*CE*(V3*STG3-V2*SIG2)
FORMAT (IFI, 'DAS = , F 15.5)
FORVAT (IF , 'DBA = , F 15.5)
109
FORMAT (IH, 'DBB = , F 15.5)
GO TO I
CADI EXIT
END
// XEQ PRED

* CCEND

```
```

APPENZIX D

```

\section*{APPENDIX D}

TERNARY INTERMEDEATE DATA

TABLE D-i.--Data az ecuimozar concentrations in the system Cnloroform(A) - Acetone(B) - Benzene (C)
\[
\begin{aligned}
& C_{A}=4.097 \text { moies } / \mathrm{Lit} . \\
& C_{E}=4.097 \mathrm{moles} / \text { Lit. } \\
& C_{C}=4.097 \text { moles/int. } \\
& \bar{V}_{A}=.0807 \text { Lit/mole } \\
& \bar{V}_{E}=.0740 \text { Lit/mole } \\
& \bar{V}_{C}=.0894 \mathrm{Lit} / \mathrm{mole} \\
& \frac{\overline{F I}}{\sigma_{\mathrm{A}}}=1.290 \times 10^{-7} \text { dynes } \\
& \frac{5 \pi}{\sigma_{B}}=1.493 \times 10^{-7} \text { dynes } \\
& \frac{R T}{\sigma_{C}}=1.307 \times 10^{-7} \text { dynes } \\
& n=.487 \mathrm{cp} \\
& \mathrm{a}=.4317 \mathrm{RT} \\
& \mathrm{~b}=.0701 \mathrm{RT} \\
& \mathrm{c}=.0978 \mathrm{RT} \\
& d=.3260 \mathrm{RT}
\end{aligned}
\]


Figure D-1.--Typical Refractive Index Gradient Curves
(taken from run \(\# 65\) ).



Figure D-3.--Linearity of Equation (188).





Figure D-7.-- \(\frac{1}{\sqrt{D_{A}}}\) vs \(\alpha_{C}\) in the System Chloroform (C) - Acetone
\[
(A) \text { - Benzene (B). }
\]

(

\[
\Pi
\]

TASLE D－2．－－Siopes and Intercents from Figures D－4
trrough D－9．

In the Acetore（A）－Eerzene（Z）－Chioroform（C）system Erom Figures コー4 and コー5：
\[
\begin{aligned}
& I_{2 m}=1.782 \times 10^{-5} \\
& I_{2 m}=I .018 \times 20^{-5} \\
& I_{A}=225.5 \\
& S_{A}=-37.0
\end{aligned}
\]

In the C：ioroiorm（C）－Acetone（A）－Eenzene（C）from Figures D－б ana Dー7：
\[
\begin{aligned}
& I_{2 m}=2.406 \times 10^{-5} \\
& S_{2 m}=-.569 \times 10^{-5} \\
& I_{A}=199.9 \\
& S_{A}=19.6
\end{aligned}
\]

Ir．tree Eerzere（シ）－CnIcroform（C）－Acetone（A）system from Figures D－8 and D－9：
\[
\begin{aligned}
& I_{2 m}=2.856 \times 20^{-5} \\
& S_{2 m}=-.470 \times 10^{-5} \\
& I_{A}=184.5 \\
& S_{A}=16.4
\end{aligned}
\]

APPENDIX E

Table E-l.--Experimental Binary Mutual Diffusivities in the System Chloroform(A) - Carbon Tetrachloride(B) at \(25^{\circ} \mathrm{C}\).
\begin{tabular}{cc}
\hline\(x_{A}\) & \(D_{A B} \times 10^{5}, \mathrm{~cm}^{2} / \mathrm{sec}\) \\
\hline 0.234 & 1.557 \\
0.24 & 1.572 \\
0.590 & 1.680 \\
0.774 & 1.757 \\
0.744 & 1.779 \\
0.946 & 1.976 \\
0.977 & 2.007 \\
\hline
\end{tabular}

TABLE E-2.--Experimentai Binary Mutual Diffusivities in the System Benzene(A) - Chloroform(B) at \(25^{\circ} \mathrm{C}\).
\begin{tabular}{lc}
\hline\(x_{A}\) & \(D_{A B} \times 10^{5}, \mathrm{~cm}^{2} / \mathrm{sec}\) \\
\hline 0.005 & 2.345 \\
0.005 & 2.359 \\
0.207 & 2.414 \\
0.207 & 2.443 \\
0.345 & 2.495 \\
0.345 & 2.419 \\
0.494 & 2.396 \\
0.785 & 2.344 \\
0.785 & 2.263 \\
0.995 & \\
\hline
\end{tabular}

TABLE E-3.--Experimental Binary Mutual Diffusivities in the System Ether(A) - Carbon Tetrachloride(B) at \(25^{\circ} \mathrm{C}\).
\(\mathrm{x}_{\mathrm{A}}\)
\(D_{A B} \times 10^{5}, \mathrm{~cm}^{2} / \mathrm{sec}\)
\begin{tabular}{ll}
0.005 & \(1.50 \pm .05\) \\
0.200 & \(1.95 \pm \pm .00\) \\
0.400 & \(2.38 \pm .14\) \\
0.600 & \(2.99 \pm .20\) \\
0.800 & \(3.76 \pm .34\) \\
0.995 & \(4.59 \pm .07\)
\end{tabular}

TA BIE E-4.--Experimental Binary Mutual Diffusivities in the System p-benzoquinone (A) - Benzene (B) at \(25^{\circ} \mathrm{C}\).
\(\times A\)
\(D_{A B} \times 10^{5}, \mathrm{~cm}^{2} / \mathrm{sec}\)
\begin{tabular}{ll}
0.0041 & 2.20 \\
0.0057 & 2.16 \\
0.0132 & 2.09 \\
0.0239 & 1.98 \\
0.0266 & 1.95 \\
0.0315 & 1.96 \\
0.0434 & 1.94
\end{tabular}

TABLE E-5.--Experimental Tracer Diffusivities in the Sy \(s t\) em 2-Butanone (A) - Carbon Tetrachloride (B) at \(25^{\circ} \mathrm{C}\).
\(x_{A}\)
\(D_{A}^{*} \times 10^{5}, \mathrm{~cm}^{2} / \mathrm{sec}\)
\(D_{B}^{*} \times 10^{5}, \mathrm{~cm}^{2} / \mathrm{sec}\)
0.000
0.037
0.478
0.678
0.925
0.982
0.995
1.611
2.260
2.720
3.183
3.300
. 30
2.973

TABTE E-6.--Experimental Tracer Diffusivities in the System p-benzoquinone(A) - Benzene(B) at \(25^{\circ} \mathrm{C}\).
\begin{tabular}{ccc}
\hline\(x_{A}\) & \(D_{A}^{*} \times 10^{5}, \mathrm{~cm}^{2} / \mathrm{sec}\) & \(D_{B}^{*} \times 10^{5}, \mathrm{~cm}^{2} / \mathrm{sec}\) \\
\hline 0.0000 & 2.32 & 2.137 \\
0.0010 & 2.11 & \\
0.0103 & 2.11 & \\
0.0464 & & \\
\hline
\end{tabular}

TABLE E-7.--Experimental Tracer Diffusivities in the System Ether (A) - Carbon Tetrachloride(B) at \(25^{\circ} \mathrm{C}\).
\begin{tabular}{ccc}
\hline \hline\(x_{A}\) & \(D_{A}^{*} \times 10^{5}, \mathrm{~cm}^{2} / \mathrm{sec}\) & \(D_{B}^{*} \times 10^{5}, \mathrm{~cm}^{2} / \mathrm{sec}\) \\
\hline 0.000 & & 2.32 \\
0.024 & \(1.629 \pm .082\) & \\
0.024 & \(2.674 \pm \pm .084\) & \\
0.332 & \(3.796 \pm \pm .132\) & \\
0.530 & \(5.383 \pm .269\) & \(4.395 \pm .220\) \\
0.850 & 7.91 & \(\pm .396\)
\end{tabular}

> TABLE E-8.--Experimental Density and Viscosity in the System p-benzoquinone(A) - Benzene(B) at \(25^{\circ} \mathrm{C}\).
\begin{tabular}{ccc}
\hline \hline \(\mathrm{x}_{\mathrm{A}}\) & density, \(\mathrm{g} / \mathrm{ml}\) & viscosity, cp \\
\hline 0.0011 & 0.8738 & 0.600 \\
0.0103 & 0.8767 & 0.608 \\
0.0283 & 0.8826 & 0.617 \\
0.0387 & 0.8861 & 0.629 \\
0.0464 & 0.8896 & 0.631 \\
\hline
\end{tabular}

TABLE E-9.--Experimertal Density and Viscosity in the System Ether(A) - Carbon Tetrachloride(B) at \(25^{\circ} \mathrm{C}\).
\begin{tabular}{ccc}
\hline \hline \(\mathrm{x}_{\mathrm{A}}\) & density, \(\mathrm{g} / \mathrm{ml}\) & viscosity, cp \\
\hline 0.000 & 1.5856 & 0.913 \\
0.1851 & 1.4177 & 0.677 \\
0.3119 & 1.3047 & 0.445 \\
0.4808 & 1.1536 & 0.583 \\
1.000 & 0.7074 & 0.225
\end{tabular}

TABLE E-10.--Experimental Density and Viscosity in the System Acetone(A) - Benzene (B) - Chloroform(C) at \(25^{\circ} \mathrm{C}\).
\begin{tabular}{ccccc}
\hline \(\mathrm{x}_{\mathrm{A}}\) & \(\mathrm{x}_{\mathrm{B}}\) & \(\mathrm{x}_{\mathrm{C}}\) & density, \(\mathrm{g} / \mathrm{ml}\) & viscosity, cp \\
\hline 0.328 & 0.339 & 0.333 & 1.0457 & 0.4869 \\
0.339 & 0.332 & 0.329 & 1.0427 & 0.4870 \\
\hline
\end{tabular}

\section*{APPENDIX F}


\section*{THERMODYNAMIC DATA}
\begin{tabular}{|c|c|c|c|c|}
\hline TABLE & \[
\begin{gathered}
\text { Acti } \\
\text { at }
\end{gathered}
\] & ta for A rom Timm & \[
\begin{aligned}
& \text { ne } \\
& \text { as }
\end{aligned}
\] & zene (2) \\
\hline \(\mathrm{X}_{2}\) & \[
\begin{aligned}
& \ln \gamma_{2}, \\
& \exp .
\end{aligned}
\] & \[
\begin{aligned}
& \ln \gamma_{2}, \\
& \text { eq. }(24)
\end{aligned}
\] & \[
\begin{aligned}
& \ln \gamma_{1}, \\
& \exp .
\end{aligned}
\] & \[
\begin{aligned}
& \ln \gamma_{1}, \\
& \text { eq. }(25)
\end{aligned}
\] \\
\hline 0.1251 & . 5002 & . 4827 & . 0011 & . 0060 \\
\hline 0.2500 & . 3937 & . 3896 & . 0265 & . 0278 \\
\hline 0.3652 & . 3122 & . 3022 & . 0662 & . 0669 \\
\hline 0.5550 & . 1829 & . 1672 & . 1802 & . 1835 \\
\hline 0.7150 & . 0898 & . 0750 & .3400 & . 3452 \\
\hline 0.8249 & . 0659 & . 0300 & . 4846 & . 4966 \\
\hline 0.8862 & . 0387 & . 0131 & . 5793 & . 5971 \\
\hline 0.9500 & . 0301 & . 0026 & . 7169 & . 7148 \\
\hline \multicolumn{2}{|l|}{\multirow[t]{2}{*}{Margules constants:}} & \multicolumn{3}{|l|}{\(A_{12}=.8169\)} \\
\hline & & \(=.568\) & & \\
\hline
\end{tabular}

TABLE F-2.--Activity Data for Acetone (1) - Chloroform (3) at \(25^{\circ} \mathrm{C}\) (from Hildebrand and Scott [21]).
\begin{tabular}{ccccc}
\hline \(\mathrm{X}_{3}\) & \begin{tabular}{c}
\(\ln \gamma_{3}\), \\
exp.
\end{tabular} & \begin{tabular}{c}
\(\ln \gamma_{3,}\), \\
eq. (24)
\end{tabular} & \begin{tabular}{c}
\(\ln \gamma_{1}\), \\
exp.
\end{tabular} & \begin{tabular}{c}
\(\ln \gamma_{1}\), \\
eq. (25)
\end{tabular} \\
\hline .0600 & -.6733 & -.6771 & -.0101 & -.0019 \\
.1840 & -.5276 & -.5502 & -.0202 & -.0198 \\
.2630 & -.4308 & -.4700 & -.0513 & -.0431 \\
.3610 & -.3711 & -.3723 & -.0943 & -.0873 \\
.4240 & -.3285 & -.3126 & -.1278 & -.1259 \\
.5080 & -.2614 & -.2379 & -.1985 & -.1913 \\
.5810 & -.1985 & -.1788 & -.2877 & -.2621 \\
.6620 & -.1287 & -.1208 & -.3857 & -.3574 \\
.8020 & -.0513 & -.0441 & -.5798 & -.5682 \\
.9180 & -.0101 & -.0079 & -.7765 & -.7917 \\
\hline
\end{tabular}

Margules constants: \(A_{13}=-.9791\)
\(A_{31}=-.7372\)
\begin{tabular}{|c|c|c|c|c|}
\hline \(\mathrm{x}_{2}\) & \[
\begin{aligned}
& \ln \gamma_{2} \\
& \exp .
\end{aligned}
\] & \[
\begin{aligned}
& \ln \gamma_{2} \\
& \text { eq. }(24)
\end{aligned}
\] & \[
\begin{aligned}
& \ln \gamma_{3} \\
& \exp .
\end{aligned}
\] & \[
\begin{aligned}
& \ln \gamma_{3} \\
& \text { eq. }(25)
\end{aligned}
\] \\
\hline 0.1340 & -. 3439 & -. 2248 & +. 0119 & -. 0066 \\
\hline 0.2600 & -. 2837 & -. 1548 & +. 0109 & -. 0237 \\
\hline 0.3180 & -. 1767 & -. 1278 & -. 0131 & -. 0347 \\
\hline 0.6400 & -. 0598 & -. 0299 & -. 0845 & -. 1225 \\
\hline 0.7160 & -. 0284 & -. 0178 & -. 1301 & -. 1480 \\
\hline 0.8660 & -. 0202 & -. 0036 & -. 1532 & -. 2012 \\
\hline
\end{tabular}

Margules Constants: \(A_{23}=-.3180\)
\[
A_{32}=-.2500
\]

TABLE F-4.--Constants for use in equations (20) through (24) for the system Acetone (1) - Benzene (2) - Chloroform (3) at \(25^{\circ} \mathrm{C}\).
\begin{tabular}{ll}
\(A_{12}\) & \(=.8169\) \\
\(A_{21}\) & \(=.5685\) \\
\(A_{13}\) & \(=-.9791\) \\
\(A_{31}\) & \(=-.7372\) \\
\(A_{23}\) & \(=-.3180\) \\
\(A_{32}\) & \(=-.2500\) \\
\(C\) & \(=0.0\)
\end{tabular}

APPENDIX G

\section*{APPENDIX G}

\section*{NOMENCLATURE}

Capitals
A interaction perameter
C concentration, interaction parameter
D diffusivity
D Onsager diffusivity
\(D_{2 m}\) reduced second moment
\(D_{A}\) reduced heigrit-area ratio
E energy of vaporization
F force
G Gibbs free energy
H entralpy of mixing
\(I_{2 m} \quad\) intercept of second-moment curve at \(\alpha=0\).
\(I_{A} \quad\) intercept of height-area ratio curve at \(\alpha=0\).
\(J \quad\) flux, fringe number
K equilibrium constant
L phenomenological coefficient; length of capillary
\(L_{2 m} \quad\) intercept of second-moment curve at \(\alpha=1.0\)
\(L_{A} \quad\) intercept of height-area ratio curve at \(\alpha=1.0\)
M magnification factor of camera
\(\mathrm{N} \quad\) number of species in solution
P, Q simplifying constants
\begin{tabular}{ll}
\(R\) & \begin{tabular}{l} 
gas law constant; refractive index constant; \\
Simplifying constant
\end{tabular} \\
\(S\) & entropy \\
\(S_{2 m}\) & slope of second-moment curve \\
\(S_{A}\) & slope of neight-area ratio curve \\
\(S^{2}\) & statistical variance \\
\(S^{y}\) & reduced sensitivity coefficient \\
\(T\) & temperature \\
\(V\) & volume \\
\(W\) & simplifying constant \\
\(Y\) & thermodynamic parameter
\end{tabular}

Small
a activity; arbitrary parameter; Miller coefficient
b,c,d Miller coefficients
f arbitrary function
\(j\) fringe number
m moment
\(n \quad\) number of moles; refractive index
t time; statistical t-test parameter
v velocity
\(x\) mole fraction
\(z\) distance

\section*{Greek Capital}
\(\Delta \quad\) difference
\(\Sigma\) summation

Greek smal1
\begin{tabular}{|c|c|}
\hline \(\alpha\) & proportionality constant; refractive-index fraction; simplifying constant \\
\hline \(\beta\) & simplifying constant \\
\hline \(\beta_{n}\) & eigen value \\
\hline \(\gamma\) & activity coefficient; simpiifying constant \\
\hline \(\delta\) & solubility parameter; Kroneker delta; simplifying constant \\
\hline \(\eta\) & viscosity \\
\hline \(\theta\) & time \\
\hline \(\lambda\) & proportiorality constant \\
\hline \(\lambda_{n}\) & eigen value \\
\hline \(\mu\) & chemical potential \\
\hline \(\pi\) & constant \(3.14159 \ldots\) \\
\hline \(\sigma\) & constant in friction coeficient \\
\hline \(\phi\) & volume fraction \\
\hline
\end{tabular}

\section*{Subscripts}
a refers to activity-defined equilibrium constant
c refers to laboratory-fixed coordinates
\(m\) refers to medium-fixed coordinates
\(\gamma\) refers to activity-coefficient-defined equilibrium constant

A,B,C refers to chemical components \(A, B, C\)
\(1, j\) refers to species i,j
1,2,3 refers to species \(1,2,3\)
d refers to driving force
\(r\) refers to resisting Sorce
\begin{tabular}{ll} 
s & refers to spinere \\
\(V\) & refers to volume-fixed coordinates \\
\(j\) & refers to iringe number \(j\) \\
\(z\) & refers to distance \(z\) \\
0 & refers to initial vaiue \\
ave & refers to average vaiue \\
\(\max\) & refers to maximum value
\end{tabular}

Superscripts
\begin{tabular}{ll}
\(m\) & refers to medium-fixed reference plane \\
\(V\) & refers to volume-fixed reference plane \\
0 & refers to standard-state \\
* & refers to tagged species \\
, & refers to related quantity \\
- & molar property \\
,
\end{tabular}
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[^0]:    Figure 4.--Tracer Diffusivity - Viscosity Products for the System 2-Butanone - Carbon Tetrachloride at $25^{\circ} \mathrm{C}$.

