TRACER AND MUTUAL DIFFUSION IN SEVERAL ISOTHERMAL NON - IDEAL LIQUID NON - ELECTROLYTE SYSTEMS

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THESIS



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C. MICHAEL KELLY

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ABSTRACT

TRACER AND MUTUAL DIFFUSION IN SEVERAL ISOTHERMAL NON-IDEAL LIQUID NON-ELECTROLYTE SYSTEMS

By

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 failure are presented. A study has been made of the method currently employed for measuring ternary diffusivities. Weaknesses in the current method 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.

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By

C. Michael Kelly

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INTRODUCTION

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 efforts 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 upon verifying the theory of Onsager based upon the principles of irreversible thermodynamics, particularly the Onsager reciprocal 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 the other upon modifications of the hydrodynamic flow model of Stokes [29]. This work will follow the hydrodynamic approach.

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 individual 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. Hartley 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

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.

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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

Hydrodynamic 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:

$$F_{id} = -\nabla \mu_i \tag{1}$$

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

$$F_{\rm sr} = - \, \delta \pi r_{\rm s} \eta v_{\rm sm} \tag{2}$$

where r_s is the radius of the sphere, η is the viscosity of the medium, and v_{sm} is the velocity of the sphere with respect to the medium, and the negative

sign is because 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

$$-\frac{d\mu_{i}}{dz} = 6\pi r_{i}\eta v_{im}$$
(3)

where $\nabla \mu_i$ has been replaced by $\frac{d\mu_i}{dz}$, denoting onedimensional diffusion.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

$$J_{i}^{m} = v_{im} C_{i} = - \frac{C_{i}}{6\pi r_{i} \eta} \frac{d\mu_{i}}{dz}$$
(4)

where J_i^{m} is the flux of species i with respect to the medium. However, most molecules are essentially non-spherical, 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 'friction coefficient' of species i. This yields

$$J_{i}^{m} = -\frac{C_{i}}{\sigma_{i}\eta} \frac{d\mu_{i}}{dz}$$
(5)

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

$$\mu_{i} = \mu_{i}^{\circ} + RT \ln a_{i}$$
 (6)

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

$$J_{i}^{m} = -\frac{C_{i}}{\sigma_{i}^{n}} \begin{bmatrix} \frac{\partial Lna_{i}}{\partial C_{i}} \end{bmatrix}_{T,P} \begin{bmatrix} \frac{\partial C_{i}}{\partial z} \end{bmatrix}_{T,P}$$
(7)

This is the expression for the flux of species i due solely to the random molecular motion of i molecules, with respect to a coordinate 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 techniques). The flux which is measured in most experiments is the flux of component i 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

$$\sum_{i=1}^{N} \overline{V}_{i} J_{i}^{m} + V_{mc} = V_{Vc}$$
(8)

where v_{mc} is the velocity of the medium with respect to laboratory-fixed coordinates, and v_{Vc} 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

> N S V_iJ^m i=1

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_{mc} .

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, v_{Vc} . The total volume flux (which is a velocity, and is represented by the left 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:

$$\mathbf{v}_{\mathrm{mc}} = -\sum_{i=1}^{N} \overline{V}_{i} J_{i}^{\mathrm{m}} + \mathbf{v}_{\mathrm{Vc}}$$
(9)

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

The measurable flux J_i^{V} is given by

$$J_{i}^{V} = J_{i}^{m} + C_{i} (v_{mc} - v_{Vc})$$
 (10)

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

$$J_{i}^{V} = -\frac{C_{i}}{\sigma_{i}\eta} \frac{\partial \mu_{i}}{\partial z} + \frac{C_{i}}{\eta} \frac{\Sigma}{j=1} \frac{C_{j}\overline{V}_{j}}{\sigma_{i}} \frac{\partial \mu_{j}}{\partial z}$$
(11)

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 ,..., B_2 , B_3 , B_4 ,..., AB, A_2B , AB_2 , and so forth, depending upon 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 constant, such as $A + B \leftrightarrow AB$. Because of K_{AB}

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 one 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

$$\Delta \overline{S}_{i} = -R \ln X_{i}$$
 (12)

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

$$\Delta \overline{H}_{i} = \overline{V}_{i} \phi_{j}^{2} (\delta_{j} - \delta_{i})^{2}$$
(13)

where ϕ_i is the volume fraction of component i (neglecting expansion on mixing) and δ_i is defined by

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

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

$$\operatorname{Ln} \gamma_{i} = \frac{\Delta \overline{H}_{i}}{RT} = \overline{V}_{i} \phi_{j}^{2} (\delta_{j} - \delta_{i})^{2}$$
(14)

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

$$\operatorname{Ln} \gamma_{i} = \frac{\overline{\nabla}_{i}}{\operatorname{RT}} \left(\delta_{i} - \overline{\delta} \right)^{2} \qquad i = 1, \dots 3 \qquad (15)$$

where

$$\overline{\delta} = \sum_{i=1}^{3} \delta_i \phi_i$$

with δ_i and ϕ_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 equilibrium 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 fit.

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.

THEORY

Solution Thermodynamics--Nonassociated Solutions

The Gibbs free energy of a system of N components is given by

$$G = \sum_{i=1}^{N} n_i G_i^{\circ} + \sum_{i=1}^{N} n_i \operatorname{RT} \operatorname{Ln} X_i + \Delta G \sum_{i=1}^{N} n_i \quad (16)$$

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 ΔG 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

$$\mu_{i} = \frac{\partial G}{\partial n_{i}} = \mu_{i}^{O} + RT Ln \gamma_{i} X_{i}$$
 (17)

where μ_i° is a function of T and P only. Carrying out the indicated differentiation on equation (16), and equating to equation (17) gives

$$Ln \gamma_{i} = \frac{1}{RT} \frac{\partial}{\partial n_{i}} \left[\Delta G \sum_{i=1}^{N} n_{i} \right]$$
(18)

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

$$\frac{\Delta G}{RT} = X_1 X_2^2 a_{12} + X_1 X_3^2 a_{13} + X_2 X_3^2 a_{23} + X_1^2 X_2^2 3a_{112} + X_1 X_2^2 3a_{122} + X_1^2 X_3^2 3a_{113} (19) + X_1 X_3^2 3a_{113} + X_2^2 X_3^2 3a_{223} + X_2 X_3^2 3a_{233} + X_1 X_2 X_3^2 6a_{123}$$

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:

Ln
$$\gamma_1 = 2X_1X_2 [A_{21} - X_1A_{21} - X_2A_{12}] + X_2^2 A_{12}$$

+ $2X_1X_3 [A_{31} - X_1A_{31} - X_3A_{13}] + X_3^2 A_{13}$ (20)
+ $(X_2X_3 - 2X_1X_2X_3) [A_{21} + A_{13} + A_{32} - C]$

$$\begin{array}{l} \text{Ln } \gamma_{2} = 2X_{2}X_{1} \left[A_{12} - X_{2}A_{12} - X_{1}A_{21}\right] + X_{1}^{2} A_{21} \\ + 2X_{2}X_{3} \left[A_{32} - X_{2}A_{32} - X_{3}A_{23}\right] + X_{3}^{2} A_{23} \end{array} \tag{21} \\ + \left(X_{1}X_{3} - 2X_{1}X_{2}X_{3}\right) \left[A_{21} + A_{13} + A_{32} - C\right] \\ \text{Ln } \gamma_{3} = 2X_{3}X_{1} \left[A_{13} - X_{3}A_{13} - X_{1}A_{31}\right] + X_{1}^{2} A_{31} \\ + 2X_{2}X_{3} \left[A_{13} - X_{3}A_{13} - X_{1}A_{31}\right] + X_{1}^{2} A_{31} \end{aligned} \tag{22} \\ + \left(X_{1}X_{2} - 2X_{1}X_{2}X_{3}\right) \left[A_{21} + A_{13} + A_{32} - C\right] \end{array}$$

where the constants are defined by

$$2a_{12} + 3a_{122} = A_{12}$$

$$2a_{12} + 3a_{112} = A_{21}$$

$$2a_{13} + 3a_{133} = A_{13}$$

$$2a_{13} + 3a_{113} = A_{31}$$

$$2a_{23} + 3a_{233} = A_{23}$$

$$2a_{23} + 3a_{223} = A_{32}$$

$$3a_{112} + 3a_{133} + 3a_{223} - 6a_{123} = C$$

$$(23)$$

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

$$Ln \gamma_{1} = 2X_{1}X_{2}[A_{21} - X_{1}A_{21} - X_{2}A_{12}] + X_{2}^{2}A_{12}$$
(24)

$$Ln \gamma_2 = 2X_2 X_1 [A_{12} - X_2 A_{12} - X_1 A_{21}] + X_1^2 A_{21}$$
(25)

Wohl [35] gives detailed derivations of equations formally similar, and algebraically identical to equations (20) through (25).

If isothermal ternary activity data are available equations (20), (21) and (22) can be fit to the data by a least-squares technique, with seven adjustable parameters. This is an unreasonably large number, but some may be specified by other means. If the ternary data are available, then binary data for each of the three pairs of components are almost sure to be available. The binary data may be fit by a least-squares technique, 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 isothermal 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} ,... are given in Tables F-1 through F-4 of Appendix F.

Solution Thermodynamics--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{V} and δ for 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

$A + B \leftrightarrow AB$

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:

$$K_{a} = \frac{a_{12}}{a_{1}a_{2}}$$
(27)

Defining K and ${\rm K}_{\gamma}$ by

$$K = \frac{X_{12}}{X_1 X_2}$$
(28)

$$K_{\gamma} = \frac{\gamma_{12}}{\gamma_{1}\gamma_{2}}$$
(29)

we see that

$$K_{a} = KK_{\gamma}$$
(30)

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

$$X_{A}Y_{A} = X_{l}Y_{l}$$
(31)

Hence, the activity coefficient of component A is given by

$$\gamma_{A} = \frac{X_{1}}{X_{A}} \gamma_{1}$$
(32)

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

For a regular solution, equation (15) holds:

$$Ln \gamma_{l} = \frac{\overline{V}_{l}}{RT} (\delta_{l} - \overline{\delta})^{2}$$
(15)

where δ_1 and $\overline{\delta}$ are defined by

$$\delta_{i} = \left[\frac{\Xi_{1}^{v}}{\overline{v}_{i}}\right]^{\frac{1}{2}}$$
(33)

$$\overline{\delta} = \sum_{i=1}^{3} \phi_i \delta_i \qquad (34)$$

$$\phi_{i} = \frac{X_{i}\overline{V}_{i}}{X_{1}\overline{V}_{1} + X_{2}\overline{V}_{2} + X_{12}\overline{V}_{12}}$$
(35)

Similar equations give the values of $Ln\gamma_2$ and $Ln\gamma_{12}$.

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

$$C_1 = C_A - C_{12}$$

 $C_2 = C_B - C_{12}$
(36)

Let us make the following approximations:

a)
$$\overline{V}_{12} = \overline{V}_1 + \overline{V}_2$$
 (37)

b)
$$E_{12}^{\mathbf{v}} = E_1^{\mathbf{v}} + E_2^{\mathbf{v}}$$
 (38)

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 ΔE for the equilibrium reaction is the same in both states. Note that ΔH 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 ln γ_A in terms of measurable quantities $(\overline{V}$'s, E^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°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--Nonassociated Systems

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

$$J_{i}^{V} * = -D_{i}^{*} \frac{dC_{i}^{*}}{dz}$$
(39)

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

$$J_{i}^{V} * = J_{i}^{m} * = -\frac{C_{i}^{*}}{\sigma_{i} \eta} \frac{d\mu_{i}}{dz}$$
(40)

For tracer diffusion equation (17) becomes

$$\mu_{i}^{*} = \mu_{i}^{0} + RT \ln \gamma_{i}^{*} X_{i}^{*}$$
(41)

Applying the chain rule gives the derivative of μ_i^* :

$$\frac{d\mu_{i}}{dz} = \frac{d\mu_{i}}{dc_{i}} \frac{dC_{i}}{dz} = RT \left[\frac{d \ln \gamma_{i}}{dc_{i}} + \frac{d \ln x_{i}}{dc_{i}} \right] \frac{d C_{i}}{dz} (42)$$

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

$$\frac{d \ln \gamma_{i}}{dC_{i}}^{*} = 0$$

$$\frac{d \ln \chi_{i}}{d \ln C_{i}}^{*} = 1$$
(43)

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

$$J_{i}^{V} = - \frac{RT}{\sigma_{i}\eta} \frac{dC_{i}}{dz}$$
(44)

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

$$D_{i}^{*} = \frac{RT}{\sigma_{i}\eta}$$
 (45)

Carman [5] suggested that the combination of physical properties on the right hand 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 AB dimer. Denoting the species present as 1, 2 and 12, the total concentration of tagged component A is given by

$$c_{A}^{*} = c_{1}^{*} + c_{12}^{*}$$
 (46)

The flux of A molecules in tracer diffusion is

$$J_{A}^{V} * = - D_{A}^{*} \frac{dC_{A}^{*}}{dz} = J_{1}^{V} * + J_{12}^{V} *$$
(47)

Substituting equation (40) for the fluxes gives

$$J_{A}^{V} = - \frac{RT}{\eta} \left[\frac{1}{\sigma_{1}} \frac{dC_{1}}{dz} + \frac{1}{\sigma_{12}} \frac{dC_{12}}{dz} \right]$$
(48)

Differentiating equation (46) with respect to C_A^* gives

$$\frac{\partial C_1}{\partial C_A^*} + \frac{\partial C_{12}}{\partial C_A^*} = 1$$
(49)

Substituting into equation (48) gives

$$J_{A}^{V} * = - \frac{RT}{\sigma_{1} \eta} \left[1 - \frac{\partial C_{2}^{*}}{\partial C_{A}^{*}}\right] \frac{dC_{A}^{*}}{dz} - \frac{RT}{\sigma_{12} \eta} \frac{\partial C_{12}^{*}}{\partial C_{A}^{*}} \frac{dC_{A}^{*}}{dz}$$
(50)

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:

$$\frac{c_{12}}{c_{12}} = \frac{c_1}{c_1} = \frac{c_A}{c_A}$$
(51)

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,

$$\frac{\partial C_{12}}{\partial C_A}^* = \frac{C_{12}}{C_A}$$
(52)

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

$$x_{12}^{\circ} = \frac{c_{12}}{c_A + c_B}$$
 (53)

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

$$J_{A}^{V} * = - \frac{RT}{\eta} \left[\frac{1}{\sigma_{1}} + \left(\frac{1}{\sigma_{12}} - \frac{1}{\sigma_{1}} \right) \frac{X_{12}^{\circ}}{X_{A}} \right] \frac{\partial C_{A}^{*}}{\partial z} \quad (54)$$

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

$$D_{A}^{*} = \frac{RT}{n} \left[\frac{1}{\sigma_{2}} + \left(\frac{1}{\sigma_{12}} - \frac{1}{\sigma_{1}} \right) \frac{X_{12}^{\circ}}{X_{A}} \right]$$
(55)

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

$$D_{\rm B}^{*} = \frac{\rm RT}{\rm n} \left[\frac{1}{\sigma_2} + \left(\frac{1}{\sigma_{12}} - \frac{1}{\sigma_2} \right) \frac{{\rm X}_{12}^{\circ}}{{\rm X}_{\rm B}} \right]$$
(56)

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 1, 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

A + B ↔ AB

 $A + C \leftrightarrow AC$

Let the true species present be designated 1, 2, 3, 12 and 13 representing A, B, C monomers, AB and AC 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:

$$J_{A}^{V} * = - D_{A}^{*} \frac{\partial C_{A}^{*}}{\partial z} = J_{1}^{V} * + J_{12}^{V} * + J_{13}^{V} *$$
(57)

$$J_{B}^{V} * = - D_{B}^{*} \frac{\partial C_{B}^{*}}{\partial z} = J_{2}^{V} * + J_{12}^{V} *$$
(58)

$$J_{C}^{V} * = - D_{C}^{*} \frac{\partial C_{C}^{*}}{\partial z} = J_{B}^{V} * + J_{13}^{V} *$$
(59)

$$c_{A}^{*} - c_{1}^{*} + c_{12}^{*} + c_{13}^{*}$$
 (60)

$$c_{B}^{*} = c_{2}^{*} + c_{12}^{*}$$
 (61)

$$c_{c}^{*} = c_{3}^{*} + c_{13}^{*}$$
 (62)

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):

$$D_{B}^{*} = \frac{RT}{\eta} \left[\frac{1}{\sigma_{2}} + \left(\frac{1}{\sigma_{12}} - \frac{1}{\sigma_{2}} \right) \frac{X_{12}^{o}}{X_{B}} \right]$$
(63)

$$D_{C}^{*} = \frac{RT}{\eta} \left[\frac{1}{\sigma_{3}} + \left(\frac{1}{\sigma_{13}} - \frac{1}{\sigma_{3}} \right) \frac{X_{13}}{X_{C}} \right]$$
(64)

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

$$J_{A}^{V} = - \left[\frac{RT}{\sigma_{1} \eta} \frac{\partial C_{1}}{\partial z} + \frac{RT}{\sigma_{12} \eta} \frac{\partial C_{12}}{\partial z} + \frac{RT}{\sigma_{13} \eta} \frac{\partial C_{13}}{\partial z}\right]$$
(65)

Differentiating equation (60) with respect to C_A^* and substituting into equation (65) gives

$$J_{A}^{V} = -\frac{RT}{\eta} \left[\frac{1}{\sigma_{1}} \left(1 - \frac{\partial C_{12}^{*}}{\partial C_{A}^{*}} - \frac{\partial C_{13}^{*}}{\partial C_{A}^{*}} \right) + \frac{1}{\sigma_{12}} \frac{\partial C_{12}^{*}}{\partial C_{A}^{*}} + \frac{1}{\sigma_{13}} \frac{\partial C_{13}^{*}}{\partial C_{A}^{*}} \right] - \frac{C_{A}^{*}}{z} (66)$$

As before, the derivatives $\frac{\partial C_{12}}{\partial C_A}^*$ and $\frac{\partial C_{13}}{\partial C_A}^*$ can be written

in terms of pseudo-mole fractions $X_{12}^{0} = \frac{C_{12}}{C_A + C_B + C_C}$ and

$$X_{13}^{\circ} = \frac{C_{13}}{C_A + C_B + C_C} \text{ to give}$$

$$J_{A}^{V} * = -\frac{RT}{n} \left[\frac{1}{\sigma_{1}} + \left(\frac{1}{\sigma_{12}} - \frac{1}{\sigma_{1}} \right) \frac{X_{12}^{\circ}}{X_{A}} + \left(\frac{1}{\sigma_{13}} - \frac{1}{\sigma_{1}} \right) \frac{X_{13}^{\circ}}{X_{A}} \right] \frac{\delta C_{A}^{*}}{\delta z}$$

(67)

From this it can easily be seen that

$$D_{A}^{*} = \frac{RT}{\eta} \left[\frac{1}{\sigma_{1}} + \left(\frac{1}{\sigma_{12}} - \frac{1}{\sigma_{1}} \right) \frac{X_{12}}{X_{A}} + \left(\frac{1}{\sigma_{13}} - \frac{1}{\sigma_{1}} \right) \frac{X_{13}}{X_{A}} \right] \quad (68)$$

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

$$D_{A}^{*} = \frac{RT}{n} \left[\frac{1}{\sigma_{1}} + \sum_{i=2}^{N+1} \left(\frac{1}{\sigma_{1i}} - \frac{1}{\sigma_{1}} \right) \frac{X_{1i}^{O}}{X_{A}} \right]$$
(69)

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 data, since it allows N adjustable parameters (the friction factors σ_{11}) if the equilibrium constants can be determined independently, or N² if they are also 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. Consider 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

$$\overline{J}_{A}^{V} = - \left[\frac{RT}{\sigma_{1}\eta} \frac{\partial C_{1}^{*}}{\partial z} + \frac{RT}{\sigma_{11}\eta} \frac{\partial C_{11}^{*}}{\partial z} + 2\frac{RT}{\sigma_{11}\eta} \frac{\partial C_{11}^{**}}{\partial z}\right] (70)$$

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

$$c_{A}^{*} = c_{l}^{*} + c_{ll}^{*} + 2c_{ll}^{**}$$
 (71)

Proceeding as before, we write

$$J_{A}^{V} + \left\{ \frac{RT}{\eta\sigma l} \frac{\partial C_{l}^{*}}{\partial C_{A}^{*}} + \frac{RT}{\eta\sigma_{ll}} \left[\frac{\partial C_{ll}^{*}}{\partial C_{A}^{*}} + 2 \frac{\partial C_{ll}^{*}}{\partial C_{A}^{*}} \right] \right\} \frac{\partial C_{A}^{*}}{\partial z} (72)$$

Differentiating (71) gives

$$\frac{\partial C_{1}}{\partial C_{A}} = 1 - \frac{\partial C_{11}}{\partial C_{A}} - 2 \frac{\partial C_{11}}{\partial C_{A}}$$
(73)

which, when substituted into (72) yields, after rearrangement,

$$J_{A}^{V} * + - \frac{RT}{\eta} \left[\frac{1}{\sigma_{1}} + \left(\frac{1}{\sigma_{11}} - \frac{1}{\sigma_{1}} \right) \frac{\partial C_{12}}{\partial C_{A}}^{*} + 2 \left(\frac{1}{\sigma_{11}} - \frac{1}{\sigma_{1}} \right) \frac{\partial C_{11}}{\partial C_{A}}^{*} \right] \frac{\partial C_{A}}{\partial z}$$

$$(74)$$

Equation (74) can be written

$$J_{A}^{V} * = -\frac{RT}{\eta} \left[\frac{1}{\sigma_{1}} + \left(\frac{1}{\sigma_{11}} - \frac{1}{\sigma_{1}} \right) \left(\frac{\partial C_{11}}{\partial C_{A}} + 2 \frac{\partial C_{11}}{\partial C_{A}} \right) \right] \quad (75)$$

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

$$D_{A}^{*} = \frac{RT}{\eta} \left[\frac{1}{\sigma_{1}} + \left(\frac{1}{\sigma_{11}} - \frac{1}{\sigma_{1}} \right) \left(\frac{\partial C_{11}^{*}}{\partial C_{A}^{*}} + 2 \frac{\partial C_{11}^{*}}{\partial C_{A}^{*}} \right) \right] \quad (76)$$

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

$$D_{A}^{*} = \frac{RT}{\eta} \left[\frac{1}{\sigma_{11}} + \left(\frac{1}{\sigma_{1}} - \frac{1}{\sigma_{11}} \right) \frac{X_{1}}{X_{A}} \right]$$
(77)

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,

 $A + A \leftrightarrow A_2$ $A_2 + A \leftrightarrow A_3$

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

$$J_{A}^{V} = -\frac{RT}{\eta} \left[\frac{1}{\sigma_{1}} \frac{\partial C_{1}}{\partial z} + \frac{1}{\sigma_{11}} \left[\frac{\partial C_{11}}{\partial z} + 2 \frac{\partial C_{11}}{\partial z} \right] + \frac{1}{\sigma_{111}} \left(\frac{\partial C_{111}}{\partial z} + 2 \frac{\partial C_{111}}{\partial z} + 3 \frac{\partial C_{111}}{\partial z} \right) \right]$$
(78)

and the stoichiometric formula is

$$c_{A}^{*} = c_{1}^{*} + c_{11}^{*} + 2c_{11}^{**} + c_{111}^{*} + 2c_{111}^{**}$$

+ $3c_{111}^{***}$ (79)

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

$$D_{A}^{*} = \frac{RT}{\eta} \left[\frac{1}{\sigma_{1}} + \left(\frac{1}{\sigma_{11}} - \frac{1}{\sigma_{1}} \right) \left(\frac{\partial C_{11}^{*}}{\partial C_{A}^{*}} + 2 \frac{\partial C_{11}^{*}}{\partial C_{A}^{*}} \right) + \left(\frac{1}{\sigma_{111}} - \frac{1}{\sigma_{1}} \right) \left(\frac{\partial C_{111}^{*}}{\partial C_{A}^{*}} + 2 \frac{\partial C_{111}^{*}}{\partial C_{A}^{*}} + \frac{\partial C_{111}^{*}}{\partial C_{A}^{*}} \right) \right]$$
(80)

The generalization of this equation by this method to a system where one molecule undergoes repeated simple self-polymerization 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 mobilities 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

| System and Association | Predicted Tracer Diffusivities |
|---|---|
| A, B, C,N no association | $D_{i}^{*} = \frac{RT}{n\sigma_{i}} \qquad i = A, B, C, \dots N$ |
| A, B A + B ↔ AB A, B, C A + B ↔ AB A + C ↔ AC | $D_{A}^{*} = \frac{RT}{n} \left[\frac{1}{\sigma_{1}} + \left(\frac{1}{\sigma_{12}} - \frac{1}{\sigma_{1}} \right) \frac{X_{12}^{\circ}}{X_{A}} \right]$ |
| | $\nu_{\rm B}^{*} = \frac{{\rm ET}}{{\rm n}} \left[\frac{1}{\sigma_2} + \left(\frac{1}{\sigma_{12}} - \frac{1}{\sigma_2} \right) \frac{{\rm X}_{12}^{-{\rm c}}}{{\rm X}_{\rm B}^{-{\rm c}}} \right]$ |
| A, B, C A + B ↔ AB A + C ↔ AC | $u_{A}^{*} = \frac{\pi T}{\eta} \left[\frac{1}{\sigma_{1}} + \left(\frac{1}{\sigma_{12}} - \frac{1}{\sigma_{1}} \right) \frac{X_{12}^{\circ}}{X_{A}} + \left(\frac{1}{\sigma_{13}} - \frac{1}{\sigma_{1}} \right) \frac{X_{13}^{\circ}}{X_{A}} \right]$ |
| | $p_{\rm B}^{*} = \frac{\rm AT}{\rm n} \left[\frac{1}{\sigma_2} + \left(\frac{1}{\sigma_{12}} - \frac{1}{\sigma_1} \right) \frac{{\rm X}_{12}^{0}}{{\rm X}_{\rm B}^{0}} \right]$ |
| | $B_{c}^{*} = \frac{RT}{n} \left[\frac{1}{\sigma_{3}} + \left(\frac{1}{\sigma_{13}} - \frac{1}{\sigma_{1}} \right) \frac{X_{13}}{X_{c}} \right]$ |
| A, B, C,N A + B ↔ C A + N ↔ AN | $D_{A}^{*} = \frac{\mathrm{HT}}{\mathrm{n}} \left[\frac{1}{\sigma_{1}} + \frac{\mathrm{HH}}{\mathrm{s}} \left(\frac{1}{\sigma_{1\mathrm{i}}} - \frac{1}{\sigma_{1}} \right) \frac{\mathrm{X}_{1\mathrm{s}}}{\mathrm{X}_{A}} \right]$ other components as in D_{B}^{*} above |
| A, B, A + A ↔ Ag B inert | $D_{A}^{*} = \frac{ET}{n} \left[\frac{1}{\sigma_{1}} + \left(\frac{1}{\sigma_{11}} - \frac{1}{\sigma_{1}} \right) \frac{\partial C_{11}}{\partial C_{A}^{*}} + 2\left(\frac{1}{\sigma_{1}} - \frac{1}{\sigma_{11}} \right) \frac{\partial C_{11}}{\partial C_{A}^{*}} \right]$ |
| | $D_{\rm B}^{*} = \frac{{\rm RT}}{{\rm n}\sigma_2}$ |
| A, B A + A + A_2 A + A_2 + A_3 | $D_{A}^{*} = \frac{RT}{n} \left[\frac{1}{\sigma_{1}} + \left(\frac{1}{\sigma_{11}} - \frac{1}{\sigma_{1}} \right) + \left(\frac{\partial}{\partial} C_{A}^{1} + \frac{\partial}{\partial} C_{A}^{1} \right) \right]$ |
| B inert | + $\left(\frac{1}{\sigma_{111}} - \frac{1}{\sigma_{1}}\right)$ $\left(\frac{\partial C_{111}}{\partial C_{A}} + 2 - \frac{\partial C_{111}}{\partial C_{A}} + 3 \frac{\partial C_{111}}{\partial C_{A}}\right)$ |
| | $D_{B}^{*} = \frac{RT}{n\sigma_{2}}$ |

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

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 considerable, as will be seen in later discussion.

Binary Mutual Diffusion--Nonassociated Systems

For a binary nonassociated system with components A and B, equation (11) gives the flux of component A:

$$J_{A} = - \frac{C_{A}}{\sigma_{A} \eta} \frac{\partial \mu_{A}}{\partial z} + \frac{C_{A}}{\eta} \left[\frac{C_{A} \overline{V}_{A}}{\sigma_{A}} \frac{\partial \mu_{A}}{\partial z} + \frac{C_{B} \overline{V}_{B}}{\sigma_{B}} \frac{\partial \mu_{B}}{\partial z} \right]$$
(81)

Substituting the definition of chemical potential gives

$$J_{A}^{V} = \frac{RT}{n} \left[-\frac{C_{A}}{\sigma_{A}} \frac{\partial \ln a_{A}}{\partial z} + C_{A} \left(\frac{C_{A} \overline{V}_{A}}{\sigma_{A}} \frac{\partial \ln a_{A}}{\partial z} + \frac{C_{B} V_{B}}{\sigma_{B}} \frac{\partial \ln a_{B}}{\partial z} \right) \right]$$
(82)

By the chain rule

$$\frac{\partial \ln a_A}{\partial z} = \frac{1}{C_A} \frac{\partial \ln a_A}{\partial \ln C_A} \frac{\partial C_A}{\partial z}$$
(83)

$$\frac{\partial \ln a_{B}}{\partial z} = \frac{1}{C_{B}} \frac{\partial \ln a_{B}}{\partial \ln C_{B}} \frac{\partial C_{B}}{\partial z}$$
(84)

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

$$J_{A}^{V} = -D_{AB} \frac{\partial C_{A}}{\partial z} = \frac{RT}{n} \left[-\frac{1}{\sigma_{A}} \frac{\partial \ln a_{A}}{\partial \ln C_{A}} + \frac{C_{A} \overline{V}_{A}}{\sigma_{B}} \frac{\partial \ln a_{B}}{\partial \ln C_{B}} + \frac{C_{A} \overline{V}_{A}}{\sigma_{A}} \frac{\partial \ln a_{A}}{\partial \ln C_{A}} \right]$$

$$(85)$$

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

$$\frac{\partial \operatorname{Ln} X_{A}}{\partial \operatorname{Ln} C_{A}} = \frac{X_{B}}{C_{B} \nabla_{B}}$$
(86)

$$\frac{\partial \ln X_{B}}{\partial L_{n} C_{B}} = \frac{X_{A}}{C_{A} V_{A}}$$
(87)

Substituting (86) and (87) into equation (85) and making use of the fact that $C_A \overline{V}_A + C_B \overline{V}_B = 1$ one obtains the well known Hartley-Crank Equation [20]:

$$D_{AB} = \frac{RT}{\eta} \left[\frac{X_B}{\sigma_A} + \frac{X_A}{\sigma_B} \right] \frac{\partial \ln a_A}{\partial \ln X_A}$$
(88)

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

$$\begin{array}{l} \text{Lim} \\ X_{A} \rightarrow 0 \end{array} D_{AB} = \frac{RT}{\eta \sigma_{A}} = D_{A} \end{array}$$

$$\tag{89}$$

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

$$J_{A}^{V} = -\frac{C_{1}}{\sigma_{1}^{\eta}} \frac{\partial \mu_{1}}{\partial z} - 2\frac{C_{11}}{\sigma_{11}^{\eta}} \frac{\partial \mu_{11}}{\partial z} + C_{A}(\frac{C_{1}V_{1}}{\sigma_{1}} \frac{\partial \mu_{1}}{\partial z} + \frac{C_{1}V_{1}}{\sigma_{1}^{\eta}} \frac{\partial \mu_{1}}{\partial z} + \frac{C_{2}V_{2}}{\sigma_{2}^{\eta}} \frac{\partial \mu_{2}}{\partial z})$$
(91)

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 $C_A \overline{V}_A + C_B \overline{V}_B = 1$, and the assumption $\overline{V}_{11} = 2\overline{V}_A$, the mutual diffusivity is found to be

$$D_{AB} = \frac{RT}{\eta} \left[\frac{X_A}{\sigma_2} + X_B \left(\frac{X_1^{\circ}}{X_A} \frac{1}{\sigma_1} + \frac{X_{11}^{\circ}}{X_A} \frac{1}{\sigma_{11}} \right) \right] \frac{\partial \ln a}{\partial \ln x}$$
(92)

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

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

A + B ↔ AB

occurs. The flux of A is given here by

$$J_{A}^{V} = -\frac{C_{1}}{\sigma_{1}n} \frac{\partial \mu_{1}}{\partial z} - \frac{C_{12}}{\sigma_{12}n} \frac{\partial \mu_{12}}{\partial z} + C_{A}(\frac{C_{1}\overline{V}_{1}}{\sigma_{1}} \frac{\partial \mu_{1}}{\partial z} + \frac{C_{12}\overline{V}_{2}}{\sigma_{2}} \frac{\partial \mu_{2}}{\partial z})$$
(93)

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

$$D_{AB} = \frac{RT}{\eta} \left[\frac{1}{\sigma_{1}} \frac{X_{1}^{\circ}}{X_{A}} X_{B} + \frac{1}{\sigma_{2}} \frac{X_{2}^{\circ}}{X_{B}} X_{A} + \frac{1}{\sigma_{12}} \frac{X_{12}^{\circ} (X_{A} - X_{B})^{2}}{X_{A} X_{B}} \right]_{\frac{\partial}{\partial} \ln X}^{\frac{\partial}{\partial} \ln X}$$
(94)

Detailed derivation is again given by Anderson [1] 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 Hartley-Crank 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 theoretical 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, thereby defining N^2 diffusion coefficients:

$$J_{i}^{V} = \sum_{j=1}^{N} D_{ij} \frac{\partial C_{j}}{\partial z} \qquad i = 1, 2, \dots N \qquad (95)$$

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:

$$J_{i}^{V} = \sum_{j=1}^{N-1} D_{ij} \frac{\partial C_{j}}{\partial z} \quad i = 1, 2, \dots N - 1 \quad (96)$$

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

$$D_{ij} = D_{ij} - \overline{\nabla}_{N} D_{iN}$$
 i, j = 1, 2,...N - 1 (97)

Since then, Gosting and coworkers have presented several methods for experimentally determining the D_{ij}'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 also 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

$$J_{1}^{V} = -\frac{c_{1}}{\sigma_{1}^{n}} \frac{\partial \mu_{1}}{\partial z} + c_{1} \left(\frac{c_{1}\overline{V}_{1}}{\sigma_{1}} \frac{\partial \mu_{1}}{\partial z} + \frac{c_{2}\overline{V}_{2}}{\sigma_{2}} \frac{\partial \mu_{2}}{\partial z} + \frac{c_{3}\overline{V}_{3}}{\sigma_{3}} \frac{\partial \mu_{3}}{\partial z} \right)$$

$$J_{2}^{V} = -\frac{c_{2}}{\sigma_{2}^{n}} \frac{\partial \mu_{1}}{\partial z} + c_{2} \left(\frac{c_{1}\overline{V}_{1}}{\sigma_{1}} \frac{\partial \mu_{1}}{\partial z} + \frac{c_{2}\overline{V}_{2}}{\sigma_{2}} \frac{\partial \mu_{2}}{\partial z} + \frac{c_{3}\overline{V}_{3}}{\sigma_{3}} \frac{\partial \mu_{3}}{\partial z} \right)$$

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From the Gibbs-Duhem relationship,

$$\frac{\partial \mu_3}{\partial z} = -\frac{C_1}{C_3} \frac{\partial \mu_1}{\partial z} - \frac{C_2}{C_3} \frac{\partial \mu_2}{\partial z}$$
(100)

Combining equations (98), (99) and (100) to eliminate the gradient of chemical potential of component 3 gives

$$J_{1} = -\frac{C_{1}}{n} \left[\left(\frac{1 - \overline{V}_{1} C_{1}}{\sigma_{1}} \right) + \frac{\overline{V}_{3} C_{1}}{\sigma_{3}} \right] \frac{\partial \mu_{1}}{\partial z} - \frac{C_{1} C_{2}}{n} \left[\frac{\overline{V}_{3}}{\sigma_{3}} - \frac{\overline{V}_{2}}{\sigma_{2}} \right] \frac{\partial \mu_{2}}{\partial z}$$
(101)

$$J_{2}^{V} = -\frac{C_{1}C_{2}}{\eta} \left[\frac{V_{3}}{\sigma_{3}} - \frac{\overline{V}_{1}}{\sigma_{1}}\right] \frac{\partial \mu_{1}}{\partial z} - \frac{C_{2}}{\eta} \left[\frac{(1-C_{2}\overline{V}_{2})}{\sigma_{2}} + \frac{\overline{V}_{3}C_{2}}{\sigma_{3}}\right] \frac{\partial \mu_{2}}{\partial z} \quad (102)$$

Mathematically, the total derivative of the chemical 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,

$$\frac{\partial c}{\partial \mu_{1}} = \frac{\partial c}{\partial \mu_{1}} \frac{\partial c}{\partial c_{1}} + \frac{\partial c}{\partial \mu_{1}} \frac{\partial c}{\partial c_{2}}$$
(103)

$$\frac{\partial \mu_2}{\partial z} = \frac{\partial \mu_2}{\partial C_1} \frac{\partial C_1}{\partial z} + \frac{\partial \mu_2}{\partial C_2} \frac{\partial C_2}{\partial z}$$
(104)

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

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

(105)

$$J_{2}^{V} = -\{\frac{C_{1}C_{2}}{\nu}, (\frac{\overline{V}_{3}}{\sigma_{3}} - \frac{\overline{V}_{1}}{\sigma_{1}})\frac{\partial\mu_{1}}{\partial C_{1}} + \frac{C_{2}}{\eta}[(\frac{1-C_{2}\overline{V}_{2}}{\sigma_{2}}) + \frac{C_{2}\overline{V}_{3}}{\sigma_{3}}]\frac{\partial\mu_{2}}{\partial C_{1}}\}\frac{\partial C_{1}}{\partial z}$$
$$-\{\frac{C_{1}C_{2}}{\eta}, (\frac{\overline{V}_{3}}{\sigma_{3}} - \frac{\overline{V}_{1}}{\sigma_{1}})\frac{\partial\mu_{1}}{\partial C_{2}} + \frac{C_{2}}{\eta}[(\frac{1-C_{2}\overline{V}_{2}}{\sigma_{2}}) + \frac{C_{2}\overline{V}_{3}}{\sigma_{3}}]\frac{\partial\mu_{2}}{\partial C_{2}}\}\frac{\partial C_{2}}{\partial z}$$
$$(106)$$

From the definition of chemical potential, these can be written

$$J_{1}^{V} = -\frac{RT}{n} \{ C_{1} \left[\left(\frac{1-C_{1}\overline{V}_{1}}{\sigma_{1}} \right) + \frac{C_{1}\overline{V}_{3}}{\sigma_{3}} \right] \frac{\partial \ln a_{1}}{\partial C_{1}} + C_{1}C_{2} \left(\frac{\overline{V}_{3}}{\sigma_{3}} - \frac{\overline{V}_{2}}{\sigma_{2}} \right) \frac{\partial \ln a_{2}}{\partial C_{1}} \} \frac{\partial C_{1}}{\partial z} + C_{1}C_{2} \left(\frac{1-C_{1}\overline{V}_{1}}{\sigma_{1}} \right) + \frac{C_{1}\overline{V}_{3}}{\sigma_{3}} \right] \frac{\partial \ln a_{1}}{\partial C_{1}} + C_{1}C_{2} \left(\frac{\overline{V}_{3}}{\sigma_{3}} - \frac{\overline{V}_{2}}{\sigma_{2}} \right) \frac{\partial \ln a_{2}}{\partial C_{2}} \} \frac{\partial C_{2}}{\partial z}$$
(107)

$$J_{2}^{V} = -\frac{RT}{n} \{ C_{1}C_{2} (\frac{\overline{V}_{3}}{\sigma_{3}} - \frac{\overline{V}_{2}}{\sigma_{2}}) \frac{\partial \ln a_{1}}{\partial C_{1}} + C_{2}[(\frac{1-C_{2}\overline{V}_{2}}{\sigma_{2}}) + \frac{C_{2}\overline{V}_{2}}{\sigma_{3}}] \frac{\partial C_{1}}{\partial z} \frac{\partial \ln a_{2}}{\partial C_{1}} \} \frac{\partial C_{1}}{\partial z}$$

$$- \frac{\mathrm{RT}}{\mathrm{\eta}} \left\{ c_{1}c_{2} \left(\frac{\overline{\mathrm{V}}_{3}}{\sigma_{3}} - \frac{\overline{\mathrm{V}}_{1}}{\sigma_{1}} \right) \xrightarrow{\partial \mathrm{Ln} a_{1}}{\partial c_{1}} + c_{2} \left[\left(\frac{1 - c_{2}\overline{\mathrm{V}}_{2}}{\sigma_{2}} \right) + \frac{c_{2}\overline{\mathrm{V}}_{3}}{\sigma_{3}} \right] \xrightarrow{\partial \mathrm{Ln} a_{2}}{\partial c_{2}} \right\} \xrightarrow{\partial c_{2}}{\partial z}$$
(108)

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

$$D_{11} = D_{AA} = \frac{RT}{n} C_1 \left[\left(\frac{1 - C_1 \overline{V}_1}{\sigma_1} \right) + \frac{C_1 \overline{V}_3}{\sigma_3} \right] \frac{\partial \ln a_1}{\partial C_1} + C_1 C_2 \left(\frac{\overline{V}_3}{\sigma_3} - \frac{\overline{V}_2}{\sigma_2} \right) \frac{\partial \ln a_2}{\partial C_1} \right]$$
(109)

$$D_{12} = D_{AB} = \frac{RT}{\eta} \{ C_1 \left[\left(\frac{1 - C_1 \overline{V}_1}{\sigma_1} \right) + \frac{C_1 \overline{V}_3}{\sigma_3} \right] \frac{\partial \ln a_1}{\partial C_2} \}$$

+
$$c_1 c_2 \left(\frac{\overline{V}_3}{\sigma_3} - \frac{\overline{V}_2}{\sigma_2} \right) \xrightarrow{\partial \text{ Ln } a_2}{\partial c_1}$$
 (110)

$$D_{21} = D_{BA} = \frac{RT}{\eta} \{ c_1 c_2 (\frac{\overline{V}_3}{\sigma_3} - \frac{\overline{V}_1}{\sigma_1}), \frac{\partial \ln a_1}{\partial c_1} + c_2 [(\frac{1-c_2 \overline{V}_2}{\sigma_2}) + \frac{c_2 \overline{V}_3}{\sigma_3}], \frac{\partial \ln a_2}{\partial c_1} \}$$
(111)

$$D_{22} = D_{BB} = \frac{RT}{n} \{ c_1 c_2 \left(\frac{\overline{V}_3}{\sigma_3} - \frac{\overline{V}_1}{\sigma_1} \right) \xrightarrow{\partial} \frac{\ln a_1}{\partial c_2} + c_2 \left[\left(\frac{1 - c_2 \overline{V}_2}{\sigma_2} \right) + \frac{c_2 \overline{V}_3}{\sigma_3} \right] \xrightarrow{\partial} \frac{\ln a_2}{\partial c_2} \}$$
(112)

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

$$D_{ij} = \frac{C_{i}}{\eta} \left[\left(\frac{1 - \overline{V}_{i} C_{i}}{\sigma_{i}} \right) + \frac{C_{i} \overline{V}_{N}}{\sigma_{N}} \right] \frac{\partial \mu_{i}}{\partial C_{j}} + \sum_{\substack{k=1\\k \neq i}}^{N-1} \frac{C_{i} C_{k}}{\eta} \left[\frac{\overline{V}_{N}}{\sigma_{N}} - \frac{\overline{V}_{k}}{\sigma_{k}} \right] \frac{\partial \mu_{k}}{\partial C_{j}}$$
(113)

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

$$T \frac{dS}{dt} = -J_1 V \frac{\partial \mu_1}{\partial z} J_2 V \frac{\partial \mu_2}{\partial z} J_3 V \frac{\partial \mu_3}{\partial z}$$

However, equation (100) can be used to eliminate μ_3 , and the constant volume relationship $J_1 \overline{V}_1 + J_2 \overline{V}_2 + J_3 \overline{V}_3 = 0$ can be used to eliminate J_3 :

$$T \frac{dS}{dt} = J_{1}^{V} Y_{1} + J_{2}^{V} Y_{2}$$
 (114)

$$Y_{i} = -\sum_{j=1}^{2} \left(\delta_{ij} + \frac{C_{i}\overline{V}_{i}}{C_{3}\overline{V}_{3}}\right) \frac{\partial \mu_{j}}{\partial z} \quad i = 1, 2 \quad (115)$$

$$\delta_{ij} = \begin{cases} 0 & j \neq i \\ 1 & j = i \end{cases}$$

Irreversible thermodynamics also states that

$$J_{1}^{V} = L_{11}Y_{1} + L_{12}Y_{2}$$
(116)
$$J_{2}^{V} = L_{21}Y_{1} + L_{22}Y_{2}$$
(117)

Substituting the expressions for Y_i from (115) into equations (116) and (117) and rearranging yields

$$J_{1}^{V} = -(\alpha L_{11} + \gamma L_{12}) \frac{\partial \mu_{1}}{\partial z} - (\beta L_{11} + \delta L_{12}) \frac{\partial \mu_{2}}{\partial z}$$
(118)

$$J_2^{V} = -(\alpha L_{21} + \gamma L_{22}) \frac{\partial \mu_1}{\partial z} - (\beta L_{21} + \delta L_{22}) \frac{\partial \mu_2}{\partial z}$$
(119)

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

$$\alpha = 1 + \frac{c_1 \overline{v}_1}{c_3 \overline{v}_3} \qquad \beta = \frac{c_2 \overline{v}_1}{c_3 \overline{v}_3}$$
$$\gamma = \frac{c_1 \overline{v}_2}{c_3 \overline{v}_3} \qquad \delta = 1 + \frac{c_2 \overline{v}_2}{c_3 \overline{v}_3}$$

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

$$L_{11}\alpha + L_{12}\gamma = \frac{C_1}{\eta} \left[\left(\frac{1 - \overline{V_1} C_1}{\sigma_1} \right) + \frac{\overline{V_3} C_1}{\sigma_3} \right]$$
(120)

$$L_{11}\beta + L_{12}\delta = \frac{C_1C_2}{\eta} \left[\frac{\overline{V}_3}{\sigma_3} - \frac{\overline{V}_2}{\sigma_2}\right]$$
(121)

$$L_{21}\alpha + L_{22}\gamma = \frac{C_1C_2}{n} \left[\frac{\overline{V}_3}{\sigma_3} - \frac{\overline{V}_2}{\sigma_2}\right]$$
(122)

$$L_{21}\beta + L_{22}\delta = \frac{C_2}{\eta} \left[\left(\frac{1 - \overline{V}_2 C_2}{\sigma_2} \right) + \frac{\overline{V}_3 C_2}{\sigma_3} \right]$$
(123)

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

$$L_{12} = \frac{\frac{C_1 C_2}{\eta} \left[\frac{\overline{V}_3}{\sigma_3} - \frac{\overline{V}_2}{\sigma_2}\right] \alpha}{\alpha \delta - \beta \gamma} - \frac{\frac{C_1}{\eta} \left[\frac{(1 - \overline{V}_1 C_1)}{\sigma_1} + \frac{\overline{V}_3 C_1}{\sigma_3}\right] \beta}{\alpha \delta - \beta \gamma}$$
(124)

$$L_{21} = \frac{\frac{C_1 C_2}{\eta} \left[\frac{\overline{V}_3}{\sigma_3} - \frac{\overline{V}_1}{\sigma_1}\right]\delta}{\alpha\delta - \beta\gamma} - \frac{C_2}{\eta} \left[\frac{(1 - \overline{V}_2 C_2)}{\sigma_2} + \frac{\overline{V}_3 C_2}{\sigma_3}\right]\gamma}{(125)}$$

Using the relation $C_1 \overline{V}_1 + C_2 \overline{V}_2 + C_3 \overline{V}_3 = 1$, and the defining expressions for α , β , γ , and δ we may obtain from equations (124) and (125) the desired result:

$$L_{12} = L_{21} = -\frac{c_1 c_2 \overline{v}_1 (1 - c_1 \overline{v}_1)}{\sigma_1 \eta} - \frac{c_1 c_2 \overline{v}_2 (1 - c_2 \overline{v}_2)}{\sigma_2 \eta} + \frac{c_1 c_2 c_3 \overline{v}_3^2}{\sigma_3 \eta}$$
(126)

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:

$$L_{12} = \frac{a D_{12} - c D_{11}}{ad - bc}$$
(127)

$$L_{21} = \frac{d D_{21} - b D_{22}}{ad - bc}$$
(128)

where

$$a = (1 + \frac{c_1 \overline{V}_1}{c_3 \overline{V}_3}) \frac{\partial \mu_1}{\partial c_1} + \frac{c_2 \overline{V}_2}{c_3 \overline{V}_3} \frac{\partial \mu_2}{\partial c_1}$$
(129)

$$b = (1 + \frac{c_2 \overline{V}_2}{c_3 \overline{V}_3}) \frac{\partial \mu_2}{\partial c_1} + \frac{c_1 \overline{V}_2}{c_3 \overline{V}_3} \frac{\partial \mu_1}{\partial c_1}$$
(130)

$$c = (1 + \frac{c_1 \overline{V}_1}{c_3 \overline{V}_3}) \frac{\partial \mu_1}{\partial c_2} + \frac{c_2 \overline{V}_1}{c_3 \overline{V}_3} \frac{\partial \mu_2}{\partial c_2}$$
(131)

$$d = (1 + \frac{c_2 \overline{v}_2}{c_3 \overline{v}_3}) \frac{\partial \mu_2}{\partial c_2} + \frac{c_1 \overline{v}_2}{c_3 \overline{v}_3} \frac{\partial \mu_1}{\partial c_2}$$
(132)

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

 $A + B \leftrightarrow AB$

where component C is inert.

Kett's equations are given here without derivation:

$$D_{AA} = \left[\frac{c_{1}}{\sigma_{1}\eta}(1-\overline{v}_{1}c_{A}) + \frac{c_{12}}{\sigma_{12}\eta}(1-\overline{v}_{12}c_{A}) + \frac{\overline{v}_{3}c_{A}}{\sigma_{3}\eta}\right]\frac{\partial\mu_{1}}{\partial c_{A}}$$

$$+ \left[-\frac{\overline{v}_{2}c_{2}c_{A}}{\sigma_{2}\eta} + \frac{c_{12}}{\sigma_{12}\eta}(1-\overline{v}_{12}c_{A}) + \frac{\overline{v}_{3}c_{A}c_{B}}{\sigma_{3}\eta}\right]\frac{\partial\mu_{2}}{\partial c_{A}}$$
(133)
$$D_{AB} = \left[\frac{c_{1}}{\sigma_{1}\eta}(1-\overline{v}_{1}c_{A}) + \frac{c_{12}}{\sigma_{12}\eta}(1-\overline{v}_{12}c_{A}) + \frac{\overline{v}_{3}c_{A}^{2}}{\sigma_{3}\eta}\right]\frac{\partial\mu_{1}}{\partial c_{B}}$$

+
$$\left[-\frac{\overline{v}_{2}c_{2}c_{A}}{\sigma_{2}\eta} + \frac{c_{12}}{\sigma_{12}\eta}(1-\overline{v}_{12}c_{A}) + \frac{\overline{v}_{3}c_{A}c_{B}}{\sigma_{3}\eta}\right]\frac{\partial\mu_{2}}{\partial c_{B}}$$
 (134)

$$D_{BA} = \left[-\frac{\overline{v}_{1}c_{1}c_{B}}{\sigma_{1}\eta} + \frac{c_{12}}{\sigma_{12}\eta} (1 - \overline{v}_{12}c_{B}) + \frac{\overline{v}_{3}c_{A}c_{B}}{\sigma_{3}\eta} \right] \frac{\partial \mu_{1}}{\partial c_{A}}$$
$$+ \left[\frac{c_{2}}{\sigma_{2}\eta} (1 - \overline{v}_{2}c_{B}) + \frac{c_{12}}{\sigma_{12}\eta} (1 - \overline{v}_{12}c_{B}) + \frac{\overline{v}_{e}c_{B}^{2}}{\sigma_{3}\eta} \right] \frac{\partial \mu_{2}}{\partial c_{A}} (135)$$

$$D_{BB} = \left[-\frac{\overline{v}_{1}c_{1}c_{B}}{\sigma_{1}\eta} + \frac{c_{12}}{\sigma_{12}\eta} (1 - \overline{v}_{12}c_{B}) + \frac{\overline{v}_{3}c_{A}c_{B}}{\sigma_{3}\eta} \right] \frac{\partial \mu_{1}}{\partial c_{B}}$$
$$+ \left[\frac{c_{2}}{\sigma_{2}\eta} (1 - \overline{v}_{2}c_{B}) + \frac{c_{12}}{\sigma_{12}\eta} (1 - \overline{v}_{12}c_{B}) + \frac{\overline{v}_{3}c_{B}^{2}}{\sigma_{3}\eta} \right] \frac{\partial \mu_{2}}{\partial c_{B}}$$
(136)

By making the assumption that \overline{V}_{12} = \overline{V}_A + \overline{V}_B he obtained

$$L_{BA} = L_{AB} = -\frac{C_{1}C_{B}\overline{V}_{1}}{\sigma_{1}\eta} (1-\overline{V}_{1}C_{A}) - \frac{C_{2}C_{A}\overline{V}_{2}}{\sigma_{2}\eta} (1-\overline{V}_{2}C_{B}) + \frac{C_{A}C_{B}\overline{V}_{3}}{\sigma_{3}\eta} (1-\overline{V}_{1}C_{A}-\overline{V}_{2}C_{B}) + \frac{C_{12}}{\sigma_{12}\eta} (1-\overline{V}_{12}C_{A}) (1-\overline{V}_{12}C_{B}) (137)$$

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 this 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

$$J_{A}^{V} = -\frac{c_{1}}{\sigma_{1} n} \frac{\partial u_{1}}{\partial z} - \frac{c_{12}}{\sigma_{12} n} \frac{\partial u_{12}}{\partial z} - \frac{c_{13}}{\sigma_{13} n} \frac{\partial u_{13}}{\partial z} + \frac{c_{A}}{\sigma_{13} n} \left[\frac{c_{1} \overline{V}_{1}}{\sigma_{1}} \frac{\partial u_{1}}{\partial z} + \frac{c_{12} \overline{V}_{12}}{\sigma_{12}} \frac{\partial u_{12}}{\partial z} + \frac{c_{13} \overline{V}_{13}}{\sigma_{13}} \frac{\partial u_{13}}{\partial z} + \frac{c_{2} \overline{V}_{2}}{\sigma_{2}} \frac{\partial u_{2}}{\partial z} + \frac{c_{3} \overline{V}_{3}}{\sigma_{3}} \frac{\partial u_{3}}{\partial z} \right]$$
(138)
$$J_{B}^{V} = -\frac{c_{2}}{\sigma_{2} n} \frac{\partial u_{2}}{\partial z} - \frac{c_{12}}{\sigma_{12} n} \frac{\partial u_{12}}{\partial z} + \frac{c_{13} \overline{V}_{13}}{\sigma_{13}} \frac{\partial u_{13}}{\partial z} + \frac{c_{13} \overline{V}_{13}}{\sigma_{13}} \frac{\partial u_{13}}{\partial z} + \frac{c_{2} \overline{V}_{2}}{\sigma_{2}} \frac{\partial u_{2}}{\partial z} + \frac{c_{3} \overline{V}_{3}}{\sigma_{3}} \frac{\partial u_{3}}{\partial z} \right]$$
(138)

For this system

$$\frac{\partial \mu_{12}}{\partial z} = \frac{\partial \mu_1}{\partial z} + \frac{\partial \mu_2}{\partial z}$$
(140)

$$\frac{\partial \mu_{13}}{\partial z} = \frac{\partial \mu_{1}}{\partial z} + \frac{\partial \mu_{3}}{\partial z}$$
(141)

Therefore, equations (138) and (139) become

$$nJ_{A}^{V} = -\left[\frac{c_{1}}{\sigma_{1}}(1-c_{A}\overline{V}_{1}) + \frac{c_{12}}{\sigma_{12}}(1-c_{A}\overline{V}_{12}) + \frac{c_{13}}{\sigma_{13}}(1-c_{A}\overline{V}_{13})\right]\frac{\partial\mu_{1}}{\partial z}$$
$$-\left[\frac{c_{12}}{\sigma_{12}}(1-c_{A}\overline{V}_{12}) - \frac{c_{A}c_{2}\overline{V}_{2}}{\sigma_{2}}\right]\frac{\partial\mu_{2}}{\partial z} - \left[\frac{c_{B}}{\sigma_{13}}(1-c_{A}\overline{V}_{13}) - \frac{c_{A}c_{3}\overline{V}_{3}}{\sigma_{3}}\right]\frac{\partial\mu_{3}}{\partial z}$$

(142)

$$nJ_{B}^{V} = -\left[\frac{c_{12}}{\sigma_{12}}(1-c_{B}\overline{V}_{12}) - \frac{c_{B}c_{1}\overline{V}_{1}}{\sigma_{1}} - \frac{c_{B}c_{13}\overline{V}_{13}}{\sigma_{13}}\right]\frac{\partial\mu_{1}}{\partialz}$$
$$-\left[\frac{c_{12}}{\sigma_{12}}(1-c_{B}\overline{V}_{2}) + \frac{c_{12}}{\sigma_{12}}(1-c_{B}\overline{V}_{12})\right]\frac{\partial\mu_{2}}{\partialz} - \left[\frac{-c_{B}c_{13}\overline{V}_{13}}{\sigma_{13}}\right]$$
$$-\frac{c_{B}c_{3}\overline{V}_{3}}{\sigma_{3}}\right]\frac{\partial\mu_{3}}{\partialz}$$
(143)

By combining the stoichiometric relationships

$$c_{A} = c_{1} + c_{12} + c_{13}$$

$$c_{B} = c_{2} + c_{12}$$

$$c_{C} = c_{3} + c_{13}$$
(144)

with the Gibbs-Duhem equation, we obtain

$$\frac{\partial \mu_{3}}{\partial z} = -\frac{C_{A}}{C_{C}} \frac{\partial \mu_{1}}{\partial z} - \frac{C_{B}}{C_{C}} \frac{\partial \mu_{2}}{\partial z}$$
(145)

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Since the chemical potentials are functions of $\rm C_A$ and $\rm C_B$ only, the expression for the total derivative gives

$$\frac{\partial \mu_{1}}{\partial z} = \frac{\partial \mu_{1}}{\partial C_{A}} \frac{\partial C_{A}}{\partial z} + \frac{\partial \mu_{1}}{\partial C_{B}} \frac{\partial C_{B}}{\partial z}$$
(146)

$$\frac{\partial \mu_2}{\partial z} = \frac{\partial \mu_2}{\partial C_A} \frac{\partial C_A}{\partial z} + \frac{\partial \mu_2}{\partial C_B} \frac{\partial C_B}{\partial z}$$
(147)

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

$$\begin{split} nJ_{A} &= -\left[\frac{\partial u_{1}}{\partial C_{A}}\left\{\frac{C_{1}}{\sigma_{1}}\left(1-C_{A}\overline{v}_{1}\right) + \frac{C_{12}}{\sigma_{12}}\left(1-C_{A}\overline{v}_{12}\right) + \left(1-\frac{C_{A}}{C_{C}}\right)\left(1-C_{A}\overline{v}_{3}\right)\frac{C_{13}}{\sigma_{13}}\right) \\ &+ \frac{C_{A}^{2}C_{3}\overline{v}_{3}}{C_{C}\sigma_{3}}\right\} + \frac{\partial u_{2}}{\partial C_{A}}\left\{\frac{C_{12}}{\sigma_{12}}\left(1-C_{A}\overline{v}_{12}\right) - \frac{C_{B}}{C_{C}}\frac{C_{13}}{\sigma_{13}}\left(1-C_{A}\overline{v}_{13}\right)\right) \\ &- \frac{C_{A}C_{2}\overline{v}_{2}}{\sigma_{2}} + \frac{C_{A}C_{B}C_{3}\overline{v}_{3}}{C_{C}\sigma_{3}}\right]\frac{\partial C_{A}}{\partial z} - \left[\frac{\partial u_{1}}{\partial C_{B}}\left\{\frac{C_{1}}{\sigma_{1}}\left(1-C_{A}\overline{v}_{1}\right)\right\}\right] \\ &+ \frac{C_{12}}{\sigma_{12}}\left(1-C_{A}\overline{v}_{12}\right) + \left(1-\frac{C_{A}}{C_{C}}\right)\left(1-C_{A}\overline{v}_{3}\right)\frac{C_{13}}{\sigma_{13}} + \frac{C_{A}^{2}C_{3}\overline{v}_{3}}{C_{C}\sigma_{3}}\right] \\ &+ \frac{\partial u_{2}}{\partial C_{B}}\left\{\frac{C_{12}}{\sigma_{12}}\left(1-C_{A}\overline{v}_{12}\right) - \frac{C_{B}}{C_{C}}\frac{C_{13}}{\sigma_{13}}\left(1-C_{A}\overline{v}_{B}\right) - \frac{C_{A}C_{2}\overline{v}_{2}}{\sigma_{2}} \\ &+ \frac{C_{A}C_{B}C_{3}\overline{v}_{3}}{C_{C}\sigma_{3}}\right\} \end{bmatrix} \frac{\partial C_{B}}{\partial z} \end{split}$$

$$(148)$$

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$$\begin{split} \mathbf{hJ}_{B} &= -\left[\frac{\partial u_{1}}{\partial C_{A}}\left\{\frac{C_{12}}{\sigma_{12}}(1-C_{B}\overline{\mathbf{v}}_{12}) - C_{B}\left(\frac{\overline{\mathbf{v}}_{1}C_{1}}{\sigma_{1}} + \frac{\overline{\mathbf{v}}_{13}C_{13}}{\sigma_{13}}\right)\right\} \\ &+ \frac{C_{A}C_{B}}{C_{C}}\left(\frac{C_{13}\overline{\mathbf{v}}_{13}}{\sigma_{13}} + \frac{C_{3}\overline{\mathbf{v}}_{3}}{\sigma_{3}}\right)\right] + \frac{\partial u_{2}}{\partial C_{A}}\left\{\frac{C_{12}}{\sigma_{12}}(1-C_{A}\overline{\mathbf{v}}_{12}) + \frac{C_{2}}{\sigma_{2}}(1-C_{B}\overline{\mathbf{v}}_{2})\right\} \\ &+ \frac{C_{B}^{2}}{C_{C}}\left(\frac{C_{13}\overline{\mathbf{v}}_{13}}{\sigma_{13}} + \frac{C_{3}\overline{\mathbf{v}}_{3}}{\sigma_{3}}\right)\right] \frac{\partial C_{A}}{\partial z} - \left[\frac{\partial u_{1}}{\partial C_{A}}\left(\frac{C_{12}}{\sigma_{12}}(1-C_{B}\overline{\mathbf{v}}_{12})\right) - C_{B}\left(\frac{\overline{\mathbf{v}}_{12}}{\sigma_{12}} + \frac{\overline{\mathbf{v}}_{13}C_{13}}{\sigma_{13}}\right) + \frac{C_{A}C_{B}}{C_{C}}\left(\frac{C_{13}\overline{\mathbf{v}}_{13}}{\sigma_{13}} + \frac{C_{3}\overline{\mathbf{v}}_{3}}{\sigma_{3}}\right)\right] \\ &- c_{B}\left(\frac{\overline{\mathbf{v}}_{1}C_{1}}{\sigma_{1}} + \frac{\overline{\mathbf{v}}_{13}C_{13}}{\sigma_{13}}\right) + \frac{C_{A}C_{B}}{C_{C}}\left(\frac{C_{13}\overline{\mathbf{v}}_{13}}{\sigma_{13}} + \frac{C_{3}\overline{\mathbf{v}}_{3}}{\sigma_{3}}\right)\right] \\ &+ \frac{\partial u_{2}}{\partial C_{A}}\left\{\frac{C_{12}}{\sigma_{12}}(1-C_{A}\overline{\mathbf{v}}_{12}) + \frac{C_{2}}{\sigma_{2}}(1-C_{3}\overline{\mathbf{v}}_{2})\right\} \\ &+ \frac{C_{B}^{2}}{C_{C}}\left(\frac{C_{13}\overline{\mathbf{v}}_{13}}{\sigma_{13}} + \frac{C_{3}\overline{\mathbf{v}}_{3}}{\sigma_{3}}\right)\right] \frac{\partial C_{B}}{\partial z} \end{split}$$

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

$$D_{AA} = \frac{1}{n} \left[\frac{c_1}{\sigma_1} (1 - c_A \overline{v}_1) + \frac{c_{12}}{\sigma_{12}} (1 - c_A \overline{v}_{12}) + (1 - \frac{c_A}{c_C}) \frac{c_{13}}{\sigma_{13}} (1 - c_A \overline{v}_{13}) \right] \\ + \frac{c_A^2 c_3 \overline{v}_3}{c_C \sigma_3} \left[\frac{\partial u_1}{\partial c_A} + \frac{1}{n} \left[\frac{c_{12}}{\sigma_{12}} (1 - c_A \overline{v}_{12}) - \frac{c_B c_{13}}{c_C \sigma_{13}} (1 - c_A \overline{v}_{13}) \right] \right] \\ - \frac{c_A c_2 \overline{v}_2}{\sigma_2} + \frac{c_A c_B c_3 \overline{v}_3}{c_C \sigma_3} \left[\frac{\partial u_2}{\partial c_A} \right] \\ D_{BB} = \frac{1}{n} \left[\frac{c_{12}}{\sigma_{12}} (1 - c_B \overline{v}_{12}) - c_B (\frac{\overline{v}_1 c_1}{\sigma_1} + \frac{\overline{v}_{13} c_{13}}{\sigma_{13}}) \right] \\ + \frac{c_A c_B}{c_C} (\frac{c_{13} \overline{v}_{13}}{\sigma_{13}} + \frac{c_3 \overline{v}_3}{\sigma_3}) \left[\frac{\partial u_1}{\partial c_B} + \frac{1}{n} \left[\frac{c_{12}}{\sigma_{12}} (1 - c_B \overline{v}_{12}) \right] \right] \\ + \frac{c_2}{\sigma_2} (1 - c_B \overline{v}_2) + \frac{c_B^2}{c_C} (\frac{c_{13} \overline{v}_{13}}{\sigma_{13}} + \frac{\overline{v}_3 c_3}{\sigma_3}) \left[\frac{\partial u_2}{\partial c_B} \right] \\ (151)$$

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

$$T \frac{dS}{dt} = -J_1 \frac{\partial \mu_1}{\partial z} - J_2 \frac{\partial \mu_2}{\partial z} - J_3 \frac{\partial \mu_3}{\partial z} - J_{12} \frac{\partial \mu_{12}}{\partial z} - J_{13} \frac{\partial \mu_{13}}{\partial z}$$
(152)

Applying equations (141) and (142) gives

$$T \frac{dS}{dt} = -(J_1 + J_{12} + J_{13})\frac{\partial \mu_1}{\partial z} - (J_2 + J_{12})\frac{\partial \mu_2}{\partial z}$$
$$- (J_3 + J_{13})\frac{\partial \mu_3}{\partial z}$$
(153)

Equation (146) allows $\frac{\partial \mu_3}{\partial z}$ to be eliminated:

$$T \frac{dS}{dt} = -[J_1 + J_{12} - \frac{C_A}{C_C}J_3 + (1 - \frac{C_A}{C_C})J_{13}]\frac{\partial \mu_1}{\partial z}$$

$$- [J_{2} + J_{12} - \frac{C_{B}}{C_{C}} (J_{3} + J_{13})] \frac{\partial \mu_{2}}{\partial z}$$
(154)

The assumption of constant volume

$$J_{1}\overline{V}_{1} + J_{2}\overline{V}_{2} + J_{3}\overline{V}_{3} + J_{12}\overline{V}_{12} + J_{13}\overline{V}_{13} = 0$$
(155)

allows J_3 to be eliminated from equation (154):

$$T \frac{dS}{dt} = -PJ_{1} - QJ_{2} - RJ_{12} - WJ_{13}$$
(156)

where the expressions P, Q, R, W are defined by
$$T \frac{dS}{dt} = -J_1 \frac{\partial \mu_1}{\partial z} - J_2 \frac{\partial \mu_2}{\partial z} - J_3 \frac{\partial \mu_3}{\partial z} - J_{12} \frac{\partial \mu_{12}}{\partial z} - J_{13} \frac{\partial \mu_{13}}{\partial z}$$
(152)

Applying equations (141) and (142) gives

$$T \frac{dS}{dt} = -(J_{1} + J_{12} + J_{13})\frac{\partial \mu_{1}}{\partial z} - (J_{2} + J_{12})\frac{\partial \mu_{2}}{\partial z}$$
$$- (J_{3} + J_{13})\frac{\partial \mu_{3}}{\partial z}$$
(153)

Equation (146) allows $\frac{\partial \mu_3}{\partial z}$ to be eliminated:

$$T \frac{dS}{dt} = -[J_1 + J_{12} - \frac{C_A}{C_C} J_3 + (1 - \frac{C_A}{C_C}) J_{13}] \frac{\partial \mu_1}{\partial z}$$

$$- [J_{2} + J_{12} - \frac{c_{B}}{c_{C}} (J_{3} + J_{13})] \frac{\partial \mu_{2}}{\partial z}$$
(154)

The assumption of constant volume

$$J_{1}\overline{V}_{1} + J_{2}\overline{V}_{2} + J_{3}\overline{V}_{3} + J_{12}\overline{V}_{12} + J_{13}\overline{V}_{13} = 0$$
(155)

allows J_3 to be eliminated from equation (154):

$$T \frac{dS}{dt} = -PJ_{1} - QJ_{2} - RJ_{12} - WJ_{13}$$
(156)

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

$$P = \frac{\partial \mu_{1}}{\partial z} + \frac{c_{A}\nabla_{1}}{c_{C}\nabla_{3}}\frac{\partial \mu_{1}}{\partial z} + \frac{c_{B}\nabla_{1}}{c_{C}\nabla_{3}}\frac{\partial \mu_{2}}{\partial z}$$

$$Q = \frac{\partial \mu_{2}}{\partial z} + \frac{c_{B}\overline{\nabla}_{2}}{c_{C}\nabla_{3}}\frac{\partial \mu_{2}}{\partial z} + \frac{c_{A}\overline{\nabla}_{2}}{c_{C}\nabla_{3}}\frac{\partial \mu_{1}}{\partial z}$$

$$R = \frac{\partial \mu_{1}}{\partial z} + \frac{\partial \mu_{2}}{\partial z} + \frac{c_{A}\overline{\nabla}_{12}}{c_{C}\nabla_{3}}\frac{\partial \mu_{1}}{\partial z} + \frac{c_{B}\overline{\nabla}_{12}}{c_{C}\nabla_{3}}\frac{\partial \mu_{2}}{\partial z}$$

$$W = \frac{\partial \mu_{1}}{\partial z} + \frac{\partial \mu_{2}}{\partial z} + \frac{c_{A}\overline{\nabla}_{12}}{c_{C}\nabla_{3}}\frac{\partial \mu_{1}}{\partial z} + (1 - \frac{c_{A}}{c_{C}})\frac{\partial \mu_{1}}{\partial z} + \frac{c_{B}\overline{\nabla}_{13}}{c_{C}\overline{\nabla}_{3}}\frac{\partial \mu_{2}}{\partial z}$$

$$- \frac{c_{B}}{c_{C}}\frac{\partial \mu_{z}}{\partial z}$$

Now substituting the stoichiometric relations

$$J_A = J_1 + J_{12} + J_{13}$$

 $J_B = J_2 + J_{12}$

yields

$$T \frac{dS}{dt} = -J_{A}P - J_{B}Q - J_{12} (R - P - Q) - J_{13} (W - P)$$
(157)

Now if we assume that $\overline{V}_{12} = \overline{V}_1 + \overline{V}_2$ and $\overline{V}_{13} = \overline{V}_1 + \overline{V}_3$, leaving

$$T \frac{dS}{dt} = -J_{A} \left(\frac{\partial \mu_{1}}{\partial z} + \frac{C_{A} \nabla_{1}}{C_{C} \nabla_{3}} \frac{\partial \mu_{1}}{\partial z} + \frac{C_{B} \nabla_{1}}{C_{C} \nabla_{3}} \frac{\partial \mu_{2}}{\partial z} \right)$$
$$-J_{B} \left(\frac{\partial \mu_{2}}{\partial z} + \frac{C_{A} \nabla_{2}}{C_{C} \nabla_{3}} \frac{\partial \mu_{1}}{\partial z} + \frac{C_{B} \nabla_{2}}{C_{C} \nabla_{3}} \frac{\partial \mu_{2}}{\partial z} \right)$$
(158)

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

$$J_{A}^{V} = -L_{AA} \left(\frac{\partial \mu_{1}}{\partial z} + \frac{c_{A} \overline{V}_{1}}{c_{C} \overline{V}_{3}} \frac{\partial \mu_{1}}{\partial z} + \frac{c_{B} \overline{V}_{1}}{c_{C} \overline{V}_{3}} \frac{\partial \mu_{2}}{\partial z} \right)$$

$$-L_{AB} \left(\frac{\partial \mu_{2}}{\partial z} + \frac{c_{A} \overline{V}_{2}}{c_{C} \overline{V}_{3}} \frac{\partial \mu_{1}}{\partial z} + \frac{c_{B} \overline{V}_{2}}{c_{C} \overline{V}_{3}} \frac{\partial \mu_{2}}{\partial z} \right) \qquad (159)$$

$$J_{B}^{V} = -L_{BA} \left(\frac{\partial \mu_{1}}{\partial z} + \frac{c_{A} \overline{V}_{1}}{c_{C} \overline{V}_{3}} \frac{\partial \mu_{1}}{\partial z} + \frac{c_{B} \overline{V}_{1}}{c_{C} \overline{V}_{3}} \frac{\partial \mu_{2}}{\partial z} \right) \qquad (159)$$

$$-L_{BB} \left(\frac{\partial \mu_{2}}{\partial z} + \frac{c_{A} \overline{V}_{2}}{c_{C} \overline{V}_{3}} \frac{\partial \mu_{1}}{\partial z} + \frac{c_{B} \overline{V}_{2}}{c_{C} \overline{V}_{3}} \frac{\partial \mu_{2}}{\partial z} \right) \qquad (160)$$

Carrying out the multiplications in equations (159) and (160), equating coefficients to equations (142) and (143) and solving for L_{AB} and L_{BA} gives

$$L_{AB} = L_{BA} = -\frac{C_{1}C_{B}\overline{V}_{1}}{\sigma_{1}\eta}(1-\overline{V}_{1}C_{A}) - \frac{C_{2}C_{A}\overline{V}_{2}}{\sigma_{2}\eta}(1-\overline{V}_{2}C_{B})$$

$$-\frac{C_{A}C_{B}\overline{V}_{3}}{\sigma_{3}\eta}(\overline{V}_{1}C_{A} + \overline{V}_{2}C_{B}-1)$$

$$+\frac{C_{12}}{\sigma_{12}\eta}(1-\overline{V}_{12}C_{A})(1-\overline{V}_{12}C_{B})$$

$$+\frac{C_{13}}{\sigma_{13}\eta}(1-\overline{V}_{13}C_{A})(1-\overline{V}_{13}C_{B})$$
(161)

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

EXPERIMENTAL

Tracer Diffusivities

Tracer diffusivities for this work were measured by means of the capillary technique, 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 material.

Ordinarily, the molecules are tagged with a radioactive isotope. In this case it is easiest to measure

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the total amount of radioactivity 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 particularly 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. Material 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

б7

end is open. The other two problems 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 technique. Wirth'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 length 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 throughout 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:

$$\frac{\partial C_{i}}{\partial t} = D_{i} \frac{\partial C_{i}}{\partial z^{2}}$$
(162)

B.C. 1:
$$\frac{\partial C_{1}^{*}}{\partial z} = 0$$
 for $z = 0, t \ge 0$
B.C. 2: $-D_{1}^{*} \frac{\partial C_{1}^{*}}{\partial z} = \frac{1}{\pi} C_{1}^{*}$ for $z = 1, t \ge 0$ (163)
I.C. $C_{1}^{*} = C_{1,0}^{*}$ for $t = 0, o \le z \le L$

where C_i^* is the concentration of tagged component i, t is the time, z is the distance coordinate, $C_{i,0}^*$ is the initial value of C_i^* and R is the constant resistance to transfer from the open end of the capillary.

This boundary value problem can be easily solved by separation of variables, to give the concentration as a function of time and distance:

$$\frac{C_{i}^{*}}{C_{i,0}^{*}} = 2\sum_{n=1}^{\infty} \left[\frac{\sin \lambda_{n}L}{\lambda_{n}L + \sin \lambda_{n}L \cos \lambda_{n}L} \exp(-\lambda_{n}^{2}D_{i}^{*}t) \cos \lambda_{n}z \right]$$
(164)

where λ_n^{ε} is given by the solution of

$$\cot (\lambda_n L) = RD_{\underline{i}}^* \lambda_n$$

A detailed solution of the boundary-value problem is given in Appendix III of reference [34]

If equation (164) is integrated over the length of the capillary, a very useful ratio results:

$$\frac{C_{i,avg}^{*}}{C_{i,o}^{*}} = 2\sum_{n=1}^{\infty} \left[\frac{\sin^{2}\beta_{n}}{\beta_{n}(\beta_{n} + \sin\beta_{n}\cos\beta_{n})}\exp(-\beta_{n}^{2}\frac{D_{i}^{*}t}{L^{2}})\right] (165)$$

where β_n is given by the solution of

$$\cot \beta_n = \beta_n \frac{RD_i}{L}$$

where $C_{i,ave}^{*}$ is the average concentration in the capillary, as defined by the expression $\int_{0}^{V} C_{i}^{*} dV = C_{i,ave}^{*}V$. 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 α depends only upon the pore geometry of the frit. Therefore the group $\frac{RD_1}{L}$ 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

$$\frac{C_{i,avg}^{*}}{C_{i,o}^{*}} vs \frac{D_{i}^{*}t}{L^{2}} \text{ for several values of } \frac{RD_{i}^{*}}{L}. \text{ Then}$$

from an experiment with a chemical whose self-diffusivity is known, the value of R may be determined. Wirth did * this, using carbon tetrachloride. He determined that $\frac{RD_{1}}{L}$ had a value of 0.012, with a variation from capillary to capillary which would lead to a .7% maximum variation in measured tracer diffusivity. Consequently, the value of $\frac{RD_{1}}{T}$ was taken as 0.012.

Using a plot of
$$\frac{C_{i,avg}}{C_{i,o}}$$
 vs $\frac{D_{i}^{*t}}{L^{2}}$ for $\frac{RD_{i}}{L} = .012$,

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 $\frac{C_{i,avg}}{C_{i,o}}$. The value of $\frac{C_{i,avg}}{C_{i,o}}$ 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-1 of Appendix B. A collimated monochromatic light beam is split into two beams by a half-silvered mirror. One beam is passed through a solution in which diffusion is occurring. The other beam is passed through a reference solution in which there is no concentration gradient. When the two beams are recombined, if the optical path lengths are only slightly different, interference produces a fringe pattern.

Since the optical path length is dependent upon the refractive index of the medium, it can be shown that the fringe pattern formed by the recombination of the beams represents a plot of refractive index vs position in the diffusing system. The refractive index is in turn related to the composition of the system. By photographically recording the changes in the fringe pattern with time, the changes in composition (and hence the diffusivities) can be determined.

The diffusion cell was constructed so that a stepchange initial condition could be approximated, and so that diffusion would be one-dimensional along the vertical axis. The cell was filled from the bottom with the denser of two solutions varying slightly in composition. The less dense solution was slowly introduced down the wall of the cell, forming a layer above the denser solution. When the cell was full, and had reached equilibrium temperature in the interferometer 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 thickness 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

$$\frac{dC}{dz} = \frac{\Delta C_o}{2\sqrt{\pi D_{AB}t}} \exp(-z^2/4 D_{AB}t)$$
(166)

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 ΔC . This solution may then be written

$$\frac{dn}{dz} = \frac{\Delta n}{2\sqrt{\pi D_{AB}t}} \exp(-z^2/4 D_{AB}t)$$
(167)

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

$$\frac{n_z - n_o}{\Delta n} = \frac{1}{2} \operatorname{erf} (z / \sqrt{4D_{AB}t})$$
 (168)

Solving this for z gives

$$z = \sqrt{4D_{AB}\tau} \operatorname{erf}^{-1} \left(2\frac{n_z - n_o}{\Delta n}\right)$$
(169)

The photographic 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 = 0z_k

Z

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 value problem. The difference between the refractive indexes of the point $z = z_i$ and z = 0 is given by

$$\frac{n_{j} - n_{o}}{\Delta n} = \frac{j - \frac{1}{2}J}{J}$$
(170)

The distance between any two fringes numbered j and k is

$$z_{j} - z_{k} = \sqrt{4D_{AB}t} \left[erf^{-1} \left(2\frac{n_{j} - n_{0}}{\Delta n} \right) - erf^{-1} \left(2\frac{n_{k} - n_{0}}{\Delta n} \right) \right]$$

(171)

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:

$$z_{j} = Mz_{j}$$
(172)

where a_j 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:

$$4M^{2}D_{AB}t = \left[\frac{z_{j} - z_{k}}{erf^{-1}(\frac{2j-J}{J}) - erf^{-1}(\frac{2k-J}{J})}\right]^{2}$$
(173)

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

$$t = t_m + t_o$$

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:

slope =
$$4M^2 D_{AB}$$
 (174)
intercept = $-4M^2 D_{AB} t_0$

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 and z_k 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 (although generally it was above .999). Otherwise, the value of D_{AB} 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 of 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 $\frac{dn}{dz}$ 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 several different initial composition differences, and the graphs of reduced 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 $\frac{dn}{dz}\Big|_{max}$ is the maximum value of $\frac{dn}{dz}$, which is at the centroid for Gaussian curves.





$$z_{c} = \frac{\int_{-\infty}^{\infty} z\left(\frac{dn}{dz}\right) dz}{\int_{-\infty}^{\infty} \left(\frac{dn}{dz}\right) dz}$$
(175)

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

$$z_{c} = \frac{1}{\lambda J} \int_{-\infty}^{\infty} z\left(\frac{dn}{dz}\right) dz$$
 (176)

where $\boldsymbol{\lambda}$ is the proportionality constant.

The second moment is defined by

$$m_{2} = \frac{\int_{-\infty}^{\infty} (z-z_{c})^{2} \left(\frac{dn}{dz}\right) dz}{\int_{-\infty}^{\infty} \left(\frac{dn}{dz}\right) dz} = \frac{1}{\lambda J} \int_{-\infty}^{\infty} (z-z_{c})^{2} \left(\frac{dn}{dz}\right) dz$$
(177)

and the total area under the curve is

area =
$$\Delta n = \int_{-\infty}^{\infty} \left(\frac{\mathrm{d}n}{\mathrm{d}z}\right) \mathrm{d}z = \lambda J$$
 (178)

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, $\frac{dn}{dz}$ can be approximated from the distance between two fringes:

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

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

$$\frac{dn}{dz_{m}} = \frac{dn}{dy} \frac{dy}{dz_{m}} = \frac{dn}{dy} \tan \theta$$
 (180)

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

$$\frac{dn}{dy} = \frac{n_{j+1} - n_j}{y_{j+1} - y_j} = \frac{\lambda(j+1 - j)}{y_{j+1} - y_j} = \frac{\lambda}{y_{j+1} - y_j} (181)$$

Equation (180) can now be written

$$\frac{dn}{dz_{m}} = \frac{\lambda}{y_{j+1} - y_{j}} \tan \theta = \frac{\lambda}{\psi} \tan \theta$$
(182)

where λ and ψ 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:

$$z_{c,m} = \frac{1}{JM} \int_{-\infty}^{\infty} z_{m} \left(\frac{1}{z_{j+1} - z_{j}} \right) \begin{vmatrix} dz_{m} \\ z_{m} \end{vmatrix}$$
(183)

$$m_{2} = \frac{1}{JM^{2}} \int_{-\infty}^{\infty} (z_{m} - z_{c,m})^{2} (\frac{1}{z_{j+1} - z_{j}}) \left| \begin{array}{c} dz_{m} \\ z_{m} \end{array} \right|^{2}$$

Note that in substituting for $\frac{dn}{dz_m}$ the constant λ cancels.

The reduced second moment is defined by

$$D_{2m} = \frac{m_2}{2t}$$
 (185)

and the reduced height-area ratio is defined by

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

The measured time is not the true time, but $t = t_m + t_0$ so these can be written

$$\frac{m_2}{2} = D_{2m} t_m + D_{2m} t_0$$
(187)

$$\frac{J^{2}}{4\pi M^{2} \left[\frac{1}{z_{j+1} - z_{j}}\right]^{2}} = D_{A} t_{m} + D_{A} t_{0} \quad (188)$$

 D_{2m} 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_{2m} 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 $n = n(C_A, C_B)$. 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

$$\alpha_{A} = \frac{R_{A} \Delta C_{A}}{R_{A} \Delta C_{A} + R_{B} \Delta C_{B}}$$
(189)

we see that

$$\alpha_{A} + \alpha_{B} = 1 \tag{190}$$

The values of R_A and R_B can be determined from measurements of Δn at several different ΔC^*s by a leastsquares technique. Since accurate direct measurements of Δn require relatively large concentration differences, the preferred method is to determine the values of R_A ' and R_B ' defined by the equation

$$J = R_{A}' \Delta C_{A} + R_{B}' \Delta C_{B}$$
(191)

where $R_A' = \lambda R_A$ and $R_B' = \lambda R_B$.

This will allow smaller composition differences to be used, since J can be measured more precisely than Δn . 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 $\frac{R'}{A}$ and intercept $\frac{1}{R'}$. 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 $\frac{R'}{R} = \frac{R_A}{R_B}$ and that only this ratio is needed in defining the refractive index fraction.

Fujita and Gosting [13] 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:

$$D_{2m} = S_{2m} \alpha_A + I_{2m}$$
 (192)

$$\sqrt{D_A} = S_A \alpha_A + I_A$$
(193)

where S_{2m} and S_A are the slopes and I_{2m} 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 α_{Λ} = 1 by the expressions

 $L_{2m} = I_{2m} + S_{2m}$ (194)

$$L_A = I_A + S_A$$
(195)

Their expressions for the diffusivities are

$$D_{AA} = - \frac{\left| D_{ij} \right| + L_{2m}}{S_{2m}} \left| D_{ij} \right|^{\frac{1}{2}} + \frac{L_{2m} S_{2m} I_{A}}{S_{A}}$$
(196)

$$D_{BB} = - \frac{\left| D_{ij} \right| + I_{2m}}{S_{2m}} \frac{\left| D_{ij} \right|^{\frac{1}{2}} + \frac{I_{2m} S_{2m} L_{A}}{S_{A}}}{S_{2m}}$$
(197)

$$D_{AB} = \frac{R_2}{R_1} (I_{2m} - D_{BB})$$
 (198)

$$D_{BA} = \frac{R_1}{R_2} (L_{2m} - D_{AA})$$
 (199)

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

$$|D_{ij}|^{3/2} + (I_{2m} - I_A \frac{S_{2m}}{S_A}) |D_{ij}| - (\frac{S_{2m}}{S_A})^2 = 0$$
 (200)

A detailed derivation of these equations is given by Fujita and Gosting, or may be found in Appendix II of reference [23]. A computer program which solves equation (200) for $|D_{ij}|^{\frac{1}{2}}$ 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 $x_B \neq 1$. 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



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 $x_A \neq 0$, and decreases as $x_A \neq 1$.

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

$$CH_3 - CH_2$$

 $CH_3 - CH_2$
 $CH_3 - CH_2$
 CL
 CL

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







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 $D_i^*\eta$ products for these systems are straight lines. Furthermore, the $D_i^*\eta$ product for CCl₄ 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 [1] 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 tetrachloride 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 $D_1^*\eta$ 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°C.







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°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°C.

The tracer diffusivity-viscosity product for quinone is also given in Figure 5. The variation of this $D_A^*\eta$ product should 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°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 $D_A^*\eta$ 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 $D_B^{*}\eta$ product of 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 puzzling, 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°C.

The author measured mutual diffusivities in the system benzene - chloroform, to further test the Hartley-Crank 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 $D_{in}^*\eta$ product of the pure component is compared to the $D_{AB}\eta$ 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 this 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



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.

Error Analysis--Mutual and 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 ±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 Bidlack 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 ±1%. Further 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 into 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 ±2%.

Again, this does 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_{2m} 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_{2m} and $\sqrt{D_A}$ 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_{AA} , D_{AB} , D_{BA} , D_{BB} or D_{AA} , D_{AC} , D_{CA} , D_{CC} or D_{BB} , D_{BC} , D_{CB} , D_{CC} . 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.

| | | Predicted | Experimental | 95% Confidence |
|---|--|------------------|-----------------|----------------|
| Diffusivity xl0 ⁵ , cm ² /sec. | D _{CC} | 3.674 | 3.70 | ±1.62 |
| | D _{CA} | 544 | 1.55 | ±7.15 |
| | D _{AC} | - .942 | 80 | ± .815 |
| | D _{AA} | 2.515 | 1.74 | ±1.52 |
| Phenomenological Coefficients | L ₁₂ RT L ₂₁ RT | -3.581 -3.581 | 2.337 -2.915 | ±9.88 ±1.40 |

TABLE 2.--Predicted and Experimental Ternary Diffusivities in the System Chloroform (C) - Acetone (A) - Benzene (B) at 25°C.

From the tracer diffusivities available for this system it was difficult to determine the association characteristics. As can be seen in Figure 9 and Figure 10, the scatter in the data is large enough to mask any curvature due to association. It is probable that there may be some cross-association in the binary acetone chloroform, but the other 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 therefore assumed that the ternary system could be considered a



Figure 9.--D^{*}_in vs Mole Fraction in the System Acetone -Chloroform at 25°C.



Benzene at 25°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 experimental precision, this can be taken as empirical verification of the Onsager Reciprocal Relations.

The 95% confidence 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 extremely sensitive to the experimentally measured intercepts, and that a very slight 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 analysis, and a consideration of the experimental data, 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 developed which will allow this method to give 95% confidence levels within 20% or so for the cross-coefficients. This would then give a rigorous test of the hydrodynamic model and the Onsager Reciprocal Relation.

Error Analysis -- Ternary 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 measurement 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, which relate the change in a calculated diffusivity to a change 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

$$y = f(a_1 a_2 \dots a_n; x_1 x_2 \dots x_m)$$
 (201)

where the a_i 's are the parameters and the x_i 's are the independent variables, then the sensitivity coefficients are defined by

$$y_{a_{i}} = (\frac{\partial f}{\partial a_{i}})_{a_{i}}, x_{K} \qquad i \neq i$$

 $i, j = 1, 2, ... n$
 $K = 1, 2, ... m$ (202)

The sensitivity coefficients measure the change 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_{2m} , S_A , and S_{2m} . The functional form of this dependence is given by equations (196) through (200). Since the functional form is rather complex, analytical evaluation of the sensitivity coefficients is rather difficult. They can easily be determined numerically with the aid of a computer, however. A small change is made in the value of one of the slopes or intercepts, keeping the others constant, and the change in the diffusivities is noted. This has been done for the system measured in this study.

If the sensitivity coefficient is multiplied by the value of the arbitrary parameter, a reduced sensitivity coefficient may be defined

$$S_{a_{i}}^{y} \equiv a_{i} y_{a_{i}} = a_{i} \left(\frac{\partial f}{\partial a_{i}}\right)$$
(203)

This gives the change in the diffusivities for a onepercent change in the parameter. This is useful, since if the percentage uncertainty in experimentally measured parameters is known, the uncertainty in the diffusivities can be determined. These same arguments also hold for the phenomenological coefficients used to test the Onsager Reciprocal Relations.

If the experimental data are to be used to test a proposed model, it would be best if the sensitivity coefficients with respect to the measured parameters were as small as possible. In the case of ternary diffusivities, three independent 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 those components for which the sensitivities are lowest. It can be seen from Table 3 that in the system acetone (A) - benzene (B) - chloroform (C), the sensitivity coefficients are generally lower when the set of diffusivities D_{CC} , D_{CA} , D_{AC} and D_{AA} is chosen to describe diffusion. This is the basis for the choice made in preparing Table 2.

If the 95% confidence levels for the parameters are known, then the 95% confidence levels for the diffusivities can be approximated from the sensitivity coefficients. By assuming that the sensitivity coefficients are constant for different values of the parameters, upper and lower limits for the diffusivities may be calculated by

95% limits of
$$D_{a,j} = \pm t \sqrt{\sum_{i} y_{a_i}^2 S_e^2(a_i)}$$
 (204)

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

95%, limits on
$$a_i = \pm t \sqrt{S_e^2(a_i)}$$
 (205)

| a _i y | I _{2m} | I _A | s _{2m} | ^S A | |
|---------------------|-----------------|----------------|-----------------|----------------|-------------------|
| D _{AA} | +.12 | +.18 | +.03 | 01 | |
| D _{AB} | 09 | 10 | +.03 | +.03 | 5 |
| D _{BA} | +.12 | +.24 | 0.0 | 0.0 | x10 - |
| D _{BB} | 09 | 13 | +.03 | +.04 | |
| D _{AA} | 19 | +.34 | 0.0 | +.01 | |
| DAC | 08 | +.12 | 02 | +.02 | ×10 ⁻⁵ |
| D _{CA} | +.38 | 78 | 0.0 | 02 | |
| D _{CC} | +.16 | 27 | +.03 | 05 | |
| D _{BB} | 21 | 36 | +.03 | 04 | |
| D _{BC} | 11 | 23 | 0.0 | 0.0 | x10 ⁻⁵ |
| D _{CB} | +.42 | +.65 | 08 | +.07 | |
| D _{CC} | +.24 | +.42 | 0.0 | 0.0 | |

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

where t stands for the statistical parameter from the t-test, and $S_e^2(a_i)$ is the statistical estimate of variance of the parameter a_i , 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_{2m} and $\sqrt{D_A}$ vs α must be reduced. The

reasons for the spread in the data are difficult to determine. One probably important cause of this spread is the quality of the initial boundary. It can be seen from Table 4 that the true initial time determined from equation (187) and the D_{2m} vs t_m curves is not the same as that determined from equation (188) and the $\frac{1}{\sqrt{D_{\star}}}$ vs t_m durves. If the initial boundary had been a true step change, and the timer started the instant that flow from the cell was stopped, the true initial time would have been $t_m = 0$. It was assumed that the initial boundary is such as would have been formed by diffusion from a step-change for a short period of time. This would have resulted in a true initial boundary in which the refractive index gradient curve was Gaussian, and the true initial time would have been the same whether determined from ecuation (187) or (188).

It can be seen that the measured refractive index gradient curves in some runs are obviously not Gaussian. The curves are slightly skewed to one side or the other. Ternary diffusion from a step change boundary always 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 true initial distributions must be Gaussian. (Note that this is the true initial distribution, not the experimental boundary.) The author believes that the error introduced by a

| Run Number | t _o , sec. eq. (187) | t _o , sec. eq. (188) |
|------------|------------------------------------|------------------------------------|
| <u></u> | | |
| 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 |

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

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 might also be worthwhile to investigate other possible methods of forming the original boundary. If this boundary could be improved, the better approximation to a step-change would undoubtedly lead to better results, and less spread in the D_{2m} and $\frac{1}{\sqrt{D_A}}$ vs α curves.

In summary, the experimental results for the system acetone - benzene - chloroform support the predictions of hydrodynamic theory, within the experimental precision of the present method. Due to the extreme sensitivity of the cross-coefficients, the method presently is not capable of providing a rigorous test of the Onsager Reciprocal Relation, although it is as valid as many previously published verifications. The author believes that the method can be improved enough, through further investigation, to give a rigorous test of the Onsager Reciprocal Relation.

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SUMMARY

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 Hartley-Crank 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 failures 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 the 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 methods 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 small 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 used here to continuous association, or simultaneous self-association and crossassociation for example.

Experimental problems which lead to low precision in measurements were discussed considerably under the Ternary Diffusion error analysis. The author feels that a thorough study of the effects of 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 possible that studies of phenomena other than diffusion would be very useful here. It has been recently proposed that the chlorine atoms of carbon tetrachloride engage in a limited form of hydrogen bonding with alcohols, and therefore they might cause some very weak bonding effects in these systems which lead to the breakdown of the Hartley-Crank equation. This seems unlikely, but perhaps spectroscopic studies directed at this particular phenomenon might provide some useful information.

Theoretical work based upon hydrodynamic theory could be directed at finding a simplification of equation (80) and its generalization which could be applied to tracer diffusivity in a system with extensive association, such as ethanol - hexane, or aniline - benzene. Or equations could be developed for application to systems like aniline - toluol where there is both selfassociation and cross-association. Equations for continuous self-association as applied to tracer diffusion could be related to similar equations for mutual diffusion. This field is again open for much investigation.

APPENDICES

APPENDIX A

APPENDIX A

PROCEDURE FOR TRACER DIFFUSION

EXPERIMENT

Figure A-1 is a schematic diagram of the diffusion capillary. Specific details regarding dimensions, materials, etc. are given by Wirth [34].

Tracer solutions of the desired compositions were prepared gravimetrically to within ±.001 mole fraction, by means of a Christian and Becker Torbal torsion balance. Bulk solutions were prepared to within ±.005 mole fraction on a large analytical balance. The tracer solutions were degassed just before an experiment for 15 minutes at about 40°C to remove air from the solution.* Six capillaries were filled by the following procedure:

The foil disc, consisting of malleable nickel
 0.001 inches thick, was rolled flat to insure
 a good seal to the teflon capillary, and placed
 in the screw cap. The capillary was inserted

Air bubbles coming out of solution during the run and drifting up to the glass disc were one of the principle experimental difficulties. They would mix the contents of the capillary as they drifted upwards, and probably changed the resistance constant in the boundary condition at the capillary end.



Figure A-1.--Schematic Diagram of the Modified Capillary Cell.
into the screw cap, and tightened with a pair of pliers to insure a good seal to the foil disc.

- 2. The capillary was immersed to within one half inch in the bulk solution, and the bulk container was placed in a thermostat to equilibrate at 25°C for one hour.
- 3. The capillaries were then filled with degassed tracer solution by a .50 cc tuberculin syringe, with a 19 ga needle cut to the same length as the capillary. Great care was taken to avoid trapping air bubbles in the capillary. The syringe was emptied of air bubbles by inverting and ejecting some of the solution. The syringe was then inserted in the capillary, and withdrawn slowly, discharging solution as it was removed. A puddle of tracer solution was left covering the top of the capillary.
- 4. The glass 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 bubbles were trapped, and with the puddle of tracer solution covering the frit.
- 5. The frit holder was then placed over the end of the capillary. By this time the excess tracer mentioned above had generally evaporated. To

prevent the frit from drying out and trapping air, the depression in the frit holder was filled with tracer solution. The entire assembly was then placed in the bulk solution, washing away the excess tracer solution in the process.

After all six capillaries had been filled, the top was placed on the bulk container, leaving the vent open until the vapor pressure could drive 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 all six capillaries.

After three to five days, depending upon the diffusivity, the bulk solution was removed from the thermostat. The six capillaries were emptied into nylon counting vials as follows:

- 5 cc of scintillation fluid was placed in the bottom of the counting vial, and a syringe was filled with 10 cc of scintillation fluid for step number (4) below.
- 2. The capillary was removed from the bulk solution, and the frit holder carefully removed without disturbing the frit. The excess solution on the frit was allowed to evaporate.
- 3. The capillary was inverted into the counting vial, which washed the frit from the end. The

end of the capillary was kept beneath the surface to avoid flash evaporation of tracer solution.

- 4. The conical depression in the screw cap was filled with fluid from the syringe mentioned in step (1). The foil disc was then punctured by the syringe needle, and tracer solution flushed from the capillary with scintillation fluid. When 2 or 3 cc remained in the syringe, the capillary was removed from the vial, and washed off with the remaining scintillation fluid, so that all the tracer solution was in the vial.
- 5. The counting vial was capped, and identified by the capillary number. It was shaken gently to thoroughly mix the contents, and the glass frit was removed. The glass frit was washed in acetone to remove scintillation material in preparation for the next experiment.

This procedure was repeated for all six capillaries, and the time recorded. The emptying process took about 20 minutes.

The capillaries and screw caps were then cleaned with acetone, dried, and prepared as before. Initial counts were then prepared as follows:

- A counting vial was prepared as in step (1) of the emptying procedure.
- 2. The capillary was filled with tracer solution as in step (3) of the filling procedure, except that the puddle was kept as small as possible, ideally covering only the opening of the capillary.*
- 3. The excess tracer solution was allowed to evaporate until level with the surface of the capillary. The capillary was then quickly inverted into the counting vial, and flushed as in the previous emptying procedure. The vial was then identified by the capillary number as an initial count.

This procedure had to be modified slightly for solutions containing a high 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 depression into the capillary before all the solution had evaporated from the surface.

The capillaries were filled with a solution for which wetting was not a problem, and emptied in the usual manner. They were then refilled with the same solution, and allowed to evaporate to the same estimated depth as the problem 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 estimated by eye, this procedure introduces 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 equipment was then cleaned and prepared for the next run.

The initial and final 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 calculated for the six capillaries) was greater than 5%, i.e. $\pm 2.5\%$ from the mean value, the experiment was discarded. This was to eliminate those runs in which there may have been convective mixing within the capillaries. Since the magnitude of such effects depends upon when during the experiment they occurred, convection would cause a spread in the values of the diffusivity as well as an increase in the apparent value. It was felt that this screening procedure would eliminate those runs in which convection occurred.

APPENDIX B

APPENDIX B

PROCEDURE FOR MUTUAL DIFFUSION

EXPERIMENT

Figure B-1 is a schematic diagram of the Mach-Zehnder 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 Bidlack [4], as are instructions for alignment and adjustment of mirrors to produce the proper fringe pattern.

Two solutions with slightly 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 the proper number of fringes, depending upon the refractive indexes of the two components. The cell was filled according to the following procedure:

- The plunger was placed in the filling syringe, and all valves were closed, except valve 2.
- 2. Approximately 40 cc of the denser solution were placed in reservoir B, and the top of the







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 cell to just below the level of the slit. The filling syringe was then used to draw fluid back and forth through valve 5 to remove air bubbles trapped near the valve stem. Solution was then allowed to fill the cell to about one half inch above the slit. Valve 5 was then closed.
- 4. Valve 4 was then opened. Solution was forced through valve 4 by the filling syringe, until the solution level in the cell was just above the slit. Care was taken not to force any air from the cell into the siphon line. Valve 4 was then closed, and valve 5 opened. Solution was allowed to flow into the cell until the level was again one half inch above the slit.
- 5. Step (4) was repeated until fluid flowed from the siphon line, to insure 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 value 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 opening 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.
- Valve 2 was closed, and the filling syringe filled with the less dense solution. The plunger was then replaced.
- 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 three 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.

11. The less dense solution was then added to reservoir A until the level was even with that in reservoir B. Reservoir A was then covered

with aluminum foil to retard evaporation. The diffusion cell was now ready to be placed in the water bath for the exteriment.

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

The cell was then placed in the water bath. Valves 1 and 5 were opened several turns each. Valve three was then opened until the flow rate from the siphon was approximately one drop every six seconds. Valve 4 was then opened until the flow rate was one drop every three seconds. It was important that the flow rate be the same from each side of the cell 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 would be symmetric about the boundary.

It usually took about 20 to 30 minutes for the cell to reach the equilibrium temperature, and for a good boundary to form. When the boundary had formed, values

3, 4, and 5 were closed and the timer started. A series of seven pictures, at intervals of 2 minutes were taken. (In the faster diffusing systems, the intervals were somewhat shorter.) In some cases, valves 3, 4 and 5 were again opened, another boundary formed, and a second set of pictures taken.

The photographic plate, a Kodak Type M plate, was developed by the following procedure:

- The plate was developed for 5 minutes in Kodak D-19 High Contrast Developer, with intermittent agitation.
- The development was then stopped by a oneminute soak, with continual agitation, in tap water.
- 3. The image was then fixed by a 5-minute soak, with intermittent agitation, in Kodak Rapidfix.
- 4. The plate was then removed from the fixer, and washed for about one minute under running water, and then allowed to dry for at least 2 hours before measurement.

The photographic plates were extremely sensitive to light, and had to be handled in absolute darkness (no safe light) throughout the entire procedure, until the 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 enough to throw the image out of focus, and perhaps change the magnification factor of the camera. The developer and fixer were replaced after every ten runs, in order to maintain a consistently high image quality in development.

APPENDIX C

APPENDIX C

COMPUTER PROGRAMS FOR DATA ANALYSIS

The following computer program uses measured values of the slopes and intercepts to calculate experimental values of the ternary diffusivities. The program language is FORTRAN IV, with specific deck structure forl the IBM 1800 computer of the College of Engineering, Michigan State University. One constant, R^2/R^1 , must be specified within the program at the designated point. Other data (the slopes and intercepts) is read by the computer.

// JØB // FØR TDIFF *IØCS (CARD, 1443 PRINTER) *EXTENDED PRECISIØN *NØNPRØCESS PRØGRAM *ØNE WØRD INTEGERS *LIST SØURCE PRØGRAM REAL 12M, IA, L2M, LA CØMMØN X READ (2, 10) I2M, IA, S2M, SA l 10 FØRMAT (4 E 10.5) LA = IA + SAL2M = I2M + S2MIF (I2M) 3, 4, 3 WRITE (3, 20) I2M, IA, S2M, SA, L2M, LA FØRMAT (1H1, 6 E 15.5) 3 20 С THE VALUE ØF R = R2/R1 MUST BE SPECIFIED С С AT THIS PØINT С R = .42999e.g.

| 40 41 42 43 | CALL PRTS (12M, IA, S2M, SA) D11 = -(X**2 + L2M * X + (L2M * IA * S2M/SA))/S2M D22 = (X**2 + I2M * X + (I2M * LA * S2M/SA))/S2M D12 = (I2M - D22) * R D21 = (L2M - D11) / R WRITE (3,40) D11 WRITE (3,42) D21 WRITE (3,43) D22 FØRMAT (8H DAA = , E15.5) FØRMAT (8H DAB = , E15.5) FØRMAT (8H DBA = , E15.5) FØRMAT (8H DBB = , E15.5) |
|--|---|
| 4 4 | GØ TØ 1 CØNTINUE CALL EXIT END |
| // FØR *EXT *ØNE *NØN *LIS | PRTS ENDED PRECISIØN WORD INTEGERS PROCESS PRØGRAM T SØURCE PRØGRAM |
| | <pre>SUBRØUTINE PRTS (CT2M, CTA, S2M, SA) DIMENSIØN A(4), B(4), C(4) CØMMØN X N = 3 N1 = N + 1 A(1) = 1 A(2) = CT2M - CTA * S2M/SA A(3) = C A(4) = -(S2M/SA)**2</pre> |
| C C C | N IS DEGREE ØF PØLYNØMIAL P IS PØLYNØMIAL EVALUATED AT X CP IS DERIVATIVE EVALUATED AT X |
| 10 | X = .000001 CALL SYND (A, B, C, X, P, DP, N, N1) XPRE = X X = XPRE - P/DP IF (1.0E-11-ABS(X-XPRE)) 10, 11, 11 |
| 11 | CØNTINUE RETURN END |

```
// FØR SYND
   *EXTENDED PRECISIÓN
   *ØNE WØRD INTEGERS
   *NØNPROCESS PRØGRAM
   *LIST SZURCE PRØGRAM
         SUBRØUTINE SYND (A, B, C, X, P, DP, N, N1)
         DIMENSI\deltaN A(4), B(4), C(4)
         B(1) = A(1)
        D\vec{z} \vec{z} \vec{z}, N\vec{z}
        B(I) = A(I) + X * B (I-1)
         C(1) = B(1)
        D\emptyset 2 I = 2, N1
        C(I) = B(I) + X * C(I-1)
         P = B(N1)
        \cdot DP = C(N)
         RETURN
         END
// XEQ TDIFF
*CC END
```

The following program predicts ternary diffusivities in a non-associated system from friction coefficients, molar volumes, viscosities and the Margules constants of the binary systems. These constants must be read as in data. The program language is FORTRAN IV, with specific deck structure for the IEM 1800 computer of the College of Engineering, Michigan State University.

// JØB // FØR PRED *IØCS (CARD, 1443 PRINTER) *LIST SØURCE PRØGRAM *NØNPROCESS PRØGRAM *EXTENDED PRECISIØN *ØNE WØRD INTEGERS REAL LNG1, LNG2, LNA, LNB READ (2, 200) A12, A21, A13, A31, A23, A32, C FØRMAT (7F 10.5) READ (2, 201) ETA

```
200
          FØRMAT (F10.5)
          IF (ETA) 1, 2, 1
          READ (2, 202)V1, V2, V3
1
          READ (2, 202) SIG1, SIG2, SIG3
          READ (2, 202) XA, XB, XC
FZRMAT (3F10.5)
202
С
С
          SIG1 REPRESENTS RT/(FRICTI2N CØEFF)
С
          ØF CØMPØNENT 1 ØR A
С
          VOLD = XA * C1 + XB * V2 + XC * V3
          CA = XA/VZLD
          CB = XE/VZLD
          CC = XC/V&LD
          LNG1 = 2 \times XA \times XB \times (A21 - XA \times A21 - XB \times A12) + XE \times XB \times A12
                + 2*XA*XC*(A31-XA*A31-XC*A13) + XC*XC*A13
       1
       2
                + (XB*XC-2*XA*XB*XC) * (A21 + A13 + A32 - C)
          XAP = XA
          XBP = XB
          XCP = XC
          LNG2 = 2.*XB*XA*(A12-XB*A12-XA*A21) + XA*XA*A21
               + 2.*XB*XC*(A32-XB*A32-XC*A23) + XC*XC*A23
       l
       2
               + (XA*XC-2.*XA*XB*XC)*(A21 + A13 + A32 - C)
          LNA = LNG1 + ALØG (XA)
          LNB = LNG2 + ALØG (XB)
          VCNEW = VÓLD - (XA + .003) * V1 - XE * V2
          CMØLS = VCNEW/V3
          TMØLS = XA + XB + .003 + CMOLS
          XA = (XA + .003)/TMØLS
          XB = XB/TMØLS
          XC = CMØLS/TMØLS
          LNG1 = 2.*XA*XB*(A21-XA*A21-XB*A12) + XB*XB*A12
                + 2.*XA*XC*(A31-XA*A31-XC*A13) + XC*XC*A13
       1
                + (XB*XC-2.*XA*XB*XC) * (A21 + A13 + A32 - C)
       2
          LNG2 = 2.*XB*XA*(A12-XB*A12-XA*A21) + XA*XA*A21
                + 2.*XB*XC*(A32-XB*A32-XC*A23) + XC*XC*A23
       1
                + (XA*XC - 2.*XA*XB*XC) * (A21 + A13 + A32 - C)
       2
          DADCA = (LNG1 + ALOG(XA) - LNA) * VOLD/.003
          DBDCA = (LNG2 + ALOG(XB) - LNB) * VOLD/.003
          VCNEW=VØLD - XAP * V1 - (XBP + .003) * V2
          CMOLS = VCNEW/V3
          TMØLS = XAP + XBP + CMØLS + .003
          XA = XAP/TMØLS
          SB = (XBP + .003)/TMØLS
          XC = CMØLS/TMØLS
```

| | LNG1 = 2.*XA*XB*(A21-XA*A21-XB*A12) + XB*XB*A12 + 2.*XA*XC*(A31-XA*A31-XC*A13) + XC*XC*A13 + (XB*XC-2.*XA*XB*XC) * (A21+A13+A32-C) LNG2 = 2.*XB*XA*(A12-XB*A12-XA+A21) + XA*XA*A21 + 2.*XB*XC*(A32-XB*S32-XC*A23) + XC*XC*A23 + (XA*XC-2.*XA*XB*XC) * (A21*A13+A32-C) DADCB = (LNG1 + ALØG(XA) - LNA) * VØLD/.003 DBDCB = (LNG2 + ALØG(XB) - LNB) * VØLD/.003 |
|---------------------------------|--|
| 100 | WRITE (3,100) WRITE (3,101) DADCA, DBDCA, DADCB, DBDCB FORMAT (1' DADCA DEDCA DADCB + DBDCB ') XA = XAP XB + XBP XC + XCP |
| | DAA = DADCA/ETA*CA*(SIGl*(1V1*SIG1) + SIG3*V3*CA) + DBDCA/ETA*CA*CB*(V3*SIG3-V2*SIG2) DAB = DADCB/ETA*CA*(SIG1*(1V1*SIG1) + SIG3*V3*CA) + DBDCB/ETA*CA*CB*(V3*SIG3-V2*SIG2) DBA = DADCA/ETA*CA*CB*(V3*SIG3-V1*SIG1) + DBDCA/ETA*CB*(SIG2*(1V2*CB) + SIG3*V3*CB) DBB = DBDCB/ETA*CB*(SIG2*(1V2*CB) + SIG3*V3*CB) + DBDCB/ETA*CB*(SIG2*(1V2*CB) + SIG3*V3*CB) |
| | WRITE (3,105) WRITE (3,106) DAA WRITE (3,107) DAB WRITE (3,108) DBA WRITE (3,109) DBB |
| 105 106 107 108 109 | <pre>FORMAT (1H , // 'THE PREDICTED DIFFUSIVITIES ARE ',/) FORMAT (1H , 'DAA = ' , F 15.5) FORMAT (1H , 'DBA = ' , F 15.5) FORMAT (1H , 'DBA = ' , F 15.5) FORMAT (1H , 'DBB = ' , F 15.5)</pre> |
| | GO TO 1 |
| | CALL EXIT END |
| // XH * C(| EQ PRED |

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APPENDIX D

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APPENDIX D

TERNARY INTERMEDIATE DATA

TABLE D-1.--Data at equimolar concentrations in the system Chloroform(A) - Acetone(B) - Benzene(C)

| CA | = | 4.097 moles/Lit. |
|----------------------------|---|-------------------------------|
| ° _B | = | 4.097 moles/Lit. |
| ° _C | = | 4.097 moles/Lit. |
| \overline{v}_{A} | = | .0807 Lit/mole |
| \overline{v}_{B} | = | .0740 Lit/mole |
| \overline{v}_{c} | = | .0894 Lit/mole |
| $\frac{RT}{\sigma_A}$ | = | $1.290 \times 10^{-7} $ dynes |
| $\frac{R_{+}}{\sigma_{B}}$ | = | 1.493×10^{-7} dynes |
| $\frac{RT}{\sigma_{C}}$ | = | 1.307×10^{-7} dynes |
| η | = | .487 cp |
| a | = | .4317 RT |
| ď | = | .0701 RT |
| с | = | .0978 RT |
| d | = | .3260 RT |
| | | |



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





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









(A) - Benzene (B).









| TABLE | D-2Slopes | and | Intercepts | from | Figures | D-4 |
|-------|-----------|-----|------------|---------------|---------|-----|
| | | | through I | D - 9. | | |

In the Acetone(A) - Benzene(B) - Chloroform(C) system from Figures D-4 and D-5: $I_{2m} = 1.782 \times 10^{-5}$ $I_{2m} = 1.018 \times 10^{-5}$ $I_{A} = 225.5$ S_A = -37.6 In the Chloroform(C) - Acetone(A) - Benzene(C) from Figures D-6 and D-7: $I_{2m} = 2.406 \times 10^{-5}$ $s_{2m} = -.569 \times 10^{-5}$ $I_{A} = 199.9$ $S_{A} = 19.6$ In the Benzene(B) - Chloroform(C) - Acetone(A) system from Figures D-8 and D-9: $I_{2m} = 2.856 \times 10^{-5}$ $S_{2m} = -.470 \times 10^{-5}$ $I_A = 184.5$ $S_{A} = 16.4$

APPENDIX E

APPENDIX E

EXPERIMENTAL RESULTS

| Table E- | 1Experimental | Binary | Mutual | Diffusivit | ;ies | in | the |
|--------------|-----------------|--------|---------|------------|------|------|-----|
| ${f System}$ | Chloroform(A) - | Carbon | Tetrach | loride(B) | at | 25°C |). |

| × _A | D _{AB} x 10 ⁵ , cm ² /sec |
|----------------|--|
| 0.234 | 1.557 |
| 0.234 | 1.572 |
| 0.690 | 1.680 |
| 0.774 | 1.757 |
| 0.774 | 1.779 |
| 0.946 | 1.976 |
| 0.977 | 2.007 |

TABLE E-2.--Experimental Binary Mutual Diffusivities in the System Benzene(A) - Chloroform(B) at 25°C.

| ×A | D _{AB} x 10 ⁵ , cm ² /sec |
|---|--|
| 0.005 0.005 0.207 0.345 0.345 0.4988 0.49889 0.779 0.79 | 2.345 2.359 2.414 2.448 2.495 2.419 2.396 2.348 2.344 2.265 |
| | |
| × _A | D _{AB} x 10 ⁵ , cm ² /sec |
|----------------|--|
| 0.005 | $1.50 \pm .05$ |
| 0.200 | $1.95 \pm .06$ |
| 0.400 | $2.38 \pm .14$ |
| 0.600 | $2.99 \pm .20$ |
| 0.800 | $3.76 \pm .34$ |
| 0.995 | $4.59 \pm .07$ |

TABLE E-3.--Experimental Binary Mutual Diffusivities in the System Ether(A) - Carbon Tetrachloride(B) at 25°C.

TABLE E-4.--Experimental Binary Mutual Diffusivities in the System p-benzoquinone(A) - Benzene(B) at 25°C.

| ×A | D _{AB} x 10 ⁵ , cm ² /sec |
|---|--|
| $\begin{array}{c} 0.0041 \\ 0.0057 \\ 0.0132 \\ 0.0239 \\ 0.0266 \\ 0.0315 \\ 0.0434 \end{array}$ | 2.20 2.16 2.09 1.98 1.95 1.96 1.94 |

TABLE E-5.--Experimental Tracer Diffusivities in the System 2-Butanone(A) - Carbon Tetrachloride(B) at 25°C.

| ×A | $D_A^* \times 10^5$, cm^2/sec | $D_B^* \times 10^5$, cm ² /sec |
|--|---|--|
| 07885N1 0347885N1 0.46999 0.999 | 1.611 2.260 2.720 3.183 3.300 | 1.320 2.973 |
| | , | |

| × _A | D _A x 10 ⁵ , cm ² /sec | D [*] _B x 10 ⁵ , cm ² /sec |
|---------------------------------------|---|--|
| 0.0000 <0.0010 0.0103 0.0464 | 2.32 2.11 2.11 | 2.137 |

TABLE E-6.--Experimental Tracer Diffusivities in the System p-benzoquinone(A) - Benzene(B) at 25°C.

TABLE E-7.--Experimental Tracer Diffusivities in the System Ether (A) - Carbon Tetrachloride(B) at 25°C.

| ×A | $D_A^* \times 10^5$, cm ² /sec | $D_B^* \times 10^5$, cm ² /sec |
|--|---|--|
| 0.000 0.024 0.024 0.332 0.530 0.850 0.999 1.000 | 1.629 ± .082 1.674 ± .084 2.636 ± .132 3.796 ± .190 5.383 ± .269 7.91 ± .396 | 1.32 4.395 ± .220 |

TABLE E-8.--Experimental Density and Viscosity in the System p-benzoquinone(A) - Benzene(B) at 25°C.

| × _A | density, g/ml | viscosity, cp |
|----------------|---------------|---------------|
| 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 |

| ×A | density, g/ml | viscosity, cp |
|--------|---------------|---------------|
| 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 |

TABLE E-9.--Experimental Density and Viscosity in the System Ether(A) - Carbon Tetrachloride(B) at 25°C.

TABLE E-10.--Experimental Density and Viscosity in the System Acetone(A) - Benzene(B) - Chloroform(C) at 25°C.

| × _A | × _B | × _C | density, g/ml | viscosity, cp |
|----------------|----------------|----------------|---------------|---------------|
| 0.328 | 0.339 | 0.333 | 1.0457 | 0.4869 |
| 0.339 | 0.332 | 0.329 | 1.0427 | 0.4870 |

APPENDIX F

APPENDIX F

THERMODYNAMIC DATA

TABLE F-1.--Activity Data for Acetone (1) - Benzene (2) at 25°C (from Timmermans [30]).

| x ₂ | lnγ ₂ , | lnγ ₂ , | lnγ _l , | lnγ _l , |
|----------------|--------------------|-------------------------|--------------------|--------------------|
| | exp. | eq. (24) | exp. | eq. (25) |
| 0.1251 | .5002 | .4827 | .0011 | .0060 |
| 0.2500 | .3937 | .3896 | .0265 | .0278 |
| 0.3652 | .3122 | .3022 | .0662 | .0669 |
| 0.5550 | .1829 | .1672 | .1802 | .1835 |
| 0.7150 | .0898 | .0750 | .3400 | .3452 |
| 0.8249 | .0659 | .0300 | .4846 | .4966 |
| 0.8862 | .0387 | .0131 | .5793 | .5971 |
| 0.9500 | .0301 | .0026 | .7169 | .7148 |
| Margules | constants: | A ₁₂ = .8169 | | |
| | | A ₂₁ = .5685 | | |

TABLE F-2.--Activity Data for Acetone (1) - Chloroform (3) at 25°C (from Hildebrand and Scott [21]).

| ×3 | lny ₃ , | lnγ ₃ , | lnγ _l , | lnγ _l , |
|----------|--------------------|----------------------------------|--------------------|--------------------|
| | exp. | eq. (24) | exp. | eq. (25) |
| .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 |
| Margules | constants: | $A_{13} =9791$ $A_{31} =7372$ | | |

| ×2 | lnγ ₂ | lnγ ₂ | lny ₃ | lnγ ₃ |
|----------|------------------|----------------------------------|------------------|------------------|
| | exp. | eq. (24) | exp. | eq. (25) |
| 0.1340 | 3439 | 2248 | +.0119 | 0066 |
| 0.2600 | 2837 | 1548 | +.0109 | 0237 |
| 0.3180 | 1767 | 1278 | 0131 | 0347 |
| 0.6400 | 0598 | 0299 | 0845 | 1225 |
| 0.7160 | 0284 | 0178 | 1301 | 1480 |
| 0.8660 | 0202 | 0036 | 1532 | 2012 |
| Margules | Constants: | $A_{23} =3180$ $A_{32} =2500$ | | |

TABLE F-3.--Activity Data for Benzene (2) - Chloroform (3) at 25°C (from Timmermans [30]).

TABLE F-4.--Constants for use in equations (20) through (24) for the system Acetone (1) - Benzene (2) - Chloroform (3) at 25° C.

| A | 12 = | .8169 | | |
|----------------------------|---|---|--|--|
| A | 21 = | .5685 | | |
| А | 13 = | 9791 | | |
| А | 31 = | 7372 | | |
| А | 23 = | 3180 | | |
| А | 32 = | 2500 | | |
| C | = | 0.0 | | |
| A A A A A C | 12 = 21 = 13 = 31 = 23 = 32 = = = | .8169 .5685 9791 7372 3180 2500 0.0 | | |

APPENDIX G

APPENDIX G

NOMENCLATURE

Capitals

| А | interaction perameter |
|-----------------|--|
| С | concentration, interaction parameter |
| D | diffusivity |
| D | Onsager diffusivity |
| D _{2m} | reduced second moment |
| D _A | reduced height-area ratio |
| EV | energy of vaporization |
| F | force |
| G | Gibbs free energy |
| Н | enthalpy of mixing |
| I _{2m} | intercept of second-moment curve at $\alpha = 0$. |
| IA | intercept of height-area ratio curve at α = 0. |
| J | flux, fringe number |
| К | equilibrium constant |
| L | phenomenological coefficient; length of capillary |
| L _{2m} | intercept of second-moment curve at α = 1.0 |
| LA | intercept of height-area ratio curve at α = 1.0 |
| М | magnification factor of camera |
| N | number of species in solution |
| P, Q | simplifying constants |

- R gas law constant; refractive index constant; simplifying constant
- S entropy
- S_{2m} slope of second-moment curve
- S_A slope of height-area ratio curve
- S² statistical variance
- S^y reduced sensitivity coefficient
- T temperature
- V volume
- W simplifying constant
- Y thermodynamic parameter

Small

| a | activity; arbitrary parameter; Miller coefficient |
|-------|---|
| b,c,d | Miller coefficients |
| f | arbitrary function |
| j | fringe number |
| m | moment |
| n | number of moles; refractive index |
| t | time; statistical t-test parameter |
| V : | velocity |
| x | mole fraction |
| Z | distance |

Greek Capital

- ∆ difference
- Σ summation

Greek small

- α proportionality constant; refractive-index fraction; simplifying constant
- β simplifying constant
- β_n eigen value
- γ activity coefficient; simplifying constant
- δ solubility parameter; Kroneker delta; simplifying constant
- η viscosity
- θ time
- λ proportionality constant
- λ_n eigen value
- μ chemical potential
- π constant 3.14159 ...
- σ constant in friction coefficient
- φ volume fraction

Subscripts

| а | refers to | activity-defined equilibrium constant |
|-------|-----------------------|--|
| с | refers to | laboratory-fixed coordinates |
| m | refers to | medium-fixed coordinates |
| Y | refers to constant | activity-coefficient-defined equilibrium |
| А,В,С | 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 force |

| S | refers to | sphere |
|-----|-----------|--------------------------|
| V | refers to | volume-fixed coordinates |
| j | refers to | fringe number j |
| Z | refers to | distance z |
| 0 | refers to | initial value |
| ave | refers to | average value |
| max | refers to | maximum value |

Superscripts

| m | refers to | medium-fixed | reference | plane |
|---|------------|---------------|-----------|-------|
| V | refers to | volume-fixed | reference | plane |
| 0 | refers to | standard-stat | e | |
| * | refers to | tagged specie | es | |
| 1 | refers to | related quant | tity | |
| _ | molar prop | erty | | |
| , | | | | |



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