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ALIMADADIAN, Abbas, 1939-MULTICOMPONENT MOLECULAR DIFFUSION IN LIQUID SYSTEMS.

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The University of Oklahoma, Ph.D., 1971 Engineering, chemical

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### THE UNIVERSITY OF OKLAHOMA

### GRADUATE COLLEGE

# MULTICOMPONENT MOLECULAR DIFFUSION

### IN LIQUID SYSTEMS

### A DISSERTATION

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### SUBMITTED TO THE GRADUATE FACULTY

## in partial fulfillment of the requirements for the

### degree of

## DOCTOR OF PHILOSOPHY

ΒY

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Norman, Oklahoma

# MULTICOMPONENT MOLECULAR DIFFUSION

# IN LIQUID SYSTEMS

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#### ACKNOWLEDGEMENTS

The author wishes to express his appreciation to the following individuals and groups for their contributions:

Dr. C. P. Colver, with whom it has been a great honor to be associated, for personal and professional guidance;

Dr. F. B. Canfield, Dr. S. Christian, Dr. C. M. Sliepcevich, and Dr. K. E. Starling for being members of my advising committee;

Mr. Charles J. Vadovic, for his assistance during the preparation of this manuscript;

Miss Mary Anne Matthews for doing the drawings;

Mr. Walt Ford for his assistance in obtaining experimental data;

The National Science Foundation for partial support of this research under Research Grant No. GK 1023.

Finally, I wish to express my deepest appreciation to my mom and dad and my wife.

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#### ABSTRACT

A modified absolute rate theory for predicting multicomponent diffusion and phenomenological coefficients was developed. The predicted values of the diffusion coefficients were in excellent agreement with experimental data obtained in this research as well as those taken from the literature. Phenomenological coefficients were also calculated and compared with those obtained from experimental data. Again, calculated values were in agreement with those obtained from the data.

Experimental data were used to test the Onsager Reciprocal Relations. For the four systems studied these relations were verified within the limits of experimental error.

The diffusion coefficients for the two ternary systems Acetone-Benzene-Methanol, and Acetone-Ethanol-Water were measured at 25°C. The binary diffusion coefficients for the systems, Acetone-Benzene; Acetone-Methanol; Benzene-Methanol; Acetone-Water; Ethanol-Water; and Acetone-Ethanol were also measured at 25°C. The diffusion apparatus consisted basically of a double Savart plate birefringent interferometer, a constant temperature air bath, and a flowing junction diffusion cell.

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Data on the Acetone-Benzene-Carbon tetrachloride system at one concentration level were measured at 25°C in order to confirm the experimental technique used to obtain the ternary diffusion data. These data were in excellent agreement with the data of Cullinan and Toor.

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### MULTICOMPONENT MOLECULAR DIFFUSION

### IN LIQUID SYSTEMS

### CHAPTER I

### INTRODUCTION

In the design of equipment for many chemical processes involving mass transfer, accurate values of multicomponent diffusivities are needed. Experimental data for such systems are virtually nonexistent and, perhaps more seriously, there exists no diffusional theory to predict these diffusivities. Our inability to estimate, a priori, multicomponent diffusivities results in large part from the lack of a usable kinetic theory for the liquid state. Consequently, we are forced to turn to semi-theoretical models for the prediction of liquid diffusivities.

If a semi-theoretical correlation is to be used with any degree of confidence, it should be checked against experimental data for a large number of systems. Further, the testing of any presently available theory requires activity data and such data are very scarce, especially for multicomponent systems. However, in the absence of experimental data, multicomponent activity coefficients

can be estimated from available binary data using relationships such as the Wilson equation (87).

To date, the diffusional behavior of only about twenty ternary systems has been experimentally studied. Unfortunately, much of the earlier data are unreliable, and for the most part ternary studies have been carried out at only one or two concentration levels. Moreover, for the great majority of systems, activity data are not available.

From the above discussion, it is clearly evident that accurate measurements of ternary diffusion coefficients are urgently needed not only for the purpose of obtaining design data but for use in the development and testing of accurate prediction methods. And further, either ternary or binary activity data should be available for the ternary systems selected. Accordingly, the purpose of this research can be summarized as follows;

- The modification and refinement of the experimental facility in general and the birefringent interferometer in particular, in order to produce accurate ternary data.
- The development of an accurate method for analyzing the data and/or modification of the available methods.
- 3) The measurement of ternary diffusion coefficients on one or more systems possessing nonideal behavior; and for which activity data are available or can be estimated.

- Development of a semi-theoretical correlation for ternary diffusion based on the modified absolute rate theory.
- 5) Testing of the correlation developed against data produced by this research as well as reliable data from the literature.
- 6) Testing of the Onsager Reciprocal Relations.

#### CHAPTER II

#### LITERATURE SURVEY

### General Background

Molecular diffusion was first treated quantitatively by Fick in 1855 (31). He postulated an equivalence between molecular transport by diffusion and thermal transport by conduction. With this Fick laid the foundation for study of the molecular transport of matter.

Two laws of molecular diffusion are attributed to Fick. The first law may be written as

$$J_{A} = -D_{AB} \text{ grad } C_{A} \tag{1}$$

where  $J_A$  is the flux of molecular species A relative to mass, molar, or volume average velocity,  $D_{AB}$  is the mutual molecular diffusion coefficient of species A in species B, and grad  $C_A$  is the concentration gradient of species A.

The second law of Fick is derived from a consideration of unsteady state diffusion. Tyrrell (80) has pointed out that Fick considered the important contribution of his work to be formulation of the differential equation, now known as Fick's second law,

$$\frac{\partial C_A}{\partial t} = \operatorname{div}(D_{AB} \operatorname{grad} C_A)$$
 (2)

where t is time. There has been considerable work in binary diffusion since Fick (31) presented his equation defining the diffusion coefficient. Although the interest in molecular diffusion for binary systems has existed for over a century, it was not until 1945 that Onsager (58) presented equations for multicomponent liquid diffusion by describing the flux of each component as the linear sum of every concentration gradient multiplied by a diffusion coefficient. Moreover, experimental work in ternary liquid diffusion was almost nonexistent until Baldwin, Dunlop, and Gosting (1,18) in 1955 presented equations similar to Onsager's relationship, along with experimental techniques for obtaining multicomponent (ternary) diffusion coefficients. This work represented the major step necessary for generation of significant new interest in the study of multicomponent liquid diffusion.

Gosting and coworkers (1,18,32,33) have periodically presented improved experimental techniques for ternary diffusion measurements utilizing Gouy interferometry. Toor and coworkers (5,8,73) have adapted the diaphragm cell method to obtain multicomponent diffusion coefficients. Furlong (34) selected an optically-monitored diaphragm cell as his experimental method. Kett (48) obtained data with an optical diffusiometer, utilizing a Mach-Zender interferometer. To date, about twenty ternary systems have

been studied with various experimental techniques.

### Generalization of Fick's Law

The linear relation between diffusional fluxes and concentration gradients may be written for a system of n components as

$$C_{i}U_{i} = -\sum_{j=1}^{n} -D_{ij} \nabla C_{j} + C_{i}U$$
(3)

The choice of concentration units and the reference velocity is arbitrary. However, the  $\mathcal{D}_{ij}$ 's are not defined before the concentration units and reference velocity are specified. A completely defined set of flux equations is obtained from equation (3) as

$$C_{i}U_{i} = -\sum_{j=1}^{n} \bigoplus_{ij}^{xc} \nabla C_{j} + C_{i}U^{x}$$
(4)

The superscripts on diffusivities  $\mathcal{D}_{ij}^{xc}$  indicate that their magnitudes depend upon the choice of concentration  $C_i$  and the weighting factors  $x_i$ , used to calculate the average velocity. Equation (4) can be rearranged to give

$$J_{i}^{xc} = C_{i}(U_{i} - U^{x}) = -\sum_{j=1}^{n} -D_{ij}^{xc} \nabla C_{j}$$
(5)

For a system which is locally at equilibrium, the n concentrations are not all independent. Thus for any one species n, chosen as "solvent", at constant T, P,

 $C_n = C_n (C_1, C_2, \dots C_{n-1})$  (6)

$$\nabla C_{n} = \sum_{j=1}^{n-1} \left( \frac{\partial C_{n}}{\partial C_{j}} \right)_{C_{\kappa}} \nabla C_{j} , \quad \kappa \neq j, n$$
 (7)

making use of equation (7) in equation (5) results in

$$J_{i}^{xc} = -\sum_{j=1}^{n-1} D_{ij}^{xc} \nabla C_{j}$$
(8)

with

$$D_{ij}^{xc} = \mathcal{D}_{ij}^{xc} + \frac{\partial C_n}{\partial C_j} \cdot \mathcal{D}_{in}^{xc}$$
(9)

The dependence of the flux on the reference frames requires a corresponding change of proportionality constants with a change of reference frame. A similar situation exists for a change of concentration units.

To complete the discussion, it is necessary to present a general relation for interconverting the  $D_{ij}^{xc}$  based on

a) different reference velocity

b) different units of the concentration gradients.

For two different reference velocities

$$D_{ij}^{xc} = \sum_{\kappa=1}^{n-1} B_{i\kappa}^{xy} D_{\kappa j}^{yc}$$
(10)

with

$$B_{i\kappa}^{xy} = \delta_{i\kappa} + (x_n \frac{Y_{\kappa}}{Y_n} x_{\kappa})$$
(11)  
$$\delta_{i\kappa} = \begin{cases} 1 \text{ if } i = \kappa \\ 0 \text{ if } i \neq \kappa \end{cases}$$

Here,  $x_i$  and  $y_i$  are the concentration fractions corres-

ponding to each reference velocity.

When the concentration units are different, then

$$D_{ij}^{xc} = \sum_{\kappa=1}^{n-1} D_{i\kappa}^{xc'} G_{\kappa j}^{c'c}$$
(12)

with

$$G_{\kappa j}^{\mathbf{C'C}} = \left(\frac{\partial \mathbf{C'}}{\partial \mathbf{C_j}}\right)_{\mathbf{C_l}}, \quad \ell \neq j, n \quad (13)$$

where c and c' indicate the different concentration units.

### Irreversible Thermodynamics

A more general framework for the macroscopic description of irreversible processes such as concentration, force, pressure, and thermal diffusion is provided by irreversible thermodynamics. This approach was originally presented by Onsager (57,58) and extended by DeGroot and Mazur (11). In the following pages this approach, as given in Chapters 3, 4, 6 of DeGroot and Mazur will be reviewed briefly. Irreversible thermodynamics is based on three postulates in addition to conservation and symmetry arguments. These postulates are:

- A linear homogeneous relation exists between "fluxes" and "driving forces".
- 2) Near equilibrium behavior prevails.
- 3) Microscopic reversibility applies.

The irreversible nature of the diffusion process suggests that there is an overall increase in the entropy of a diffusing system. In the development of flux relations, advantage is taken of this fact by starting with an entropy balance of the form

$$\rho \frac{dS}{dt} = -div \quad \underline{J}_{S}^{\omega} + \sigma \qquad (14)$$

where  $\underline{J}_{S}^{\omega}$  is the entropy flux relative to the mass average velocity  $\underline{U}^{\omega}$ , S the entropy per unit mass,  $\sigma$  the rate of entropy production per unit volume,  $\rho$  the mass density, and  $\frac{d}{dt}$  the time derivative for a path following the fluid velocity  $\underline{U}^{\omega}$ . The total differential of S is given by the Gibbs relation as

$$TdS = dU + Pdv - \sum_{\kappa=1}^{n} \mu_{\kappa} d\omega_{\kappa}$$
(15)

where P is the equilibrium pressure, U the internal energy per unit mass, v is the specific volume, T is the absolute temperature,  $\mu_{\kappa}$  is the chemical potential of component  $\kappa$ , and  $\omega_{\kappa}$  is the mass fraction of component  $\kappa$ . Assuming that equation (15) is valid for a path which describes the motion of the center of mass of an element, the following equation is obtained

$$T \frac{dS}{dt} = \frac{dU}{dt} + P \frac{dv}{dt} - \sum_{\kappa=1}^{n} \mu_{\kappa} \frac{d\omega_{\kappa}}{dt}$$
(16)

In order to find the explicit form of the entropy balance given by equation (14), the expressions for  $\frac{dU}{dt}$  and  $\frac{d\omega_{\kappa}}{dt}$  are utilized in the form

$$\rho \frac{dU}{dt} = -div \underline{J}_{q}^{\omega} - \rho P \frac{dv}{dt} - \underline{I} : grad \underline{U}^{\omega} + \sum_{\kappa=1}^{n} \underline{J}_{\kappa}^{\omega\rho} \cdot \underline{F}_{\kappa} (17)$$

$$\rho \frac{d\omega_{\kappa}}{dt} = -div \underbrace{J}_{\kappa}^{\omega\rho} (\kappa = 1, 2, ... n)$$
(18)

where  $\underline{J}_{\kappa}^{\omega\rho}$  and  $\underline{J}_{q}^{\omega}$  are the mass flux and the multicomponent energy flux relative to the mass average velocity respectively,  $\underline{F}_{\kappa}$  is the external force of conservative type per unit mass exerted on the chemical component  $\kappa$ , and  $\underline{I}$  is the pressure tensor. Substitution of equations (17) and (18) into equation (16) leads to

$$\rho \frac{dS}{dt} = -\frac{1}{T} \operatorname{div} \underline{J}_{q}^{\omega} - \frac{1}{T} \underline{I} : \operatorname{grad} \underline{U}^{\omega} + \frac{1}{T} \sum_{\kappa=1}^{n} \underline{J}_{\kappa}^{\omega\rho} \cdot \underline{F}_{\kappa}$$
$$+ \frac{1}{T} \sum_{\kappa=1}^{n} \mu_{\kappa} \operatorname{div} \underline{J}_{\kappa}^{\omega\rho} \qquad (19)$$

In the case of an isothermal, isobaric system with negligible viscous dissipation, and no external forces equation (19) reduces to

$$\rho \frac{dS}{dt} = -\frac{1}{T} \operatorname{div} \underline{J}^{\omega}_{q} + \frac{1}{T} \sum_{\kappa=1}^{n} \mu_{\kappa} \operatorname{div} \underline{J}^{\omega\rho}_{\kappa}$$
(20)

Equation (20) can be rearranged to give

$$\rho \frac{\mathrm{dS}}{\mathrm{dt}} = -\mathrm{div} \left[ \frac{J_{q}^{\omega} - \sum_{\kappa=1}^{n} \mu_{\kappa} J_{\kappa}^{\omega\rho}}{\mathrm{T}} \right] - \frac{1}{\mathrm{T}} \sum_{\kappa=1}^{n} J_{\kappa}^{\omega\rho} \cdot \mathrm{grad}_{\mu_{\kappa}}(21)$$

On comparison of equation (21) with equation (14), it follows that the expression for the entropy flux and entropy production are given by

$$\underline{J}_{s}^{\omega} = \frac{1}{T} \left( \underline{J}_{q}^{\omega} - \sum_{\kappa=1}^{n} \mu_{\kappa} \underline{J}_{\kappa}^{\omega\rho} \right)$$
(22)

$$\sigma = -\frac{1}{T} \sum_{\kappa=1}^{n} \frac{J^{\omega\rho}}{\kappa} \cdot \text{grad } \mu_{\kappa}$$
(23)

At thermodynamic equilibrium the gradients of chemical potential are zero therefore,  $\sigma$  vanishes. Since equation (23) (under condition given in the earlier paragraphs) is a complete expression for the entropy production, it is evident that the diffusional mass fluxes in such a system are functions only of chemical potential. The assumption of linear homogeneous relations between fluxes and driving forces leads to

$$\mathbf{J}_{i}^{\omega\rho} = -\sum_{\kappa=1}^{n} \mathbf{L}_{i\kappa}^{\omega\rho} \text{ grad } \boldsymbol{\mu}_{\kappa}$$
(24)

where the phenomenological coefficients  $L_{i\kappa}^{\omega\rho}$  depend only on the state of the system. This simple linear relations ship is analogous to the other common phenomenological laws, such as Newton's law and Fourier's law, which have been introduced <u>ad hoc</u> through the purely phenomenological theories of irreversible processes.

The assumption of symmetry of the phenomenological coefficients leads to "Onsager Reciprocal Relations" (ORR)

$$L_{ij} = L_{ji}$$
(25)

These relations have been justified by Onsager (57) on the basis of statistical mechanical arguments and have been verified experimentally for several systems (15,16,

23,84,88). The Onsager Reciprocal Relations (ORR) are valid for the coefficients of the phenomenological equations if the independent "fluxes" are written as linear functions of the independent "thermodynamic forces". However, it has been shown (11) that a linear homogeneous dependency among the fluxes does not impair the validity of the ORR. Nevertheless, for the case of n independent driving forces and n linearly dependent fluxes

$$\sum_{\kappa=1}^{n} a_{\kappa} J_{\kappa} = 0$$
 (26)

and the following relations hold

$$L_{i\kappa} = L_{\kappa i}$$
 (i,  $\kappa = 1, 2, ..., n-1$ ) (27)

$$\sum_{\kappa=1}^{n} a_{\kappa} L_{i\kappa} = 0 \quad (i = 1, 2, ... n)$$
(28)

$$\sum_{\kappa=1}^{n} a_{i} L_{i_{\kappa}} = 0 \quad (\kappa = 1, 2, ... n)$$
(29)

For one-dimensional diffusion of a ternary system, the entropy production per unit volume given by equation (23), reduces to

$$T_{\sigma} = -J_{1}^{\phi c} \frac{\partial^{\mu} 1}{\partial X} - J_{2}^{\phi c} \frac{\partial^{\mu} 2}{\partial X} - J_{3}^{\phi c} \frac{\partial^{\mu} 3}{\partial X}$$
(30)

However, only two of the fluxes and two of the chemical potential gradients are independent. This is due to linear dependence of the fluxes and the Gibbs-Duhem relation.

For a volume fixed frame of reference, the linear dependence of the fluxes is expressed as

$$\overline{\nabla}_{1}J_{1}^{\phi C} + \overline{\nabla}_{2}J_{2}^{\phi C} + \overline{\nabla}_{3}J_{3}^{\phi C} = 0$$
(31)

provided that partial molar volumes  $\overline{v}_{i}$  are constant.

From the Gibbs-Duhem relation

$$C_{1} \frac{\partial^{\mu} 1}{\partial x} + C_{2} \frac{\partial^{\mu} 2}{\partial x} + C_{3} \frac{\partial^{\mu} 3}{x} = 0$$
 (32)

Inserting  $J_3^{\phi C}$  and  $\frac{\partial \mu}{\partial x}$  from equations (31) and (32) into equation (30) results in

$$T\sigma = J_{1}^{\phi C}Y_{1} + J_{2}^{\phi C}Y_{2}$$
(33)

where

$$Y_{i} = -\sum_{j=1}^{2} \left[ \delta_{ij} + \frac{C_{j} \overline{V}_{i}}{C_{3} \overline{V}_{3}} \right] \frac{\partial \mu_{j}}{\partial x} , \quad i = 1, 2 \quad (34)$$

According to irreversible thermodynamics, the linear relations are therefore,

$$J_{1}^{\phi c} = L_{11}^{\phi c} Y_{1} + L_{12}^{\phi c} Y_{2}$$
(35a)

$$J_{2}^{\phi c} = L_{21}^{\phi c} Y_{1} + L_{22}^{\phi c} Y_{2}$$
(35b)

According to Miller (53) the mutual independence of  $J_i^{\phi c}$ , as well as  $Y_i$ , is a sufficient condition for the validity of the ORR, namely

$$L_{12}^{\phi c} = L_{21}^{\phi c}$$
(36)

Equation (35) can be rewritten in terms of chemical potential gradients, by inserting Y<sub>i</sub> from equation (34) as  $J_{1}^{\phi C} = -(L_{11}^{\phi C} \alpha_{11} + L_{12}^{\phi C} \alpha_{21}) \frac{\partial \mu_{1}}{\partial x} - (L_{11}^{\phi C} \alpha_{12} + L_{12}^{\phi C} \alpha_{22}) \frac{\partial \mu_{2}}{\partial x} (37a)$ 

$$J_{2}^{\phi C} = -(L_{21}^{\phi C} \alpha_{11} + L_{22}^{\phi C} \alpha_{21}) \frac{\partial^{\mu} 1}{\partial x} - (L_{21}^{\phi C} \alpha_{12} + L_{22}^{\phi C} \alpha_{22}) \frac{\partial^{\mu} 2}{\partial x}$$
(37b)

where

$$\alpha_{ij} = \delta_{ij} + \frac{C_j V_i}{C_3 \overline{V}_3}$$
(38)

Unfortunately, chemical potential gradients can not be measured directly. However, they can be expressed as products of chemical potential derivatives with respect to concentration, and concentration gradients as

$$\frac{\partial \mu_{i}}{\partial x} = \sum_{j=1}^{2} \left( \frac{\partial \mu_{i}}{\partial C_{j}} \right)_{T,P,C_{\kappa}} \frac{\partial C_{j}}{\partial x}, \quad \kappa \neq j,3$$
(39)

Substituting  $\frac{\partial \mu_i}{\partial x}$  from equation (39) into equation (37) results in

$$J_{1}^{\phi C} = -\left[ \left( L_{11}^{\phi C} {}_{11}^{\alpha} {}_{11}^{\alpha} + L_{12}^{\phi C} {}_{21}^{\alpha} \right)^{\mu} {}_{11}^{\mu} + \left( L_{11}^{\phi C} {}_{12}^{\alpha} + L_{12}^{\phi C} {}_{22}^{\alpha} \right)^{\mu} {}_{21}^{\beta} \frac{\partial C_{1}}{\partial x} - \left[ \left( L_{11}^{\phi C} {}_{11}^{\alpha} + L_{12}^{\phi C} {}_{21}^{\alpha} \right)^{\mu} {}_{12}^{\mu} + \left( L_{11}^{\phi C} {}_{11}^{\alpha} + L_{12}^{\phi C} {}_{22}^{\alpha} \right)^{\mu} {}_{22}^{\beta} \frac{\partial C_{2}}{\partial x} \right]$$
(40a)

$$J_{2}^{C} = -\left[\left(L_{21}^{\phi C}_{11} + L_{22}^{\phi C}_{21}\right)^{\mu}_{11} + \left(L_{21}^{\phi C}_{12} + L_{22}^{\phi C}_{22}\right)^{\mu}_{21}\right]^{\frac{\partial C_{1}}{\partial x}}_{\frac{\partial C_{2}}{\partial x}}$$
(40b)  
$$-\left[\left(L_{21}^{\phi C}_{11} + L_{22}^{\phi C}_{22}\right)^{\mu}_{12} + \left(L_{21}^{\phi C}_{12} + L_{22}^{\phi C}_{22}\right)^{\mu}_{22}\right]^{\frac{\partial C_{2}}{\partial x}}_{\frac{\partial C_{2}}{\partial x}}$$

where

$${}^{\mu}_{ij} = \left(\frac{\partial {}^{\mu}_{i}}{\partial {}^{C}_{j}}\right)_{T,P,C_{\kappa}}, \quad \kappa \neq j,3$$
(41)

For one-dimensional diffusion of a ternary system, equation (8) reduces to

$$J_{1}^{\phi C} = -D_{11}^{\phi C} \frac{\partial C_{1}}{\partial x} - D_{12}^{\phi C} \frac{\partial C_{2}}{\partial x}$$
(42a)

$$J_{2}^{\phi c} = -D_{21}^{\phi c} \frac{\partial C_{1}}{\partial x} - D_{22}^{\phi c} \frac{\partial C_{2}}{\partial x}$$
(42b)

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Comparing equations (40) and (42), the following four equations are obtained

$$(L_{11}^{\phi C} \alpha_{11} + L_{12}^{\phi C} \alpha_{21}) \mu_{11} + (L_{11}^{\phi C} \alpha_{12} + L_{12}^{\phi C} \alpha_{22}) \mu_{21} = D_{11}^{\phi C} (43a)$$

$$(L_{11}^{\phi C} \alpha_{11} + L_{12}^{\phi C} \alpha_{21}) \mu_{12} + (L_{11}^{\phi C} \alpha_{12} + L_{12}^{\phi C} \alpha_{22}) \mu_{22} = D_{12}^{\phi C} (43b)$$

$$(L_{21}^{\phi C} \alpha_{11} + L_{22}^{\phi C} \alpha_{21}) \mu_{11} + (L_{21}^{\phi C} \alpha_{12} + L_{22}^{\phi C} \alpha_{22}) \mu_{21} \neq D_{21}^{\phi C} (43c)$$

$$(L_{21}^{\phi C} \alpha_{11} + L_{22}^{\phi C} \alpha_{21}) \mu_{12} + (L_{21}^{\phi C} \alpha_{12} + L_{22}^{\phi C} \alpha_{22}) \mu_{22} = D_{22}^{\phi C} (43c)$$

$$(L_{21}^{\phi C} \alpha_{11} + L_{22}^{\phi C} \alpha_{21}) \mu_{12} + (L_{21}^{\phi C} \alpha_{12} + L_{22}^{\phi C} \alpha_{22}) \mu_{22} = D_{22}^{\phi C} (43d)$$
Equations (43) may be rearranged to yield

$$a_{11}L_{11}^{\phi c} + a_{12}L_{12}^{\phi c} = D_{11}^{\phi c}$$
 (44a)

$$a_{21}L_{11}^{\phi c} + a_{22}L_{12}^{\phi c} = D_{12}^{\phi c}$$
 (44b)

$$a_{11}L_{21}^{\phi c} + a_{12}L_{22}^{\phi c} = D_{21}^{\phi c}$$
 (44c)

$$a_{21}L_{21}^{\phi c} + a_{22}L_{22}^{\phi c} = D_{22}^{\phi c}$$
 (44d)

where

$$a_{ij} = \sum_{\kappa=1}^{2} \alpha_{j\kappa} \mu_{\kappa i}$$
(45)

Equations (44a,44b) may be solved for  $L_{12}^{\phi c}$  as

$$L_{12}^{\phi C} = \frac{a_{11}}{a_{11}} \frac{D_{12}^{\phi C} - a_{21}}{a_{22}} \frac{D_{11}^{\phi C}}{a_{12}}$$
(46)

Equations (44c,44d) result in

$$L_{21}^{\phi c} = \frac{a_{22}}{a_{11}} \frac{D_{21}^{\phi c} - a_{12}}{a_{12}} \frac{D_{22}^{\phi c}}{a_{12}}$$
(47)

The necessary and sufficient condition for  $L_{12}^{\phi C} = L_{21}^{\phi C}$  is

$$a_{11} D_{12}^{\phi C} - a_{21} D_{11}^{\phi C} = a_{22} D_{21}^{\phi C} - a_{12} D_{22}^{\phi C}$$
 (48)

$$a_{11}a_{22} - a_{12}a_{21} \neq 0$$
 (49)

Equations (48) and (49) provide explicit relationships in terms of experimental diffusion coefficients which may be used to test the Onsager Reciprocal Relations.

### Theoretical

The inherent complexity of the diffusion process and the numerous molecular variables which affect the rate of the process have been known for a long time. It is obvious that a rigorous theory of diffusion can be derived at the present time only through statistical mechanical investigations. This requires a knowledge of intermolecular potentials and particle distribution functions. Yet, the present knowledge of molecular multi-particle interactions does not allow the quantitative prediction of transport properties in liquids from basic principles. This forces us to resort to less basic approaches which lead to "semiempirical" theories.

Semi-empirical methods for quantitatively predicting diffusivities in liquid systems have generally been based on either of two model dependent theories: The hydrodynamic theory and the absolute rate theory.

Hydrodynamic Theory. This theory is much simpler and more directly related to macroscopic behavior and is based

on the independent studies of Einstein (19,20,21,22) and Sutherland (77), in which the diffusional flow is regarded as a balance between a driving force and a resistance to flow. In the original papers the gradient of osmotic pressure was taken to be the driving force. However, irreversible thermodynamics suggests that the proper driving force is the gradient of chemical potential. For a binary mixture the diffusional force per molecule of component A may be expressed as

$$\left(-\nabla \mu_{A}\right)_{T,P} = \frac{-RT}{C_{A}} \left(\frac{d \ell n a_{A}}{d \ell n C_{A}}\right) \nabla C_{A}$$
(50)

If the viscous resistance per molecule is  $\zeta$ , the velocity of the solute in the direction of diffusion is  $U_A$ , and the volume average velocity is U, then for a one dimensional system, a force balance results in

$$U_{A} - U = - \frac{RT}{C_{A}N\varsigma} \left( \frac{d\ln a_{A}}{d\ln C_{A}} \right) \frac{dC_{A}}{dx}$$
(51)

The diffusion coefficient  $D_{AB}$  is related to  $U_A^{-U}$  by

$$J_{A} = C_{A} (U_{A} - U) = -D_{AB} \frac{dC_{A}}{dx}$$
(52)

Substitution of equation (51) into equation (52) yields

$$D_{AB} = \frac{\kappa T}{\zeta} \left( \frac{d \ln a}{d \ln C_A} \right)$$
(53)

For ideal solutions, the thermodynamic factor  $\left(\frac{d \ln A}{d \ln C_A}\right)$ 

is unity and equation (53) reduces to the Nernst-Einstein equation

$$D_{AB} = \frac{\kappa T}{\zeta}$$
(54)

The viscous resistance per molecule,  $\zeta$ , for the spherical particle of radius  $r_A$  moving in a continuous medium of viscosity  $n_B$ , was calculated by Stokes (76) and was found to be

$$\zeta = 6\pi \eta_{B} r_{A} \left( \frac{1 + 2\eta_{B} / \beta r_{A}}{1 + 3\eta_{B} / \beta r_{A}} \right)$$
(55)

 $\beta$  is the coefficient of sliding friction between the diffusing molecule and its surroundings. There are two limiting cases, namely,

$$\beta = 0 \quad \zeta = 4\pi \eta_B r_A \tag{56}$$

$$\beta \rightarrow \infty \quad \zeta = 6\pi \eta_B r_A$$
 (57)

For large spherical solute molecules diffusing in a medium of low molecular weight, Sutherland (77) suggested that little "slip" in a hydrodynamic sense would occur, and equation (57) would be applicable. Equations (54) and (57) can be combined to give the Stokes-Einstein equation

$$D_{AB} = \frac{\kappa T}{6\pi n_B r_A}$$
(58)

For the systems consisting of large solute molecules including sucrose-water (41), equation (58) is correct.

According to Sutherland, diffusion of a small solute molecule through a solvent of comparable size corresponds

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fairly closely to the limiting case of  $\beta=0$ . He reasoned that there would be free spaces between solvent molecules through which the solute molecule could move freely. For this case, equations (56) and (54) may be combined to give

$$D_{AB} = \frac{\kappa T}{4\pi \eta \mathbf{g} \mathbf{r}_{A}}$$
(59)

It should be mentioned that in this case the assumption of solvent as a continuous medium with respect to the motion of the solute molecule is not valid.

Gordon (37) extended expression (58) to moderate concentrations by the substitution of  $\eta_{AB}$  for  $\eta_{B}$  and inclusion of the activity correction term as

$$D_{AB} = \frac{\kappa T}{6\pi \eta_{AB} r_{A}} \left( \frac{d \ln a_{A}}{d \ln C_{A}} \right)$$
(60)

where  $a_A$  is the activity of species A, and  $n_{AB}$  is the solution viscosity. Gordon's use of  $n_{AB}$  to account for concentration dependence of D is an empiricism rather than a theoretical extension of Stokes law. The consistency of Gordon's results with statistical mechanics has been confirmed by Bearman (2) for regular solutions.

Hartley and Crank (40) expressed the concentration dependence of  $D_{AB}^{}$  as

$$D_{AB} = \frac{\kappa T}{\eta_{AB}} \left( \frac{x_A}{\sigma_A} + \frac{x_B}{\sigma_B} \right) \left( \frac{d \ln a_A}{d \ln x_A} \right)$$
(61)

where  $\sigma_i$  are the concentration-independent resistance coefficients which are functions of molecular size, shape, and solvent viscosity. Bearman (2) showed that equation (61) is equivalent to

$$D_{AB} = (x_B D_{AB}^{\circ} + x_A D_{BA}^{\circ}) \left(\frac{d \ell n a_A}{d \ell n x_A}\right)$$
(62)

where  $D^{\circ}_{AB}$  is the mutual diffusion coefficient of A in B at the limit of zero concentration of A.

Pyun and Fixman (63) correlated the added resistance to diffusion in concentrated systems through the concept of interactions of the velocity fields of neighboring solute particles. They considered the viscosity of the solution as constant and equal to the viscosity of the pure solvent  $n_B$ . The dependence of the friction factor on the volume fraction of solute particles  $\phi_A$  for large rigid spheres in a continuum was represented by.

$$\zeta_{AB} = \zeta_{AB}^{\circ} (1 + 7.16\phi_{A} + 0\phi_{A}^{2} + ...)$$
 (63)

As a result, their concentration dependence of the mutual diffusion coefficient is independent of the solution viscosity. Cussler and Lightfoot (10) extended this development to multicomponent systems. Their results for the system Polystyrene(1)-Polystyrene(2)-Toluene, is in reasonable agreement with experimental data.

Furlong (34) applied an independent extension of Pyun and Fixman's approach (the method of reflections) to multicomponent systems. He made the following assumptions: 1) The solvent is a continuum with respect to the solute molecules. 2) The diffusing species is a large, spherical particle and includes any bound solvent. 3) The pointforce approximation to the complete solution of the Navier-Stokes equation is valid. 4) The particle radius is independent of concentration, <u>i.e.</u>, sufficient solvent is present to solvate all solute molecules. His result for a binary system is

$$D_{AB} = D_{AB}^{\circ} \frac{\phi_{B}[1 + \phi_{A}(\theta_{A} - 1 - 2\tau_{A}) + \phi_{A}^{2}(2\tau_{A})]}{(1 + k\phi_{A})}$$
(64)

where

$$\theta_{A} = \frac{\overline{\nabla}_{A}}{\overline{\nabla}_{B}}$$
(65a)

$$\tau_{A} = A_{AB} \frac{\overline{V}_{A}}{RT}$$
(65b)

 $A_{AB}$  is some energy of interaction between the solute A and solvent B, and k is a hydrodynamic parameter.

For the ternary system consisting of solutes 1 and 2 in a solvent 3 the results are:

$$D_{11}^{\phi_{C}} = \frac{\phi_{3}[H_{2}Q_{11}D_{13}^{\circ} - \kappa_{2}Q_{21}D_{23}^{\circ}]}{(H_{1}H_{2} - \kappa_{1}\kappa_{2})}$$

$$\frac{+ \phi_{2}[(H_{2}+\kappa_{1})Q_{11}D_{13}^{\circ} - (\kappa_{2}+H_{1})Q_{21}D_{23}^{\circ}]}{(H_{1}H_{2} - \kappa_{1}\kappa_{2})}$$
(66a)

$$D_{12}^{\phi C} = \frac{C_1}{C_2} \frac{\phi_3 [H_2 Q_{12} D_{13}^{\circ} - \kappa_2 Q_{22} D_{23}^{\circ}]}{(H_1 H_2 - \kappa_1 \kappa_2)} + \phi_2 [(H_2 + \kappa_1) Q_{12} D_{13}^{\circ} - (\kappa_2 + H_1) Q_{22} D_{23}^{\circ}]}{(H_1 H_2 - \kappa_1 \kappa_2)}$$
(66b)

$$D_{21} = \frac{C_2}{C_1} \frac{\phi_3 [Q_{21}H_1D_{23}^2 - Q_{11}\kappa_1D_{13}^2]}{(H_1H_2 - \kappa_1\kappa_2)} + \phi_1 [(H_1+\kappa_2)Q_{21}D_{23}^2 - (H_2+\kappa_1)Q_{11}D_{13}^2]}{(H_1H_2 - \kappa_1\kappa_2)}$$
(66c)

$$D_{22} = \frac{\phi_{3} [\Omega_{22}^{H_{1}} D_{23}^{2} - \Omega_{12}^{\kappa} D_{13}]}{(H_{1}^{H_{2}} - \kappa_{1}^{\kappa} 2)} + \phi_{1} [(H_{1}^{+\kappa} 2) \Omega_{22} D_{23}^{2} - (H_{2}^{+\kappa} 1) \Omega_{12} D_{13}^{*}]}{(H_{1}^{H_{2}} - \kappa_{1}^{\kappa} 2)}$$
(66d)

where

$$H_{i} = 1 + k_{i}\phi_{i}$$
,  $i = 1,2$  (67a)

$$\kappa_{1} = \frac{3}{2} \left(\frac{k_{2}}{6}\right) \left(\frac{r_{1}+r_{2}}{r_{1}}\right)^{2} \phi_{1}$$
 (67b)

$$\kappa_2 = \frac{3}{2} \left(\frac{k_1}{6}\right) \left(\frac{r_1 + r_2}{r_2}\right)^2 \phi_2$$
 (67c)

$$Q_{ij} = \frac{C_j}{RT} \left( \frac{\partial \mu_i}{\partial C_j} \right)_{T,P,C_{\ell}} \quad \ell \neq j,3 \quad (67d)$$

and k<sub>i</sub> are hydrodynamic parameters.

Starting with the fundamental postulate of hydrodynamic theory (a balance between a driving force and a resistance to flow), Kett (48) developed relations expressing the multicomponent diffusion coefficients  $D_{ij}$ , in terms of friction coefficients  $\sigma_i$ , concentrations, partial molar volumes, solution viscosity, and concentration derivatives of the chemical potentials; for both non-associating and associating systems. His derivation is based on the definition of the resisting force

$$F_{i,r} = -f_{i}N\eta U_{i,m} = -\sigma_{i}\eta U_{i,m}$$
(68)

where  $F_{i,r}$  is the resisting force to intrinsic diffusion per molecule of component i,  $f_i$  is a coefficient which is a function of the size and shape of the molecule and includes effects of the medium, n is the viscosity of the medium,  $\sigma_i$  is defined as the friction coefficient of component i. The negative sign is a result of the velocity of component i being in the opposite direction to the resisting force. The driving force corresponding to the resisting force given by equation (68) was taken to be the negative of the chemical potential gradient of component i,

$$\mathbf{F}_{i,d} = -\nabla \boldsymbol{\mu}_i \tag{69}$$

By equating  $F_{i,d}$  with  $-F_{i,r}$  and solving the resultant equations for  $U_{i,m}$  and then multiplying  $U_{i,m}$  by the concentration  $C_i$  he obtained the intrinsic flux of component i. From these intrinsic fluxes the volume fixed fluxes may be calculated by

$$J_{i}^{v} = J_{i}^{m} - C_{i} \sum_{j=1}^{n} \overline{v}_{j} J_{j}^{m}$$

The diffusion coefficients may then be obtained by combining the Gibbs-Duhem equation with the volume fixed fluxes; for a non-associating ternary system these are

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

$$+ C_1 C_2 \left( \frac{\overline{\nabla}_3}{\sigma_3} - \frac{\overline{\nabla}_2}{\sigma_2} \right) \left( \frac{\partial \ln a_2}{\partial C_1} \right) C_2 \right]$$

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

$$(70b)$$

+ 
$$C_1 C_2 \left( \frac{\overline{v}_3}{\sigma_3} - \frac{\overline{v}_2}{\sigma_2} \right) \left( \frac{\partial \ln a_2}{\partial C_2} \right)_{C_1}$$

$$D_{21} = \frac{RT}{\eta} \left[ C_1 C_2 \left( \frac{V_3}{\sigma_3} - \frac{V_1}{\sigma_1} \right) \left( \frac{\partial \ln a_1}{\partial C_1} \right) C_2 + C_2 \left( \frac{1 - C_2 \overline{V}_2}{\sigma_2} + \frac{C_2 \overline{V}_3}{\sigma_3} \right) \left( \frac{\partial \ln a_2}{\partial C_1} \right) C_2 \right]$$
(70c)

$$D_{22} = \frac{RT}{n} \left[ C_1 C_2 \left( \frac{\overline{V}_3}{\sigma_3} - \frac{\overline{V}_1}{\sigma_1} \right) \left( \frac{\partial \ln a_1}{\partial C_2} \right) \right] + C_2 \left( \frac{1 - C_2 \overline{V}_2}{\sigma_2} + \frac{C_2 \overline{V}_3}{\sigma_3} \right) \left( \frac{\partial \ln a_2}{\partial C_2} \right) \right]$$
(70d)

In the derivation of equations (70), partial molar volumes were assumed to be constant. For a ternary system with components A, B, and C in which an A molecule links with a B molecule to form an A-B complex, the diffusion coefficients were given as

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

$$+ \left[ -\frac{\overline{\nabla}_{2}C_{2}C_{A}}{\sigma_{2}^{n}} + \frac{C_{12}}{\sigma_{12}^{n}}(1-\overline{\nabla}_{12}C_{A}) + \frac{C_{A}C_{B}\nabla_{3}}{\sigma_{3}^{n}} \right] \left( \frac{\partial\mu_{2}}{\partial C_{A}} \right)_{C_{B}}$$
(71a)  
$$D_{AB} = \left[ \frac{C_{1}}{\sigma_{1}^{n}}(1-C_{A}\overline{\nabla}_{1}) + \frac{C_{12}}{\sigma_{12}^{n}}(1-\overline{\nabla}_{12}C_{A}) + \frac{C_{A}^{2}\overline{\nabla}_{3}}{\sigma_{3}^{n}} \right] \left( \frac{\partial\mu_{1}}{\partial C_{B}} \right)_{C_{A}}$$
$$+ \left[ -\frac{\overline{\nabla}_{2}C_{2}C_{A}}{\sigma_{2}^{n}} + \frac{C_{12}}{\sigma_{12}^{n}}(1-\overline{\nabla}_{12}C_{A}) + \frac{C_{A}C_{B}\overline{\nabla}_{3}}{\sigma_{3}^{n}} \right] \left( \frac{\partial\mu_{2}}{\partial C_{B}} \right)_{C_{A}}$$
(71b)  
$$= \left[ -\frac{\overline{\nabla}_{1}C_{1}C_{B}}{\sigma_{2}^{n}} + \frac{C_{12}}{\sigma_{12}^{n}}(1-\overline{\nabla}_{12}C_{A}) + \frac{C_{A}C_{B}\overline{\nabla}_{3}}{\sigma_{3}^{n}} \right] \left( \frac{\partial\mu_{2}}{\partial C_{B}} \right)_{C_{A}}$$
(71b)

$$D_{BA} = \left[ -\frac{1}{\sigma_{1}} \frac{1}{\sigma_{1}} \frac{1}{\sigma_{1}} + \frac{1}{\sigma_{12}} \frac{1}{\sigma_{12}} (1 - \overline{V}_{12}C_{B}) + \frac{C_{A}C_{B}V_{3}}{\sigma_{3}} \right] \left( \frac{\partial \mu_{1}}{\partial C_{A}} \right)_{C_{B}} + \left[ \frac{C_{2}}{\sigma_{2}} (1 - \overline{V}_{2}C_{B}) + \frac{C_{12}}{\sigma_{12}} (1 - \overline{V}_{12}C_{B}) + \frac{C_{B}^{2}\overline{V}_{3}}{\sigma_{3}} \right] \left( \frac{\partial \mu_{2}}{\partial C_{A}} \right)_{C_{B}} (\hat{\eta}_{1}c)$$

$$D_{BB} = \left[ -\frac{\overline{\nabla}_{1}C_{1}C_{B}}{1^{\eta}} + \frac{C_{12}}{\sigma_{12}^{\eta}}(1-\overline{\nabla}_{12}C_{B}) + \frac{\overline{\nabla}_{3}C_{A}C_{B}}{\sigma_{3}^{\eta}} \right] \left( \frac{\partial \mu_{1}}{\partial C_{B}} \right)_{A} + \left[ \frac{C_{2}}{\sigma_{2}^{\eta}}(1-\overline{\nabla}_{2}C_{B}) + \frac{C_{12}}{\sigma_{12}^{\eta}}(1-\overline{\nabla}_{12}C_{B}) + \frac{C_{B}^{2}\overline{\nabla}_{3}}{\sigma_{3}^{\eta}} \right] \left( \frac{\partial \mu_{2}}{\partial C_{B}} \right)_{C_{A}}$$
(71d)

where  $C_A = C_1 + C_{12}$ ,  $C_B = C_2 + C_{12}$ ,  $C_C = C_3$ . The terms  $\sigma_{12}$ ,  $\overline{V}_{12}$  are the friction coefficient and the partial molar volume of the 12 complex respectively.

Similar results for a system in which one component dimerizes was given as

$$D_{AA} = \left[\frac{C_{1}}{\sigma_{1}^{\eta}}(1-C_{A}\overline{V}_{1}) + \frac{2C_{11}}{\sigma_{11}^{\eta}}(2-C_{A}\overline{V}_{11}) + \frac{\overline{V}_{3}C_{A}^{2}}{\sigma_{3}^{\eta}}\right] \left(\frac{\partial\mu_{1}}{\partial C_{A}}\right)_{C_{B}} + \left[-\frac{C_{A}C_{B}\overline{V}_{2}}{\sigma_{2}^{\eta}} + \frac{C_{A}C_{B}\overline{V}_{3}}{\sigma_{3}^{\eta}}\right] \left(\frac{\partial\mu_{2}}{\partial C_{A}}\right)_{C_{B}}$$
(72a)
$$\begin{split} \mathbf{D}_{\mathbf{AB}} &= \left[ \frac{\mathbf{C}_{\mathbf{1}}}{\sigma_{\mathbf{1}}^{n}} (\mathbf{1} - \mathbf{C}_{\mathbf{A}}^{\mathbf{\overline{V}}} \mathbf{1}) + \frac{\mathbf{2C}_{\mathbf{1}\mathbf{1}}}{\sigma_{\mathbf{1}\mathbf{1}}^{n}} (\mathbf{2} - \mathbf{C}_{\mathbf{A}}^{\mathbf{\overline{V}}} \mathbf{1}_{\mathbf{1}}) + \frac{\mathbf{\overline{V}}_{\mathbf{3}} \mathbf{C}_{\mathbf{A}}^{2}}{\sigma_{\mathbf{3}}^{n}} \right] \left( \frac{\partial \mathbf{u}_{\mathbf{1}}}{\partial \mathbf{C}_{\mathbf{B}}} \right)_{\mathbf{C}_{\mathbf{A}}} (72b) \\ &+ \left[ - \frac{\mathbf{C}_{\mathbf{A}}^{\mathbf{C}}_{\mathbf{B}}^{\mathbf{\overline{V}}} \mathbf{2}}{\sigma_{\mathbf{2}}^{n}} + \frac{\mathbf{C}_{\mathbf{A}}^{\mathbf{C}}_{\mathbf{B}}^{\mathbf{\overline{V}}} \mathbf{2}}{\sigma_{\mathbf{3}}^{n}} \right] \left( \frac{\partial \mathbf{u}_{\mathbf{2}}}{\partial \mathbf{C}_{\mathbf{B}}} \right)_{\mathbf{C}_{\mathbf{A}}} (72b) \\ &+ \left[ - \frac{\mathbf{C}_{\mathbf{1}}^{\mathbf{C}}_{\mathbf{B}} \mathbf{\overline{V}}_{\mathbf{1}}}{\sigma_{\mathbf{1}}^{n}} - \frac{2\mathbf{C}_{\mathbf{1}\mathbf{1}}^{\mathbf{C}}_{\mathbf{B}} \mathbf{\overline{V}}_{\mathbf{1}\mathbf{1}}}{\sigma_{\mathbf{1}\mathbf{1}}^{n}} + \frac{\mathbf{C}_{\mathbf{A}}^{\mathbf{C}}_{\mathbf{B}} \mathbf{\overline{V}}_{\mathbf{3}}}{\sigma_{\mathbf{3}}^{n}} \right] \left( \frac{\partial \mathbf{u}_{\mathbf{1}}}{\partial \mathbf{C}_{\mathbf{A}}} \right)_{\mathbf{C}_{\mathbf{B}}} \\ &+ \left[ \frac{\mathbf{C}_{\mathbf{B}}}{\sigma_{\mathbf{2}}^{n}} (\mathbf{1} - \mathbf{C}_{\mathbf{B}} \mathbf{\overline{V}}_{\mathbf{2}}) + \frac{\mathbf{C}_{\mathbf{B}}^{2} \mathbf{\overline{V}}_{\mathbf{3}}}{\sigma_{\mathbf{3}}^{n}} \right] \left( \frac{\partial \mathbf{u}_{\mathbf{2}}}{\partial \mathbf{C}_{\mathbf{A}}} \right)_{\mathbf{C}_{\mathbf{B}}} \\ &+ \left[ \frac{\mathbf{C}_{\mathbf{B}}}{\sigma_{\mathbf{2}}^{n}} (\mathbf{1} - \mathbf{C}_{\mathbf{B}} \mathbf{\overline{V}}_{\mathbf{2}}) + \frac{\mathbf{C}_{\mathbf{B}}^{2} \mathbf{\overline{V}}_{\mathbf{3}}}{\sigma_{\mathbf{3}}^{n}} \right] \left( \frac{\partial \mathbf{u}_{\mathbf{2}}}{\partial \mathbf{C}_{\mathbf{A}}} \right)_{\mathbf{C}_{\mathbf{B}}} \\ &+ \left[ \frac{\mathbf{C}_{\mathbf{B}}}{\sigma_{\mathbf{2}}^{n}} (\mathbf{1} - \mathbf{C}_{\mathbf{B}} \mathbf{\overline{V}}_{\mathbf{2}}) + \frac{\mathbf{C}_{\mathbf{B}}^{2} \mathbf{\overline{V}}_{\mathbf{3}}}{\sigma_{\mathbf{3}}^{n}} \right] \left( \frac{\partial \mathbf{u}_{\mathbf{2}}}{\partial \mathbf{C}_{\mathbf{B}}} \right)_{\mathbf{C}_{\mathbf{A}}} \end{aligned}$$
(72d) 
$$&+ \left[ \frac{\mathbf{C}_{\mathbf{B}}}{\sigma_{\mathbf{2}}^{n}} (\mathbf{1} - \mathbf{C}_{\mathbf{B}} \mathbf{\overline{V}}_{\mathbf{2}}) + \frac{\mathbf{C}_{\mathbf{B}}^{2} \mathbf{\overline{V}}_{\mathbf{3}}}{\sigma_{\mathbf{3}}^{n}} \right] \left( \frac{\partial \mathbf{u}_{\mathbf{2}}}{\partial \mathbf{C}_{\mathbf{B}}} \right)_{\mathbf{C}_{\mathbf{A}}} \end{aligned}$$

where  $C_A = C_1 + 2C_{11}$ ,  $C_B = C_2$ ,  $C_C = C_3$ ;  $C_{11}$ ,  $\overline{v}_{11}$ , and  $\sigma_{11}$  are concentration, partial molar volume, and friction coefficient of the dimer complex respectively.

Accurate values of friction coefficients in Kett's derivations can be obtained through the use of tracer diffusion measurements only. This means that at each composition, three tracer diffusion measurements are required. Therefore, the theory involves quite a number of measurements of the tracer diffusion coefficients. To eliminate this difficulty Kett proposed to predict these friction coefficients from self-diffusion and binary diffusion coefficients at the limit of infinite dilution. These predicted values of friction coefficients are in good agreement with measured values for the systems in which the friction coefficients are not strong functions of composition. In summary, Kett's derivations produce fairly good results in the case of non-associating systems with weak composition dependent friction coefficients.

Absolute Rate Theory. This theory pioneered by Eyring and co-workers (24,25,27,28,29,30,36,42,49,60,67,68,69, 75), is an application of the theory of rate processes in conjunction with a lattice structured model for the liquid state. This approach is more closely related to molecular behavior and statistical mechanics than hydrodynamic theory; and has provided a means of developing equations for the transport properties in general and for the coefficients of diffusion and viscosity in particular. This theory may be summarized as follows:

 Almost all processes which occur at a measurable rate can be regarded as proceeding through a transition state.
 If there is no force (in the general sense) acting on the system, then the energy of the transition state exceeds that of the initial state by an amount E° per mole.
 The overall rate of change is determined by the rate at which the transition state is acquired and is given by

$$v = H \frac{\kappa T}{h} \exp\left(-\frac{\Delta G^{\neq}}{RT}\right) = H \frac{\kappa T}{h} \frac{F^{\neq}}{F} \exp\left(-E^{\circ}/RT\right)$$
 (73)

where H is a "transmission coefficient" normally assumed to be unity,  $\kappa$  is the Boltzmann constant, h is Planck's constant, T is the absolute temperature,  $\Delta G^{\neq}$  is the Gibbs

free energy of formation of the transition state from the initial state,  $F^{\neq}$  is the partition function per unit volume of the molecule in the activated state, and F is the partition function of the normal state.

4. The liquid has a cell or lattice structure in which there are vacancies or holes.

5. The motion of molecules is a result of jumps, the distance of which is on the order of the magnitude of a lattice spacing. (A molecule that has gained the activation energy required for motion leaves its initial equilibrium state and passes through the activated state to the neighboring hole which then becomes the new equilibrium state.)
6. The presence of a driving force reduces the activation energy of the forward process while increasing the activation.

Applying this theory, the coefficient of diffusion for a binary system is expressed as

$$D_{AB} = \frac{\lambda^2}{\psi} v$$
 (74)

where  $\psi$  is the number of nearest neighbors in the same plane as the diffusing molecules, and

$$v = \frac{\kappa T}{h} \frac{F^{\neq}}{F_{AB}} \exp\left(\frac{-E_{D,AB}}{RT}\right)$$
(75)

Here  $F_{AB}^{\neq}$ ,  $F_{AB}$  and  $E_{D,AB}$  are, respectively, the partition functions for the activated and normal state of the mole-cule; and the activation energy per mole for the diffu-

sion process.

The Eyring theory has also been applied to viscous flow to predict liquid viscosity coefficients

$$n_{\rm B} = \frac{h_{\rm A} \lambda_{\rm B}}{\lambda_{\rm 2B} \lambda_{\rm 3B} \lambda_{\rm B}^2} \frac{F_{\rm BB}}{F_{\rm BB}^2} \exp\left(\frac{En_{\rm B}}{RT}\right)$$
(76)

where  $\lambda_{1B}$ ,  $\lambda_{2B}$ , and  $\lambda_{3B}$  represent the distances between molecules in the three coordinate directions;  $E_{n,B}$  is the activation energy for viscosity per mole.

Equations (74,75,76) can be combined to yield the following expression

$$D_{AB} = \frac{\kappa T}{\psi \eta_{B}} \frac{\lambda_{1B}}{\lambda_{2B}^{\lambda_{3B}}} \frac{F_{BB}}{F_{BB}^{\sharp}} \frac{F_{AB}^{\sharp}}{F_{AB}} \exp\left(\frac{E_{\eta,B} - E_{D,AB}}{RT}\right)$$
(77)

To simplify equation (77), two assumptions are made. First,

$$\lambda_{1B} = \lambda_{2B} = \lambda_{3B} = (V_B/N)^{\frac{1}{3}}$$

in which  $V_B$  is the molar volume and N is Avogadro's number. The second assumption states that the rotational and vibrational modes are equal for the normal and activated states, thus only the translational contributions to the partition functions are considered. This results in

$$\frac{F_{BB}}{F_{BB}^{\neq}} \frac{F_{AB}^{\neq}}{F_{AB}} = \left(\frac{M_{B}}{M_{A}}\right)^{\frac{1}{2}} \left(\frac{V_{f,BB}}{V_{f,AB}}\right)^{\frac{1}{3}}$$
(78)

where  $M_A$  and  $M_B$  are molar masses of A and B respectively; and  $V_{f,AB}$  and  $V_{f,BB}$  are the free volumes of molecules A,B surrounded by molecules B respectively. Olander (56) has suggested that the product of the ratios of the partition functions may be approximated by unity. He considered the ratios of equation (78) as follows: If  $M_A$  is larger than  $M_B$ , then the free volume of A in B will be smaller than the free volume of B in B. But if  $M_A$  is smaller than  $M_B$  then  $V_{f,AB}$  will be larger than  $V_{f,BB}$ . Therefore, the change of one ratio is offset by the change in the other ratio, so that the product remains nearly constant and may be set equal to unity. With these considerations, equation (77) reduces to

$$D_{AB} = \frac{\kappa_{T}}{\psi \eta_{B}} (N/V_{B})^{\frac{1}{3}} \exp \left(\frac{E_{\eta,B} - E_{D,AB}}{RT}\right)$$
(79)

In the case of self-diffusion  $E_{n,B}$  may be taken to be equal to  $E_{D,AB}$ , then equation (79) takes the form

$$D_{BB} = \frac{\kappa T}{\psi \eta_B} \left( N / V_B \right)^{\frac{1}{3}}$$
(80)

Applying equation (80) to self-diffusion data available in the literature,  $\psi$  can be evaluated. The investigations of Gainer and Metzner (35) show that except for methyl and ethyl alcohols, the value of  $\psi$  can be taken as six. Olander (56) proposed that the assumption of equal activation energy for diffusion and viscosity was not valid for mutual diffusion and was responsible for differences between observed values of diffusivity and those predicted by Eyring's equation. He suggested the following relation for the difference between the two energies

$$E_{n,B} - E_{D,AB} = \frac{E_{n,B}}{2} - f(E_{n,A} E_{n,B})^{\frac{1}{2}}$$
 (81)

where f denotes the fraction of the activation energy associated with the jumping of a molecule from its initial equilibrium position to a new equilibrium position, and its value for a non-associating system is assumed to be equal to 1/2. This correction has reduced the error in the estimation of mutual diffusivities.

Several modifications of the absolute rate theory have been published. In the following pages some of these are reviewed in detail.

Eyring, Henderson, and Ree (26) presented a modified lattice ("significant structure") theory which treats the liquid state as a combination of solid particles (occupied lattice sites) and gaseous particles (holes or particles in transit). They defined  $\overline{V}_s$  as the solid volume per mole of liquid and  $\overline{V}_s/\overline{V}$  the solid fraction; and expressed the liquid properties as

$$\kappa_{l} = \kappa_{s} \left( \overline{\nabla}_{s} / \overline{\nabla} \right) + \kappa_{g} \left( \frac{\overline{\nabla} - \overline{\nabla}_{s}}{\overline{\nabla}} \right)$$
(82)

where K is the thermal conductivity. Their result for self-diffusion may be given as

$$D_{self} = \frac{\kappa T}{\chi (\overline{V}_{s}/\overline{V})^{\frac{1}{3}\eta}}$$
(83)

There,  $\chi$  is an empirical number of the nearest neighbors, e.g., 5.4 for sodium. Their results for liquid metals

and liquified gases are in general agreement with experimental data. However, for fluids which are normally liquid at ambient conditions this agreement has not been achieved.

It was shortly after Vignes (81) published his excellent correlation for the concentration dependence of the binary diffusion coefficient in nearly ideal systems,

$$D_{AB} = (D_{AB}^{\circ})^{X_{B}} (D_{BA}^{\circ})^{X_{A}} \left(1 + \frac{d \ln \gamma_{A}}{d \ln \chi_{A}}\right)$$
(84)

that Cullinan (7) applied a modified version of the absolute rate theory to derive the Vignes equation. In his developments, Cullinan made the following assumptions: l) the lattice size is the same despite the difference in the size and energy of the particles.

2)  $\exp(-\Delta G_{ij}/RT) = X_i \exp(-\Delta G_{jo}/RT) + X_j \exp(-\Delta G_{io}/RT)$ and 3)  $\Delta G_{ij} = X_j \Delta G_{ij}^{\circ} + X_i \Delta G_{ji}^{\circ}$ . Here,  $\Delta G_{io}$  is the free energy barrier for diffusion of species i in a homogeneous mixture, and  $\Delta G_{ij}^{\circ}$  is the net activation energy for the diffusion process at the limit of infinite dilution of component i.

Cullinan and Cusick (9) extended the previous development to multicomponent systems and derived expressions for the concentration dependence of the multicomponent friction coefficients. They started their analysis with

$$U_{i} = \frac{-a^{2}}{hN} e^{-\Delta G_{i0}/RT} \nabla_{\mu}$$
(85)

Then, they used the Gibbs-Duhem equation to eliminate one of the n chemical potential gradients and obtained

$$-\nabla \mu_{i} = -\frac{hN}{Ca^{2}} \sum_{j=1}^{n} e^{\Delta G_{ij}/RT} C_{j} (U_{j} - U_{i})$$
(86)

where

$$e^{\Delta G_{ij}/RT} = \frac{\prod_{\substack{\substack{\kappa \neq i,j \\ \\ k \neq l}} n - \Delta G_{\kappa 0}/RT}}{\sum_{\substack{k \neq i,j \\ k \neq l}} n - \Delta G_{\kappa 0}/RT}$$
(87)

Comparing equation (86) with the equations defining the multicomponent friction coefficients as

$$-\nabla \mu_{i} = F_{ij} C_{j} (V_{i} - V_{j})$$
(88)

They then made the identification

$$F_{ij} = \frac{hN}{Ca^2} e^{\Delta G_{ij}/RT}$$
(89)

using the following mixing rule

$$\Delta G_{ij} = \sum_{\kappa=1}^{n} X_{\kappa} \lim_{X_{\nu} \to 1} \Delta G_{ij}$$
(90)

The relationship between  $\mbox{F}_{\mbox{ij}}$  and corresponding limiting values is then

$$F_{ij} = \frac{1/C}{\prod_{\kappa} (\overline{V}_{\kappa})^{X_{\kappa}}} \prod_{\kappa}^{n} \left( \lim_{X_{\kappa} \to 1} F_{ij} \right)^{X_{\kappa}}$$
(91)

Cullinan and Cusick expressed the limiting values of friction coefficients at each of the corners of the ternary composition field as

$$\lim_{\substack{X_{i} \to 1 \\ X_{\kappa} \to 0}} F_{ij} = \frac{RTV_{i}}{D_{ji}^{\circ}}$$
(92)

$$\lim_{\substack{X_{j} \neq 1 \\ X_{r} \neq 0}} F_{ij} = \frac{RT\overline{V}_{j}}{D_{ij}}$$
(93)

$$\lim_{X_{\kappa} \to 1} F_{ij} = \frac{-1}{D_{j\kappa}^{c}} \lim_{X_{\kappa} \to 1} \left( \frac{\partial^{\mu} i}{\partial C_{j}} \right)_{C_{i}, T, P} j \neq \kappa$$
(94)

and since  $F_{ij} = F_{ji}$  then,

$$\lim_{X_{\kappa} \to 1} F_{ij} = \frac{-1}{D_{i\kappa}^{\circ}} \lim_{X_{\kappa} \to 1} \left( \frac{\partial^{\mu} j}{\partial C_{i}} \right)_{C_{j}, T, P}$$
(95)

Vignes (82) showed that equations (94,95) are incorrect and it was necessary to make the assumption

$$\lim_{X_{3} \to 1} (\overset{\circ}{D_{12}^{\mu}}_{11}) \stackrel{\sim}{\to} RT \lim_{X_{3} \to 1} (\overset{D_{12}^{\nu}}{C_{1}}) \to 0$$
(96)

to insure the validity of equation (94).

Cullinan and Cusick reported an average absolute deviation of 5% between the calculated and experimental values for the main diffusion coefficients, for the two ternary systems tested. Since the thermodynamic terms appearing in equation (95) can not be evaluated with any accuracy at all, in testing the theory, Cullinan and Cusick determined these terms so as to minimize the sum of squares of deviations of the inverse of the actual  $F_{ij}$ (calculated from experimental diffusion coefficients) from those calculated from equations (91) through (95). The following questions arise immediately:

1) What procedure should be used to calculate  $F_{ij}$  in absence of diffusion data?

2) Are the thermodynamic terms so determined correct values or is this just a method for forcing the calculated values of the diffusion coefficients to closely reproduce the data?

Lane and Kirkaldy (50) developed a prediction method for ternary systems by applying the absolute rate theory in conjunction with a quasi-lattice model for the liquid state. They assumed that diffusion proceeded through the interchange of species between neighboring lattice sites. Their expression for the phenomenological coefficients of Onsager are

$$L_{ii}^{vc} = \sum_{\substack{j \neq i \\ J=0}}^{n-1} \kappa_{ij} C_{i} C_{j}$$
(97)

$$L_{ij}^{vc} = -\kappa_{ij} C_i C_j \quad i \neq j$$
 (98)

where the  $\kappa_{ij}$  are related to the lattice spacing and the activation energy. The  $\kappa_{ij}$ 's are expected to vary slowly with concentration and are evaluated from binary diffusion coefficients at the limit of infinite dilution by

$$\kappa_{\rm io} = D_{\rm io}/C_{\rm o} RT \cdot 10^3 \tag{99}$$

$$\kappa_{ij} = (\kappa_{i0} + \kappa_{j0})/2 \tag{100}$$

where the subscript o denotes solvent. They obtained good greeement between their predicted values and experimental values for ternary electrolytic solutions of less than lN.

#### Empirical Correlations

Lack of a general theoretical description of the diffusion process from the first principles forces us to turn to empirical correlations. To date, there is not any empirical correlation for the prediction of the diffusion coefficients in ternary or multicomponent systems. However, several correlations are available for binary systems. In the following sections these empirical correlations will be reviewed briefly.

By plotting the logarithm of diffusion coefficients versus the logarithm of the vapor pressure of water; and the logarithm of the viscosity of water versus the vapor pressure of water at corresponding temperatures, Othmer and Thakar (59) noticed the similarity in functional relationship of the diffusion in water of various materials with vapor pressure, and the viscosity of water versus the vapor pressure of water. They suspected that a plot of log  $D_{A_{\omega}}$  versus log  $n_{\omega}$  for corresponding temperatures would yield a straight line with a slope equal to  $-E_{D,AB}/E_{n,B}$ , where  $E_{D,AB}$  and  $E_{n,B}$  are the energy of activation for diffusion and viscosity respectively. Based on this fact and information obtained from a logarithmic plot of diffusion coefficients at 20°C. against molal volume of diffusing substances, they proposed the following empirical relationship

$$D_{AB}^{\circ} = \frac{14 \times 10^{-5}}{\eta_{\omega}^{(1.1 \ L_{B}/L_{\omega})} \eta_{B} \ \overline{V}_{A}^{0.6}}$$
(101)

where  $D_{AB}^{\circ}$  is the diffusion coefficient of a dilute solution of A in B,  $n_{\omega}$ , and  $n_{B}$  are the viscosities of water and the solvent respectively; and  $L_{B}$ ,  $L_{\omega}$  are the latent heats of vaporization of solvent and water respectively. Equation (101) has been tested against experimental systems with absolute deviations of a few percent for water as the solvent, to as much as 35% for other materials as solvents.

Wilke and Chang (86) modified the predictive equation for infinite dilution diffusion coefficients, proposed by Wilke (85). The modified form, known as Wilke-Chang equation is

$$D_{AB}^{\circ} = \frac{7.4 \times 10^{-8} (\Omega M_{B})^{\frac{1}{2}} \pi}{\eta_{B} V_{A}^{0.6}}$$
(102)

**.** .

where  $\Omega$  is the "association" parameter of the solvent. They reported that for more than two hundred systems tested the average deviation of 10 per cent between observed and predicted values was found. However, Olander (55) found that, for diffusion of water in organic solvents, the values predicted by the Wilke-Chang equation were higher than the experimental data by a factor of 2.3. He recommended that the predicted values for this case be divided by 2.3. Another modified version of the Wilke equation is given by Scheibel (72) in the form

$$D_{AB}^{\circ} = \frac{8.2 \times 10^{-8} \left| 1 + \left(\frac{3 \overline{V}_B}{\overline{V}_A}\right)^{\frac{1}{3}} \right| T}{n_B \overline{V}_A^{\frac{1}{3}}}$$
(103)

As is evident from equation (103), the association parameter has been eliminated. Average errors of 10 percent have been reported.

Reddy and Doraiswamy (65) have modified the Wilke-Chang equation and proposed two different equations for two different ranges of solvent to solute molar volume ratios as

Case 1: For 
$$\frac{V_B}{V_A} \le 1.5$$
  
 $D_{AB}^{\circ} = \frac{10 \times 10^{-8} \text{ M}^{\frac{1}{2}} \text{ T}}{n_B V_A^{\frac{1}{3}} V_B^{\frac{1}{3}}}$  (104)  
Case 2: For  $\frac{V_B}{V_A} > 1.5$   
 $D_{AB}^{\circ} = \frac{8.5 \times 10^{-8} \text{ M}^{\frac{1}{2}} \text{ T}}{n_B V_A^{\frac{1}{3}} V_B^{\frac{1}{3}}}$  (165)

These authors reported average deviations of 13.5 and 18 percent between predicted and observed values for case 1 and case 2 respectively.

By combining the characteristics of hydrodynamic and absolute rate theories, Lusis and Ratcliff (51) developed a correlation for estimation of diffusion coefficients in organic solvents as

$$D_{AB}^{\circ} = \frac{8.52 \times 10^{-10} \text{T}}{n_{B} \overline{V}_{B}^{\frac{1}{3}}} \left| 1.4 \left( \frac{\overline{V}_{B}}{\overline{V}_{A}} \right)^{\frac{1}{3}} + \left( \frac{\overline{V}_{B}}{\overline{V}_{A}} \right) \right|$$
(106)

A comparison of the various equations presented here, using data cited by Reid and Sherwood (70), was made by Lusis and Ratcliff (51) yielding the following average errors: Wilke-Chang, 20 percent; Othmer-Thakar, 33 percent; Scheibel, 23 percent; and Lusis-Ratcliff, 16 percent.

Based on the principles of non-equilibrium thermodynamics, Rathbun and Babb (64) developed an empirical equation for predicting the concentration dependence of the mutual diffusion coefficient in a binary liquid system containing one component which is associated due to hydrogen bonding. The equation contains one empirical constant which permits the equation to be applied to a wide variety of binary systems including systems with negative deviations from Raoult's law, by assuming a different value for the constant with each system. The equation has the form

$$D_{AB} = \left( X_{B} D_{AB}^{\circ} + X_{A} D_{BA}^{\circ} \right) \left( \frac{d \ln a_{A}}{d \ln X_{A}} \right)^{S}$$
(107)

For systems possessing a positive deviation from Raoult's law, they recommended a value of S equal to 0.6; for negative deviations from Raoult's law, the recommended value was equal to 0.3.

This equation has been largely applied to systems containing a non-polar, and an associated compound.

As previously discussed, cf equation (84), Vignes (81) has presented the following empirical expression for the concentration dependence of mutual diffusion coefficients for binary systems:

$$D_{AB} = (D_{AB}^{\circ})^{X_{B}} (D_{BA}^{\circ})^{X_{A}} \left(1 + \frac{d \ln \gamma_{A}}{d \ln X_{A}}\right)$$
(108)

Vignes stated that this relationship is valid for both ideal and non-ideal systems. However, Dullien (12) tested equation (108) against available experimental data and suggested that Vignes correlation is excellent for prediction of diffusion coefficients in ideal systems but for non-ideal, non-associated systems the general validity is not verified.

## Previous Experimental Work

Considering that there is an indefinite number of diffusional processes involving multicomponent liquid systems, there have been relatively few experimental studies reported, and of these very few have covered the entire concentration range.

Using either a Gouy interferometer or a diaphragm cell, ternary diffusion coefficients have been determined for the systems sucrose-water-glucose (6,41,83), sucrosewater-glycine (17), sucrose-water-fructose (41), sucrosewater-mannitol (23,54), sucrose-water-KC1 (41,71), NaClmannitol-water (16), NaCl-LiCl-water (18), NaCl-KCl-water (15), LiCl, KCl-water (18), KCl-glycine-water (88), raffinose-KCl-water (14), raffinose-urea-water (13), Toluenechlorobenzene-bromobenzene (5), methyl alcohol-n-propyl alcohol-isobutyl alcohol (73), NaCl-water-Pentaery-thritol (89), Na<sub>2</sub>So<sub>4</sub>-water-H<sub>2</sub>So<sub>4</sub> (84), acetone-benzene-carbontetrachloride (8), and Polystyrene 1 - Polystyrene 2 - toluene (10).

Using a diaphragm cell Holmes, Olander and Wilke (43) investigated diffusion of toluene at low concentrations in binary mixtures of n-hexane-n-tetradecane, nhexane-cyclohexane, and cyclohexane-n-decane. Furlong (34), using a diaphragm cell equipped with a Mach-Zender interferometer measured ternary diffusion coefficients for the systems sucrose-glucose-water, sucrose-raffinosewater, and glucose-raffinose-water.

Graff and Drew (38) in an article describing a steadystate method for measuring ternary diffusion, report diffusion coefficients for the system benzene - 2-propanol carbon tetrachloride. Kett (48), using a flowing junction cell equipped with a Mach-Zender interferometer measured ternary diffusion coefficients for the systems dodecanehexadecane-dexane, and diethyl ether-chloroform-carbon tetrachloride at only one composition point.

# CHAPTER III

# DEVELOPMENT OF A NEW THEORETICAL EQUATION FOR PREDICTION OF MULTICOMPONENT DIFFUSION COEFFICIENTS

It was shown in the previous chapter that both the hydrodynamic and the absolute rate theories can lead to reasonable results. However, the hydrodynamic theory yields better results for cases where a large solute molecule diffuses into a continuum of small molecules.

In this chapter a modified absolute rate theory, in conjunction with the principles of irreversible thermodynamics, is applied to the prediction of multicomponent diffusion coefficients in liquid systems.

According to the absolute rate theory (36) the specific rates (frequencies) for the diffusion of species i are

$$v_{i}^{\pm} = \frac{\kappa T}{h} e^{-\Delta G_{i}^{\pm}/RT}$$
(109)

where  $\Delta G_{i}^{\pm}$  is the free energy of formation for the activated state from the initial state. This free energy of formation exists even in a completely homogeneous (on a macroscopic scale) mixture. For the case when a macroscopic chemical potential gradient is present, the free energy of formation may be expressed as

$$\Delta G_{i}^{\pm} = \Delta G_{i0} \pm \frac{1}{2} a \nabla_{\mu}$$
(110)

Here,  $\pm$  refers to the direction of a jump, a is the distance between equilibrium positions,  $\Delta G_{io}$  the free energy of formation for the activated state from the initial state in a homogeneous mixture, and  $\nabla \mu_i$  is the macroscopic gradient of chemical potential. Substitution of equation (110) into equation (109) results in

$$v_{i}^{\pm} = \frac{\kappa T}{h} e^{-(\Delta G_{i0} \pm \frac{1}{2} a \nabla \mu_{i})/RT}$$
(111)

A Taylor series expansion of the exponential term, assuming that 2RT >>  $a \nabla \mu_i$ , yields

$$v_{i}^{\dagger} - v_{i}^{-} = \frac{-a}{hN} e^{-\Delta G_{i0}/RT} \nabla \mu_{i}$$
(112)

The velocity of species i, in the lattice frame of reference may be expressed as

$$U_{i} - U^{\ell} = a(v_{i}^{\dagger} - v_{i}^{-})$$
(113)

where  $U_i$  is the velocity of species i, and  $U^{\ell}$  is the lattice velocity with respect to a fixed coordinate. Combining equations (112) and (113) one obtains

$$U_{i} - U^{\ell} = \frac{-a^{2}}{hN} e^{-\Delta G_{io}/RT} \nabla_{\mu_{i}}$$
(114)

The flux of component i relative to the lattice velocity

is related to  $U_i - U^{\ell}$  by

$$J_{i}^{\ell c} = C_{i} (U_{i} - U^{\ell}) = -L_{ii}^{\ell c} \nabla_{\mu}$$
(115)

where  $L_{ii}^{lc}$  is the phenomenological coefficient given by

$$L_{ii}^{lC} = \frac{a^2}{hN} C_i e^{-\Delta G_i o/RT}$$
(116)

Most experimental data reported in the literature have been measured relative to a volume average velocity. Therefore, it is desirable to obtain relations between coefficients relative to the volume average velocity, and those relative to lattice velocity. In a multicomponent system consisting of N components equation (115) may be rewritten as

$$C_{i}(U_{i}-U^{\ell}) = -L_{ii}^{\ell C} \nabla_{\mu}, \quad i = 1, 2, \dots N-1$$
 (117)

$$C_{N}(U_{N}-U^{\ell}) = -L_{NN}^{\ell C} \nabla \mu_{N}$$
 (118)

Equation (118) can be solved for  $U^{\ell}$  to give

$$U^{\ell} = U_{N} + \frac{1}{C_{N}} L_{NN}^{\ell C} \nabla \mu_{N}$$
(119)

The Gibbs-Duhem equation may be expressed as

$$\nabla \mu_{\mathbf{N}} = -\sum_{j=1}^{\mathbf{N}-1} \frac{\mathbf{C}_{j}}{\mathbf{C}_{\mathbf{N}}} \nabla \mu_{j}$$
(120)

Substitution of  $\nabla \mu_{\mbox{$N$}}$  from equation (120) into equation (119) results in

$$U^{\ell} = U_{N} - \sum_{j=1}^{N-1} \frac{C_{j}}{C_{N}^{2}} L_{NN} \nabla_{\mu} j$$
 (121)

Inserting equation (121) into equation (117) one obtains

$$U_{i} = U_{N} - \frac{1}{C_{i}} \sum_{j=1}^{N-1} \left( \delta_{ij} L_{jj}^{\ell c} + \frac{C_{i}C_{j}}{C_{N}^{2}} L_{NN}^{\ell c} \right) \nabla \mu_{j}$$
(122)

where  $\delta_{ii}$  is the Kronecker delta.

The fluxes relative to the volume average velocity are defined as

$$J_{i}^{\phi C} = C_{i} (U_{i} - U^{\phi}) = -\sum_{j=1}^{N-1} L_{ij}^{\phi C} \nabla_{\mu}$$
(123)

where

$$\mathbf{U}^{\phi} = \sum_{\kappa=1}^{N} C_{\kappa} \overline{\mathbf{V}}_{\kappa} \mathbf{U}_{\kappa}$$
(124)

Here, the  $\overline{V}_{\kappa}$ 's are the partial molar volumes. (Recall that  $C_{\kappa}\overline{V}_{\kappa}$  = volume fraction of component  $\kappa$ .) Substitution of  $U^{\phi}$  from equation (124) into equation (123) results in

$$C_{i} \sum_{\kappa=1}^{N-1} (\delta_{i\kappa} - C_{\kappa} \overline{\nabla}_{\kappa}) U_{\kappa} - C_{i} C_{N} \overline{\nabla}_{N} U_{N} = -\sum_{j=1}^{N-1} L_{ij}^{\phi c} \nabla_{\mu} j \qquad (125)$$

Inserting U  $_{\rm K}$  from equation (122) into equation (125) one obtains

$$C_{i\kappa=1}^{N-1} (\delta_{i\kappa} - C_{\kappa} \overline{\nabla}_{\kappa}) [U_{N} - \frac{1}{C_{\kappa}} \sum_{j=1}^{N-1} (\delta_{\kappa j} L_{jj}^{\ell C} + \frac{C_{j}C}{C_{N}^{2}} L_{NN}^{\ell C}) \nabla_{\mu}_{j}]$$
$$-C_{i}C_{N} \overline{\nabla}_{N} U_{N} = -\sum_{j=1}^{N-1} L_{ij}^{\phi C} \nabla_{\mu}_{j}$$
(126)

Equation (126) may be rearranged to give

$$C_{i_{\kappa=1}}^{N-1}(\delta_{i_{\kappa}}-C_{\kappa}\overline{v}_{\kappa})\frac{1}{C_{\kappa}}\sum_{j=1}^{N-1}(\delta_{\kappa j}L_{jj}^{\ell c}+\frac{C_{j}C}{C_{N}^{2}}L_{NN}^{\ell c})\nabla_{\mu}_{j} = \sum_{j=1}^{N-1}L_{ij}^{\phi c}\nabla_{\mu}_{j} \quad (127)$$

From equation (127) the following relation is obtained

$$\mathbf{L}_{ij}^{\phi c} = C_{i} \sum_{\kappa=1}^{N-1} (\delta_{i\kappa} - C_{\kappa} \overline{V}_{\kappa}) \frac{1}{C_{\kappa}} (\delta_{\kappa j} \mathbf{L}_{jj}^{\ell c} + \frac{C_{j} C_{\kappa}}{C_{N}^{2}} \mathbf{L}_{NN}^{\ell c}) \quad (128)$$

Upon algebraic simplification, equation (128) reduces to

$$L_{ij}^{\phi c} = (\delta_{ij} - C_j \overline{V}_j \frac{C_i}{C_j}) L_{jj}^{\ell c} + C_N \overline{V}_N \frac{C_i C_j}{C_N^2} L_{NN}^{\ell c}$$
(129)

Substitution of equation (129) into equation (123) results in

$$J_{i}^{\phi c} = -\sum_{j=1}^{N-1} [(\delta_{ij} - C_{j}\overline{\nabla}_{j} \frac{C_{i}}{C_{j}})L_{jj}^{\ell c} + C_{N}\overline{\nabla}_{N} \frac{C_{i}C_{j}}{C_{N}^{2}}L_{NN}^{\ell c}]\nabla_{\mu} ]$$
(130)  
$$i = 1, 2, \dots N-1$$

Combining equations (39) and (130) one obtains

$$J_{i}^{\phi C} = -\sum_{\kappa=1}^{N-1} \sum_{j=1}^{N-1} [(\delta_{ij} - C_{j} \overline{V}_{j} \frac{C_{i}}{C_{j}}) L_{jj}^{\ell C} + C_{N} \overline{V}_{N} \frac{C_{i} C_{j}}{C_{N}^{2}} L_{NN}^{\ell C}]$$

$$\left(\frac{\partial \mu}{\partial C_{\kappa}}\right)_{\substack{C_{\ell} \neq \kappa, N}} \nabla C_{\kappa} \quad i = 1, 2, \dots N-1 \qquad (131)$$

The fluxes  $J_i^{\phi C}$  can be expressed in terms of the diffusion coefficients, as

$$J_{i}^{\phi c} = -\sum_{\kappa=1}^{N-1} D_{i\kappa}^{\phi c} \nabla C_{\kappa}$$
(132)

Comparing equations (131) and (132) one obtains

$$D_{i\kappa}^{\phi c} = \sum_{j=1}^{N-1} \left[ \left( \delta_{ij} - C_j \overline{\nabla}_j \frac{C_i}{C_j} \right) L_{jj}^{\ell c} + C_N \overline{\nabla}_N \frac{C_i C_j}{C_N^2} L_{NN}^{\ell c} \right] \left( \frac{\partial^{\mu} j}{\partial C_{\kappa}} \right)_{\ell \neq \kappa, N}$$
(133)

$$i, \kappa = 1, 2, \dots N-1$$

For a ternary system equation (133) takes the form

$$D_{11}^{\phi c} = [(1-C_1 \overline{V}_1) L_{11}^{\ell c} + \frac{C_1^2 \overline{V}_3}{C_3} L_{33}^{\ell c}]_{\mu_{11}}$$

$$+ [-C_{1}\overline{\nabla}_{2}L_{22}^{\&c} + \frac{C_{1}C_{2}\overline{\nabla}_{3}}{C_{3}}L_{33}^{\&c}]_{\mu}_{21}$$
(134a)  

$$D_{12}^{\downarrow C} = [(1-C_{1}\overline{\nabla}_{1})L_{11}^{\&c} + \frac{C_{1}^{2}\overline{\nabla}_{3}}{C_{3}}L_{33}^{\&c}]_{\mu}_{12}$$
(134b)  

$$+ [-C_{1}\overline{\nabla}_{2}L_{22}^{\&c} + \frac{C_{1}C_{2}\overline{\nabla}_{3}}{C_{3}}L_{33}^{\&c}]_{\mu}_{22}$$
(134b)  

$$D_{21}^{\downarrow C} = [-C_{2}\overline{\nabla}_{1}L_{11}^{\&c} + \frac{C_{1}C_{2}\overline{\nabla}_{3}}{C_{3}}L_{33}^{\&c}]_{\mu}_{11}$$
(134c)  

$$+ [(1-C_{2}\overline{\nabla}_{2})L_{22}^{\&c} + \frac{C_{2}^{2}\overline{\nabla}_{3}}{C_{3}}L_{33}^{\&c}]_{\mu}_{21}$$
(134c)  

$$D_{22}^{\downarrow C} = [-C_{2}\overline{\nabla}_{1}L_{11}^{\&c} + \frac{C_{1}C_{2}\overline{\nabla}_{3}}{C_{3}}L_{33}^{\&c}]_{\mu}_{12}$$

+ 
$$[(1-C_2\overline{V}_2)L_{22}^{\&c} + \frac{C_2^2\overline{V}_3}{C_3}L_{33}^{\&c}]_{\mu_{22}}$$
 (134d)

where

$$\mu_{ij} = \left(\frac{\partial \mu_{i}}{\partial C_{j}}\right)_{C_{\kappa}}, \quad \kappa \neq j, N$$

The following linear mixing rule for the energy of activation is assumed

$$\Delta G_{io} = \sum_{j=1}^{3} X_j \Delta G_{ij}^{\circ}$$
(135)

where  $\Delta G_{ij}^{\circ}$  is the energy of activation for diffusion of infinite dilution of component i in j,  $\Delta G_{io}$  is the energy of activation for diffusion of component i in the mixture, relative to lattice velocity. Substitution of  $\Delta G_{io}$  from equation (135) into equation (116) results in

$$L_{ii}^{\ell C} = \frac{a^2}{hN} C_i \exp \begin{bmatrix} -(\frac{3}{j \leq 1} X_j \Delta G_{ij}^\circ) / RT \end{bmatrix}$$
(136)

On rearrangement, equation (136) yields

$$L_{ii}^{lc} = C_{ij} \prod_{j=1}^{3} \left[\frac{a^2}{hN} e^{-\Delta G_{ij}^{\circ} / RT}\right]_{j}^{X_{j}}$$
(137)

For the case of a binary system at the limit of infinite dilution, equation (115) reduces to

$$J_{i}^{\ell c} = J_{i}^{\phi c} = \lim_{X_{i} \to 0} - L_{ii}^{\ell c} \nabla \mu_{i}$$
(138)

and equation (116) reduces to

$$\lim_{X_{i} \to 0} L_{ii}^{\ell C} = C_{i} \frac{a^{2}}{hN} e^{-\Delta G_{ij}^{\circ}/RT}$$
(139)

The gradient of chemical potential at this limit can be expressed as

$$\nabla \mu_{i} = \left(\frac{\partial \mu_{i}}{\partial C_{i}}\right) \nabla C_{i}$$
(140)

The chemical potential of component i may be written as

$$\mu = \mu_{i}^{\circ} + RT \ln a \qquad (141)$$

where  $\mu_{i}^{\circ}$  is a function of T and P, and a is the activity of component i. At constant T,P for a binary solution at the limit of infinite dilution, equation (141) yields

$$\lim_{\substack{C_{i} \to 0}} \left(\frac{\partial^{\mu} i}{\partial C_{i}}\right) = \frac{RT}{C_{i}}$$
(142)

Combining equations (140) and (142) one obtains

$$\nabla \mu_{i} = \frac{RT}{C_{i}} \nabla C_{i}$$
(143)

Substitution of equations (143) and (139) into equation (138) results in

$$J_{i}^{\phi C} = -RT \frac{a^{2}}{hN} e^{-\Delta G_{ij}^{\circ}/RT} \nabla C_{i}$$
(144)

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The flux of component i at the limit of infinite dilution for a binary system may be expressed in terms of diffusion coefficient as

$$J_{i}^{\phi c} = -D_{ij}^{\circ} \nabla C_{i}$$
(145)

Comparing equations (144) and (145) one obtains

$$D_{ij}^{\circ} = RT \frac{a^2}{hN} e^{-\Delta G_{ij}^{\circ}/RT}$$
(146)

A similar result is obtained for self diffusion coefficient. Inserting equation (146) into equation (137) yields

$$L_{ii}^{\ell c} = \frac{C_i}{RT} \prod_{j=1}^{3} (D_{ij}^{\circ})^{X_j}$$
(147)

Combining equation (147) and equations (134) yields

$$D_{11}^{\phi C} = [(1-C_{1}\overline{V}_{1})C_{1} \prod_{j=1}^{3} (D_{1j}^{\circ})^{X_{j}} + C_{1}^{2}\overline{V}_{3} \prod_{j=1}^{3} (D_{3j}^{\circ})^{X_{j}}]_{RT}^{\frac{\mu}{11}} + [-C_{1}C_{2}\overline{V}_{2} \prod_{j=1}^{3} (D_{2j}^{\circ})^{X_{j}} + C_{1}C_{2}\overline{V}_{3} \prod_{j=1}^{3} (D_{3j}^{\circ})^{X_{j}}]_{RT}^{\frac{\mu}{21}}$$
(148a)

$$D_{12}^{\phi C} = [(1-C_{1}\overline{\nabla}_{1})C_{1} \prod_{j=1}^{3} (D_{1j}^{\circ})^{X_{j}} + C_{1}^{2}\overline{\nabla}_{3} \prod_{j=1}^{3} (D_{3j}^{\circ})^{X_{j}}]_{RT}^{\frac{\mu_{12}}{RT}} + [-C_{1}C_{2}\overline{\nabla}_{2} \prod_{j=1}^{3} (D_{2j}^{\circ})^{X_{j}} + C_{1}C_{2}\overline{\nabla}_{3} \prod_{j=1}^{3} (D_{3j}^{\circ})^{X_{j}}]_{RT}^{\frac{\mu_{22}}{RT}}$$
(148b)

$$D_{21}^{\phi c} = [-C_{1}C_{2}\overline{V}_{1} \prod_{j=1}^{3} (D_{1j}^{\circ})^{X_{j}} + C_{1}C_{2}\overline{V}_{3} \prod_{j=1}^{3} (D_{3j}^{\circ})^{X_{j}}]_{\overline{RT}}^{\mu}$$

$$+ [(1-C_{2}\overline{V}_{2})C_{2} \prod_{j=1}^{3} (D_{2j}^{\circ})^{X_{j}} + C_{2}^{2}\overline{V}_{3} \prod_{j=1}^{3} (D_{3j}^{\circ})^{X_{j}}]_{\overline{RT}}^{\mu} (148c)$$

$$D_{22}^{\phi c} = \left[-C_{1}C_{2}\overline{V}_{1} \prod_{j=1}^{3} (D_{1j}^{\circ})^{X_{j}} + C_{1}C_{2}\overline{V}_{3} \prod_{j=1}^{3} (D_{3j}^{\circ})^{X_{j}}\right]_{RT}^{\mu}$$

$$+ \left[(1-C_{2}\overline{V}_{2})C_{2} \prod_{j=1}^{3} (D_{2j}^{\circ})^{X_{j}} + C_{2}^{2}\overline{V}_{3} \prod_{j=1}^{3} (D_{3j}^{\circ})^{X_{j}}\right]_{RT}^{\mu} (148d)$$

The chemical potential derivatives  $\mu_{ij}$  can be obtained from equation (141) as

$$\mu_{11} = RT \left(\frac{\partial \ln a_1}{\partial C_1}\right)_{C_2}$$
(149a)

$$\mu_{12} = RT \left(\frac{\partial \ln a_1}{\partial C_2}\right)_{C_1}$$
(149b)

$$\mu_{21} = RT \left(\frac{\partial \ln a_2}{\partial C_1}\right)_{C_2}$$
(149c)

$$\mu_{22} = RT \left(\frac{\partial \ln a_2}{\partial C_2}\right)_{C_1}$$
(149d)

Substitution of equations (149) into equations (148) results in

$$D_{11}^{\phi c} = [(1-c_{1}\overline{v}_{1})c_{1} \prod_{j=1}^{3} (D_{1j}^{\circ})^{X_{j}} + c_{1}^{2}\overline{v}_{3} \prod_{j=1}^{3} (D_{3j}^{\circ})^{X_{j}}] (\frac{\partial \ln a_{1}}{\partial c_{1}})_{\partial c_{1}} c_{2} + [-c_{1}c_{2}\overline{v}_{2} \prod_{j=1}^{3} (D_{2j}^{\circ})^{X_{j}} + c_{1}c_{2}\overline{v}_{3} \prod_{j=1}^{3} (D_{3j}^{\circ})^{X_{j}}] (\frac{\partial \ln a_{2}}{\partial c_{1}})_{c_{2}} (150a)$$

$$D_{12}^{\phi c} = [(1-C_{1}\overline{V}_{1})C_{1} \prod_{j=1}^{3} (D_{1j}^{\circ})^{X_{j}} + C_{1}^{2}\overline{V}_{3} \prod_{j=1}^{3} (D_{3j}^{\circ})^{X_{j}}] (\frac{\partial \ln a_{1}}{\partial C_{2}})_{C_{1}} + [-C_{1}C_{2}\overline{V}_{2} \prod_{j=1}^{3} (D_{2j}^{\circ})^{X_{j}} + C_{1}C_{2}\overline{V}_{3} \prod_{j=1}^{3} (D_{3j}^{\circ})^{X_{j}}] (\frac{\partial \ln a_{2}}{\partial C_{2}})_{C_{1}}$$
(150b)

$$D_{21}^{\phi C} = [-C_{1}C_{2}\overline{V}_{2} \prod_{j=1}^{3} (D_{1j}^{\circ})^{X_{j}} + C_{1}C_{2}\overline{V}_{3} \prod_{j=1}^{3} (D_{3j}^{\circ})^{X_{j}}] \left(\frac{\partial \ln a_{1}}{\partial C_{1}}\right)_{C_{2}} + [(1-C_{2}\overline{V}_{2})C_{2} \prod_{j=1}^{3} (D_{2j}^{\circ})^{X_{j}} + C_{2}^{2}\overline{V}_{3} \prod_{j=1}^{3} (D_{3j}^{\circ})^{X_{j}}] \left(\frac{\partial \ln a_{1}}{\partial C_{1}}\right)_{C_{2}} (150c)$$

$$D_{22}^{\phi C} = \left[ -C_{1}C_{2}\overline{V}_{1} \right]_{j=1}^{3} \left( D_{1j}^{\circ} \right)^{X_{j}} + C_{1}C_{2}\overline{V}_{3} \right]_{j=1}^{3} \left( D_{3j}^{\circ} \right)^{X_{j}} \left( \frac{\partial \ln a_{1}}{\partial C_{2}} \right)_{l} (150d)$$
$$+ \left[ \left( 1 - C_{2}\overline{V}_{2} \right)C_{2} \right]_{j=1}^{3} \left( D_{2j}^{\circ} \right)^{X_{j}} + C_{2}^{2}\overline{V}_{3} \right]_{j=1}^{3} \left( D_{3j}^{\circ} \right)^{X_{j}} \left( \frac{\partial \ln a_{2}}{\partial C_{2}} \right)_{l} (150d)$$

Equations (150) express the ternary diffusion coefficients in terms of binary diffusion coefficients at the limit of infinite dilution, self diffusion coefficients, and thermodynamic factors. It remains to show that the modified absolute rate theory satisfies the "Onsager Reciprocal Relations". This can be accomplished by first rewriting equations (130) for a ternary system as

$$J_{1}^{\phi c} = -\left[\left(1 - C_{1}\overline{\nabla}_{1}\right)L_{11}^{\ell c} + \frac{C_{1}^{2}\overline{\nabla}_{3}}{C_{3}}L_{33}^{\ell c}\right]\nabla\mu_{1} - \left[-C_{1}\overline{\nabla}_{2}L_{22}^{\ell c} + \frac{C_{1}C_{2}\overline{\nabla}_{3}}{C_{3}}L_{33}^{\ell c}\right]\nabla\mu_{2}$$
(151a)  
$$J_{1}^{\phi c} = -\left[-C_{1}\overline{\nabla}_{2}L_{33}^{\ell c}\right]\nabla\mu_{2}$$
(151a)

$$J_{2}^{\phi C} = -\left[-C_{2}\overline{\nabla}_{1}L_{11}^{\chi C} + \frac{12}{C_{3}}L_{33}^{\chi C}\right]\nabla_{\mu_{1}} - \left[(1-C_{2}\overline{\nabla}_{2})L_{22}^{\chi C} + \frac{C_{2}^{2}\overline{\nabla}_{3}}{C_{3}}L_{33}^{\chi C}\right]\nabla_{\mu_{2}}$$
(151b)

Equating the like coefficients of the independent equations (37) and (151) one obtains

$$L_{11}^{\phi c} + L_{12}^{\phi c} = (1 - C_1 \overline{V}_1) L_{11}^{\ell c} + \frac{C_1^2 \overline{V}_3}{C_3} L_{33}^{\ell c}$$
(152a)

$$L_{11\alpha_{12}}^{\phi c} + L_{12\alpha_{22}}^{\phi c} = -C_1 \overline{V}_2 L_{22}^{\ell c} + \frac{C_1 C_2 V_3}{C_3} L_{33}^{\ell c}$$
(152b)

$$L_{21}^{\phi c}{}_{11} + L_{22}^{\phi c}{}_{21} = -C_2 \overline{V}_1 L_{11}^{\ell c} + \frac{C_1 C_2 \overline{V}_3}{C_3} L_{33}^{\ell c}$$
(152c)

$$L_{21}^{\phi C}{}_{12} + L_{22}^{\phi C}{}_{22} = (1 - C_2 \overline{V}_2) L_{22}^{\ell C} + \frac{C_2^2 \overline{V}_3}{C_3} L_{33}^{\ell C}$$
(152d)

Equations (152a) and (152b) may be solved to yield the expression for  $L_{12}^{\phi C}$  in terms of  $L_{1i}^{\ell C}$ , and equations (152c) and (152d) can be solved to give the corresponding expression for  $L_{21}^{\ell C}$ . These are

$$L_{12}^{\phi C} = \frac{\alpha_{21} (-C_1 \overline{\nabla}_2 L_{22}^{\ell C} + \frac{C_1 C_2 \nabla_3}{C_3} L_{33}^{\ell C})}{\alpha_{11}^{\alpha_{22}} - \alpha_{12}^{\alpha_{22}} L_{21}^{\ell C}} \\ - \frac{-\alpha_{12} ((1 - C_1 \overline{\nabla}_1) L_{11}^{\ell C} + \frac{C_1^2 \overline{\nabla}_3}{C_3} L_{33}^{\ell C})}{\alpha_{11}^{\alpha_{22}} - \alpha_{12}^{\alpha_{21}} 21}$$
(153a)

$$L_{21}^{\phi c} = \frac{\alpha_{11} [(1 - C_2 \overline{V}_2) L_{22}^{\ell c} + \frac{C_2^2 \overline{V}_3}{C_3} L_{33}^{\ell c}]}{\alpha_{11}^{\alpha_{22}} - \alpha_{12}^{\alpha_{21}}}$$
$$\frac{-\alpha_{12} (-C_2 \overline{V}_1 L_{11}^{\ell c} + \frac{C_1 C_2 \overline{V}_3}{C_3} L_{33}^{\ell c})}{\alpha_{11}^{\alpha_{22}} - \alpha_{12}^{\alpha_{21}}}$$
(153b)

Equations (153) can be combined with equations (38) to yield

$$L_{12}^{\phi c} = L_{21}^{\phi c} = -C_2 \overline{v}_1 (1 - C_1 \overline{v}_1) L_{11}^{\ell c} - C_1 \overline{v}_2 (1 - C_2 \overline{v}_2) L_{22}^{\ell c} + C_1 C_2 \overline{v}_3^2 L_{33}^{\ell c}$$
(154)

Therefore, the modified absolute rate theory predicts that  $L_{12}^{\phi c} = L_{21}^{\phi c}$ .

In the above derivations it was assumed: 1) The distance between equilibrium positions, a, is not a function of composition.

2) Partial molar volumes are constant and are taken as pure molar volumes.

3) The energy of activation for a given component in a solution is a linear function of its values in the various binaries at infinite dilution and during self diffusion. This is given by equation (135).

#### CHAPTER IV

## EXPERIMENTAL INVESTIGATIONS

# Selection of Experimental Method

There exists a wide variety of methods which may be employed to investigate the rates of molecular diffusion. A detailed description of these methods is given by Tyrrell (80) and will not be discussed here. In general, methods which utilize optical techniques are advantageous because they are capable of accurate measurements and do not require calibration. The method which employs a birefringent interferometer is of particular interest for the study of infinite diffusion. Bryngdahl (4) analyzed this method and found that it possesses a high degree of precision unattainable by previous methods in which the optical power of resolution limits accuracy. The most advantageous feature of the birefringent interferometer is its high degree of resolution making it capable of detecting very small differences in refractive index. As a result, it is possible to use very small concentration differences between the two diffusing solutions. This condition assures that the experimental diffusion coefficients correspond to the Fickian diffusion coefficients.

A double savart plate birefringent interferometer was used to obtain the diffusion coefficients for both binary and ternary systems studied in the present work.

# Experimental Apparatus

The experimental equipment used to determine the diffusion coefficients for both binary and ternary systems consists basically of a double Savart plate birefringent interferometer, a constant temperature air bath, a flowing junction test cell, a 35 mm still camera, a time measurement system, and a fringe measurement system.

The basic experimental apparatus was designed by Merliss (52) on the basis of work by Bryngdahl and Ljunggren (3) and Ingelstam (45,46). Modification of the apparatus was carried out by Haluska (39). However, the accuracy obtained was not high enough to allow accurate measurement of the ternary diffusion coefficients. Consequently, the need for major modifications of the experimental apparatus was recognized, and it was taken as the first objective of this research. Modification was focused on the two critically important elements of the apparatus, namely, the birefringent interferometer and the diffusion test cell. A brief description of the experimental equipment, including the modifications made in this work, will be presented in the following sections.

The interferometer. The birefringent interferometer has been described in detail by Merliss (52) and consisted

basically of an optical bench, a lens system, and a laser light source. Figure 1. is a schematic drawing of the interferometer system used in this work. The interferometer's function can be explained briefly with reference to the Figure 1. as follows: A spatially and temporally coherent, polarized light beam from a helium-neon gas laser (Electro Optics Associates, Model 201) is expanded and collimated by meshing the focal points of the lenses  $L_1$  and  $L_2$ , to pass through the diffusion test cell. After passing through the test cell the beam is reconverged to a diameter of about 1/2 inch and recollimated by meshing the focal points of the lenses  $L_2$  and  $L_4$  for passage through the first savart plate S1. Then, the beam is converged by the lens L<sub>5</sub> through the second savart plate S<sub>2</sub> to form the fringe patterns on the photographic plate (camera), after passing through the polarizer P.

The modification made in this work was the complete . redesign of the portion between lens  $L_4$  and the photographic plate. The new design consisted of the following changes:

The lens after the second savart plate was removed.
 The lens L<sub>5</sub> was replaced by a lens with a focal length of 25 mm, which is short compared to the original 64 mm lens.

3) The optical components between lens  $L_4$  and the photographic plate were repositioned in a very compact arrangement. These changes resulted in extremely sharp fringe



Figure 1. Interferometer Optical Arrangement.

patterns and an increase in the number of fringes from two to eight, which, in turn, reduced the fringe width considerably, and yielded far more accurate fringe measurements. Moreover, the new design provided a very easy focusing procedure. That is, with every component of the interferometer fixed in place, the position of the lens  $L_5$ could be adjusted to obtain a sharp image of the fringes and the test cell on the photographic plate.

The diffusion cell. The flowing junction diffusion cell and its supporting elements (fluid reservoirs, tubings, and valve system) were built by Merliss (52), based on the design of Svensson (78) and Skinner (74). In the present study a new diffusion cell was utilized. A schematic representation of this diffusion cell is gi-The new cell was made of two 316 stainven in Figure 2. less steel plates held together with two machine bolts. The cell cavity was machined from one cell plate to the dimensions 1/4 inch wide by 3-1/2 inches high by 3 inches thick, giving a geometrical light path through the cell of three inches. All faces of the cell forming sealing surfaces were machined and ground to high tolerance to insure leak free seals. The cell could be taken apart for cleaning and the plates could be reassembled in exactly the same relative position by means of two positioning pins. All inlet holes were drilled and tapped for 5/16 inch, 24 thread per inch, special O-ring seal



Figure 2. Flowing Junction Test Cell.

fittings, with 1/8 inch compression tubing connections on the opposite end of the fittings. The slits were 0.006 inch wide and were deep enough to intersect the 1/3 inch circular channels drilled parallel to the walls with a horizontal orientation. Each of these channels was, in turn, intersected perpendicularly by five holes drilled from the back of the plates. The withdrawn fluid was collected by manifolds leading to the drain line. Each fluid inlet was connected to a stainless steel fluid reser-The cell was vented by a 1/8 inch stainless steel voir. tube located adjacent to the top inlet port. Adjustable brackets held the cell windows in place. Each cell window was made of schott BK-7 optical glass polished flat to 1000 angstroms or less with surfaces parallel to 15 seconds or less.

A detailed description of the supporting elements was given by Merliss (52) and Haluska (39) and will not be discussed here. Advantages gained by the new cell design are:

1) Uniform withdrawal of the fluid from the entire length of the slits considerably improved the quality of initial interface.

2) All contamination problems were eliminated.

3) Cleaning of the cell became an easy matter by elimination of cements which were originally used for sealing purposes.

The constant temperature air bath. The constant temperature air bath consisted of a double wall box, the annular space of which was filled with perlite insulation. Windows constructed of two glass plates with internal air space were mounted in the walls to align with the optical The two side walls were equipped with similar doupath. ble glass viewing ports. The air bath was equipped with heater elements, baffles, an air circulating fan and temperature sensing elements. Temperatures in the bath were controlled within 0.01° C by means of a temperature controller (Hallikainen, Thermotrol serial No. 14672); temperature fluctuations were continuously recorded with a (Hallikainen Thermograph, serial No. 13058). Unshielded nickel-wound resistance probes were used for sensing the bath temperature. The equilibrium temperatures were measured by a calibrated platinum resistance thermometer (Leeds and Northrup, No. 8164) located on the inner bath wall. A Mueller Temperature Bridge (Leeds and Northtup, serial No. 1699588) and a D.C. null voltmeter (Hewlett Packard Co., serial No. 646-014808) were used for resistance measurements of the thermometer.

<u>Camera and film.</u> A Nikkormat (model FT) 35 mm camera without a lens was used to photograph the interference patterns. The camera was bolted to the camera mount, possessing five degrees of freedom for adjustments. The camera mount was in turn mounted on the optical bench.
Kodak plus-X Panchromatic film was selected for the following reasons: (1) the fine grain provided excellent picture sharpness and (2) short exposure time required because of the relatively high exposure index (ASA 125).

<u>Time measurement.</u> A precision electric timer (Precision Timer Co., Inc.) was used to measure the elapsed time during a diffusion run. The timer was accurate to one-tenth of a second and had a range of 0 to 9999.9 seconds. The timer was located in a control box mounted on the optical bench adjacent to the camera.

Fringe measurement system. A coordinate measuring microprojector (George Sherr Co., Inc.) was used for the measurement of the fringe patterns recorded on the photographic negatives.

<u>Chemicals.</u> All chemicals used in this study were of very high purity. The following is a listing of chemicals together with the manufacturers' purity specifications:

J. T. Baker Co.

Acetone	"Analyzed" Reagent Lot 35055
	Spectrophotometric quality
	Boiling Range 56.1°-56.4°C
	Residue after evaporation 0.0002%
Methyl Alcohol	"Analyzed" Reagent Lot 38735
	Spectrophotometric quality
	Boiling Range 64.6°-65.0°C
	Residue after evaporation 0.0001%

Benzene	"Analyzed" Reagent Lot 38769
	Boiling Range 80.1°-80.5°C
	Residue after evaporation 0.0001%
Merck	

Carbon tetra-	"Analyzed" Reagent Lot 7244
chloride	Boiling Range 76.7°-77.7°C
	Residue after evaporation 0.001%

U.S.I.

Ethyl	alcohol	U.S.I S.D.A. /17
		Boiling Point 78.38°C
		Maximum impurities 0.1%

The water used was triple distilled and deionized and had impurities of less than 0.1 ppm.

## Experimental Procedures

Alignment of diffusion apparatus. The alignment procedures developed by Merliss (68) were used to align the interferometer.

Solution preparation. The test solutions for both binary and ternary experiments were prepared by gravimetric methods through several weight measurements. The test solutions for each binary run were prepared immediately prior to the start of a diffusion experiment. For each binary experiment, two test solutions with slight difference in solute mole fraction were required. In order to obtain these two solutions a stock solution near the desired mole fraction of the solute component was prepared by the following procedure: A clean and dry bottle and its Teflon-lined screw cap were weighed. Then an amount of solvent, nearly equal to the predetermined amount, was added and the total weight was measured. The solute was added and weighed in a similar manner. The exact weight of both solute and solvent were obtained by subtraction of the consecutive recorded weights. These values were then used to calculate the mole fractions. The stock solution was then divided into two portions, one of which was again weighed and a known amount of solute was added to make up the required compositional difference between the two portions. The exact values of average solute mole fraction and the mole fraction difference were then calcu-In the case of ternary diffusion experiments at lated. least two experimental runs at the same average concentrations of the constituents were required to permit calculation of the diffusion coefficients. The stock solution was prepared in the same manner as for binaries. To make the concentration difference between two solutions used in an experimental run a portion of stock solution was weighed in a clean bottle, then a small precleaned and dried test tube held in a brass tube holder was used to weigh a small amount of one or both solute components and was added to the bottle containing the weighed portion of the stock solution. The cap was tightened and the solution was thoroughly mixed. This completed the process of preparing solutions. . . .

Procedure for diffusion runs. The first step in preparation for each diffusion run was the thorough cleaning of the diffusion cell, fluid reservoirs, valve system, and tubings. Use of the new cell enabled application of the following simple cleaning procedure: at the beginning of each run the remainder of the solutions from a previous run was drained completely. Then, the fluid reservoirs were washed, rinsed and finally filled with The cell was filled and drained several times. acetone. Then the cell was filled and the vent line as well as the drain line connected to the bottom of the cell were closed and acetone withdrawal from the center slits began. This withdrawal went on until both fluid reservoirs were completely drained and the fluid level in the cell was only as high as the center slits. At this point the valve on the drain line connected to the bottom of the cell was opened and the remaining acetone was drained. Then, a flow of compressed air was supplied to the cell through the vent line. All the valves were left open so that air would flow through all the tubings, valves, fluid reservoirs and fluid withdrawal slits and manifolds. This was continued for about two hours to insure discharge of every trace of acetone from the cell assembly. The flow of air to the cell was then stopped and the valves on the fluid reservoirs were closed. Then, high density (heavy) and low density (light) solutions were transferred to the reservoirs leading to the bottom and top of the cell respec-

tively. The valve on the fluid reservoir leading to the bottom of the cell was opened and the heavy solution was permitted to fill the drain line leading to the bottom of the cell and to drain from it to insure discharge of the air from this line. Then the valve on this drain line was closed permitting the heavy solution to flow into the cell while the valve on the drain line connected to the withdrawal slits were kept open. As soon as the fluid level in the cell passed the withdrawal slits the fluid started to flow through these slits to the drain line. This was continued until about 50 ml. of solution was drained to assure discharge of air from this line. Then, this valve was also closed and the cell was completely filled by the heavy solution. The valve on the heavy solution reservoir was closed and the one on the light fluid reservoir was opened. After a two-minute interval the valve on the withdrawal slits was opened to permit a withdrawal rate of about twenty drops per minute. The withdrawn fluid was replaced by the light fluid flowing into the cell from the top thus forming a moving interface between light and heavy solutions. As more fluid was withdrawn this interface moved toward the center slits with its motion observed visually. As soon as this interface reached the center, interface sharpening started by slowly opening the valve on the heavy fluid reservoir. This permitted flow of the heavy and light solutions from the bottom and the top to the cell while withdrawing from the center slits. At this point the laser

was turned on and process of interface sharpening was followed by observation of the interference patterns formed on the photographic plate. The rate of fluid withdrawal was reduced slowly down to about eight drops per minute. After a sharp interface was formed, withdrawal was continued for about two hours.

The necessary steps for achieving thermal equilibrium at the desired temperature were taken during the time period when the cell was cleaned and the interface was established (except for short time when the solutions were transferred to the fluid reservoirs). As soon as the fluid reservoirs were washed and filled up with acetone, the lid of constant temperature bath was installed and the fan was started. Power to the auxiliary bath heater was turned on, and control rheostat for the auxiliary bath heater was set at the desired level. To start the operation of the control heater, the Thermotrol was set for the desired control temperature. The rheostat on the control heater was adjusted for maximum power to the control heater. When the Thermotrol began to function on control, the power to the auxiliary heater was reduced gradually in such a way as to maintain the Thermotrol on control. This was continued until power to the auxiliary heater was reduced to nearly zero. Then the power to the auxiliary heater was cut off completely and reduction of power of the control heater was initiated. The power to the control heater was slowly reduced until the ratio of off time to on time of the control heater was approximately four. This was the optimum ratio specified for the controller by the manufacturer. The air temperature in the air bath was periodically measured by the platinum capsule thermometer located on the bath wall. Minor adjustments on the Thermotrol setting were made as it became necessary to maintain the desired temperature.

The thermal equilibrium was usually achieved before the interface was established. Therefore, by the time the initial interface was established thermal equilibrium had already been achieved and two hours of maintaining the interface insured that the liquid in the cell as well as every other part of the system was at the desired experimental temperature. To start the diffusion process, the timer was activated and the valves on the drain line as well as those on the fluid reservoirs were closed simultaneously and thus permitted the two solutions in the cell to diffuse. The diffusion process was monitored by taking photographs of the interference patterns at proper time intervals.

<u>Confirmation of technique.</u> The validity of birefringent interferometry when utilized to measure binary diffusion coefficients has been tested and confirmed by Merliss (52) and Haluska (39). To further extend this validity to the measurement of the ternary diffusion coefficients, the diffusion coefficients of a previously studied ternary system (8) was measured at one concentration level. A comparison of the diffusion coefficients produced by this technique with previously reported data is given in Table 1.

# TERNARY DIFFUSION COEFFICIENTS FOR THE SYSTEM ACETONE(1) - BENZENE(2) - CARBON TETRACHLORIDE(3) AT 25°C.

Average Mo	ole fractions	
$x_1 = 0.35$	$x_2 = 0.30$	$x_3 = 0.35$
Diffusion	Coefficients	
D <sub>11</sub> ×10 <sup>5</sup> , cm <sup>2</sup> /sec.	1.8134*	1.887#
$D_{12} \times 10^5$ , $cm^2/sec$ .	-0.2438*	-0.213#
$D_{21} \times 10^5$ , $cm^2/sec$ .	-0.0467*	<b>-0.</b> 037 <sup>#</sup>
$D_{22} \times 10^5$ , cm <sup>2</sup> /sec.	2.1989*	2.225#

\* Data obtained in the present research.

# Data obtained by Cullinen and Toor (8).

## Interpretation of Data

The equations defining one dimensional diffusion

$$\frac{\partial C_1}{\partial t} = D_{11} \frac{\partial^2 C_1}{\partial x^2} + D_{12} \frac{\partial^2 C_2}{\partial x^2}$$
(155a)

$$\frac{\partial C_2}{\partial t} = D_{21} \frac{\partial^2 C_1}{\partial x^2} + D_{22} \frac{\partial^2 C_2}{\partial x^2}$$
(155b)

where,  $C_1$ ,  $C_2$  are solute concentrations,  $D_{11}$ ,  $D_{22}$  are main diffusion coefficients, and  $D_{12}$ ,  $D_{21}$  are cross-term diffusion coefficient. For free diffusion with a sharp initial boundary between solutions A and B, above and below the boundary respectively, the initial concentrations for the two solutes (i=1,2) are

$$C_{i} = \overline{C}_{i} + \frac{\Delta C_{i}}{2} \text{ for } X>0, t=0 \qquad (156 a)$$

$$C_{i} = \overline{C}_{i} - \frac{\Delta C_{i}}{2} \text{ for } X < 0, t=0$$
 (156 b)

where

$$\overline{C}_{i} = \frac{1}{2} [(C_{i})_{A} + (C_{i})_{B}]$$
(156 c)

$$\Delta C_{i} = (C_{i})_{B} - (C_{i})_{A}$$
 (156 d)

and the boundary conditions are

$$C_i \rightarrow \overline{C}_i + \frac{\Delta C_i}{2} \text{ for } x \rightarrow \infty, t > 0$$
 (157a)

$$c_i \rightarrow \overline{c}_i - \frac{\Delta C_i}{2}$$
 for  $x \rightarrow -\infty$ ,  $t > 0$  (157b)

A matrix solution of equations (155) with initial and boundary conditions (156) and (157) yields (cf Appendix A)

$$C_{1} - \overline{C}_{1} = \frac{1}{2} \{ \frac{\lambda_{2}^{-D} 1}{\lambda_{2}^{-\lambda_{1}}} \Delta C_{1} - \frac{D_{12}}{\lambda_{2}^{-\lambda_{1}}} \Delta C_{2} \} \operatorname{erf}(n_{1})$$
  
+ 
$$\frac{1}{2} \{ - \frac{\lambda_{1}^{-D} 1}{\lambda_{2}^{-\lambda_{1}}} \Delta C_{1} + \frac{D_{12}}{\lambda_{2}^{-\lambda_{1}}} \Delta C_{2} \} \operatorname{erf}(n_{2})$$
(158a)

$$C_{2}-\overline{C}_{2} = \frac{1}{2} \{ \frac{(\lambda_{2}-D_{11})(\lambda_{1}-D_{11})}{D_{12}(\lambda_{2}-\lambda_{1})} \Delta C_{1} - \frac{\lambda_{1}-D_{11}}{\lambda_{2}-\lambda_{1}} \Delta C_{2} \} erf(n_{1})$$

+ 
$$\frac{1}{2} \{ -\frac{(\lambda_2 - D_{11})(\lambda_1 - D_{11})}{D_{12}(\lambda_2 - \lambda_1)} \Delta C_1 + \frac{\lambda_2 - D_{11}}{\lambda_2 - \lambda_1} \Delta C_2 \} erf(n_2)$$
(158b)

where

$$\lambda_{1} = \frac{1}{2} \{ (D_{11} + D_{22}) + [ (D_{11} + D_{22})^{2} - 4 (D_{11} D_{22} - D_{12} D_{21}) ]^{\frac{1}{2}} \}$$
(159a)

$$\lambda_{2} = \frac{1}{2} \{ (D_{11} + D_{22}) - [(D_{11} + D_{22})^{2} - 4 (D_{11} D_{22} - D_{12} D_{21})]^{\frac{1}{2}} \}$$
(159b)

$$n_1 = \frac{X}{2\sqrt{\lambda_1 t}}$$
,  $n_2 = \frac{X}{2\sqrt{\lambda_2 t}}$  (159c)

$$\operatorname{erf}(q) = \frac{2}{\sqrt{\pi}} \int_{0}^{q} e^{-q^{2}} dq$$
 (159d)

In order to relate solute concentrations to the refractive index of solutions, it is assumed that the dependence of refractive index, n, on the two independent concentrations can be represented by the first three terms of a Taylor series, namely,

$$n = n_{c} + R_{1}(C_{1}-\overline{C}_{1}) + R_{2}(C_{2}-\overline{C}_{2})$$
(160)

where  $n_{\overline{C}}$  is the refractive index of a solution in which

the solute concentrations are  $\overline{C}_1$  and  $\overline{C}_2$ ,

$$R_{i} \equiv \left(\frac{\partial n}{\partial C_{i}}\right)_{T,P,C_{j\neq i,N}}$$
(161)

The refractive index fractions of solutes are defined as

$$\alpha_{1} = R_{1} \frac{\Delta C_{1}}{\Delta n}$$
 (162a)

$$\alpha_2 = R_2 \frac{\Delta C_2}{\Delta n}$$
(162b)

where  $\Delta n = R_1 \Delta C_1 + R_2 \Delta C_2$ . (162c) Equation (160), after inserting equations (158) and making use of equations (162), becomes

$$n = n_{\overline{c}} + \frac{\Delta n}{2} \{ L_1 \operatorname{erf}(n_1) + L_2 \operatorname{erf}(n_2) \}$$
(163a)

where

$$L_{1} = \frac{R_{1}}{\Delta n} \left\{ \frac{\lambda_{2}^{-D} 1}{\lambda_{2}^{-\lambda_{1}}} \Delta C_{1} - \frac{D_{12}}{\lambda_{2}^{-\lambda_{1}}} \Delta C_{2} \right\} + \frac{R_{2}}{\Delta n} \left\{ \frac{(\lambda_{2}^{-D} 1)(\lambda_{1}^{-D} 1)}{D_{12}(\lambda_{2}^{-\lambda_{1}})} \Delta C_{1} - \frac{\lambda_{1}^{-D} 1}{\lambda_{2}^{-\lambda_{1}}} \Delta C_{2} \right\}$$
(163b)

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$$L_2 = 1 - L_1$$
 (163c)

The product of the refractive index, n, and the geometrical length,  $\alpha$ , through the test cell is defined as the length of the optical path Z and is given by

$$Z = \alpha n = Z_{\overline{c}} + \frac{\alpha \Delta n}{2} [L_1 \operatorname{erf}(n_1) + L_2 \operatorname{erf}(n_2)]$$
(164)

Differentiation of equation (164) with respect to X yields

$$\left(\frac{\partial Z}{\partial X}\right)_{t} = \frac{\alpha \Delta n}{2\sqrt{\pi t}} \left\{\frac{L_{1}}{\sqrt{\lambda_{1}}} \exp\left(-\frac{X^{2}}{4\lambda_{1}t}\right) + \frac{L_{2}}{\sqrt{\lambda_{2}}} \exp\left(-\frac{X^{2}}{4\lambda_{2}t}\right)\right\} \quad (165)$$

Assuming that refractive index gradient profile, (consequently optical path gradient curve) possesses only one maximum at the center (X=0), then from equation (165) this maximum is obtained as

$$\left[\left(\frac{\partial Z}{\partial X}\right)_{t}\right]_{\max} = \frac{\alpha \Delta n}{2\sqrt{\pi t}} \left(\frac{L_{1}}{\sqrt{\lambda_{1}}} + \frac{L_{2}}{\sqrt{\lambda_{2}}}\right)$$
(166)

Equation (165) represents the interference patterns produced by the birefringent interferometer and equation (166) represents the corresponding maximums. Thus, the relations between interference patterns and the concentration gradient profiles of the diffusing solutions have been established. In the following sections, the method for calculating the diffusion coefficients from the measurements of the interference pattern photographs will be presented.

#### Evaluation of Photographs

A sample consisting of four photographs taken during a diffusion run with Acetone-Benzene-Methanol system is given in Figure 3. The straight lines represent the region of zero optical path gradients. Therefore, the gradient at a given point is measured using these lines as references. The distances h and W, as depicted in Figure  $4_i$ , are measured with the microprojector. The known width of



Figure 3. Photographs of Initial Interface and Interference Patterns



Figure 4. Illustration of Measurement Performed on each Interference Pattern.

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the cell cavity is used as a scale factor. These scaled measurements, together with their respective coordinate times, provide the necessary data for the calculation of the ternary diffusion coefficients.

## Reduction of Data

In this study, a non-linear least squares method for analyzing the data was developed. The mathematical model for this least-squares process was obtained by dividing equation (165) by equation (166). This model may be written as

$$y = \kappa_1 \exp\left(\frac{-X^2}{4\lambda_1 t}\right) + \kappa_2 \exp\left(\frac{-X^2}{4\lambda_2 t}\right)$$
(167)

where

$$y = \frac{\left(\frac{\partial Z}{\partial X}\right)_{t}}{\left[\left(\frac{\partial Z}{\partial X}\right)_{t}\right]_{max}} = \frac{h}{h_{max}}$$
(168)

$$\kappa_{1} = \frac{L_{1}/\sqrt{\lambda_{1}}}{L_{1}/\sqrt{\lambda_{1}} + L_{2}/\sqrt{\lambda_{2}}}$$
(169)

$$\kappa_{2} = 1 - \kappa_{1}$$

$$x = \frac{W}{2M}$$
(170)

and M is the magnification factor.

It should be pointed out that, it is not possible to establish an infinitely sharp interfacial boundary between the top and bottom solutions. However, it is possible to mathematically correct for this imperfect initial condition by inclusion of a zero time correction,  $t_c$ . On considering this zero time correction and adding it to each experimentally measured time, equation (167) takes the form

$$y = \kappa_1 \exp \left(\frac{-X^2}{4\lambda_1(t+t_c)}\right) + \kappa_2 \exp \left(\frac{-X^2}{4\lambda_2(t+t_c)}\right)$$
(172)

Equation (172) is then used as the regression model for determining the "best" values of  $\kappa_1$ ,  $\lambda_1$ ,  $\lambda_2$ , and t<sub>c</sub> from a set of experimental measurements made on a diffusion run.

The non-linear least squares analysis was based on a Gauss-Newton regression procedure. Development of the computational scheme is given in Appendix (B). The computer program to carry out the necessary computations is given in Appendix (F).

Equation (169), after substitution of the calculated values of  $\kappa_1$ ,  $\lambda_1$ , and  $\lambda_2$ , yields values of  $L_1$  for each experimental run. Combining equations (161), (162), and (163b); and recalling that

$$\lambda_1 + \lambda_2 = D_{11} + D_{22}$$
 (173a)

$$\lambda_1 \lambda_2 = D_{11} D_{22} - D_{12} D_{21}$$
 (173b)

$$\alpha_2 = 1 - \alpha_1 \tag{173c}$$

the following expression is obtained

$$L_{1} = \frac{D_{22} - D_{11} + \frac{R_{1}}{R_{2}} D_{12} - \frac{R_{2}}{R_{1}} D_{21}}{\lambda_{2} - \lambda_{1}} \alpha_{1} + \frac{D_{11} - \lambda_{1} - \frac{R_{1}}{R_{2}} D_{12}}{\lambda_{2} - \lambda_{1}} (174)$$

A linear regression of  $L_1$  versus  $\alpha_1$  for several experimental runs at the same average solute concentrations, yields the values of  $L_1$  at  $\alpha_1=0$ , and  $\alpha_1=1$ . The corresponding expressions for these limiting values of  $L_1$  are obtained from equation (174) as

$$L_{1}^{0} = \frac{D_{11} - \lambda_{1} - \frac{R_{1}}{R_{2}} D_{12}}{\lambda_{2} - \lambda_{1}}$$
(175a)

$$L_{1}^{1} = \frac{-\frac{R_{2}}{R_{1}}D_{21} - D_{11} + \lambda_{2}}{\lambda_{2} - \lambda_{1}}$$
(175b)

where  $L_1^0$ ,  $L_1^1$  are the values of  $L_1$  at  $\alpha_1=0$ , and  $\alpha_1=1$  respectively. Equations (175a,b) may be rearranged to yield the explicit expressions for  $D_{12}$ , and  $D_{21}$  as

$$D_{12} = (D_{11} - N_1^0) \frac{R_2}{R_1}$$
(176a)

$$D_{21} = (-D_{11} + N_1^1) \frac{R_1}{R_2}$$
 (176b)

where

$$N_{1}^{0} = \lambda_{1} + L_{1}^{0} (\lambda_{2} - \lambda_{1})$$
 (176c)

$$N_{1}^{1} = \lambda_{2} - L_{1}^{1}(\lambda_{2} - \lambda_{1})$$
(176d)

Multiplying equation (176a) by equation (176b) one obtains

$$D_{12}D_{21} = (D_{11} - N_{1}^{0}) (-D_{11} + N_{1}^{1})$$
(177)

Equation (173a) may be solved for  $D_{22}$  to give

$$D_{22} = \lambda_1 + \lambda_2 - D_{11}$$
(178)

Equation (178), after multiplication by D<sub>11</sub> becomes

$$D_{11}D_{22} = D_{11}(\lambda_1 + \lambda_2 - D_{11})$$
(179)

Substitution of equation (177) and equation (179) in equation (173b) results in

$$D_{11}(\lambda_{1}+\lambda_{2}-D_{11}) - (D_{11}-N_{1}^{0})(-D_{11}+N_{1}^{1}) = \lambda_{1}\lambda_{2}$$
(180)

Equation (180) may be solved for D<sub>11</sub> to give

$$D_{11} = \frac{\lambda_1 \lambda_2 - N_1^0 N_1^1}{\lambda_1 + \lambda_2 - N_1^0 - N_1^1}$$
(181)

Substitution of  $D_{11}$  into equations (176a,176b,178) yields the values of  $D_{12}$ ,  $D_{21}$ , and  $D_{22}$  respectively, provided  $R_1/R_2$  is known. The quantity  $R_1/R_2$  can be calculated from the measurement of the areas under optical path gradient profiles of two or more diffusion runs. The computational procedures of  $R_1/R_2$  from the measurements of the areas is given in Appendix (C).

A non-linear least squares fit of the data to a model such as the one given by equation (172) requires the initial guesses which are very close to actual values of the parameters of the model under consideration. These initial guesses may be obtained from the values of the diffusion coefficients obtained from the moment-area method. This method is discussed in Appendix (D) and the computer program for carrying out the necessary computations is given in Appendix (F).

#### CHAPTER V

### RESULTS AND DISCUSSION

This chapter is devoted to the presentation of results and discussion. The experimental data are presented and discussed in detail. Also, the ternary diffusion coefficients calculated from the theoretical expressions developed in Chapter III are compared with the experimental data.

#### Experimental Results and Discussion

In this research the diffusion coefficients for the two ternary systems, (1) Acetone-Benzene-Methanol; (2) Acetone-Ethanol-Water, as well as the binary systems (1) Acetone-Benzene; (2) Acetone-Methanol; (3) Benzene-Methanol; (4) Acetone-Water; (5) Ethanol-Water; (6) Acetone-Ethanol were obtained at atmospheric pressure and at a temperature of 25°C. These data are tabulated in tables 2 through 9. The ternary data are listed at the average composition at which the diffusion coefficients were measured. The binary data are given along with the initial concentrations and the average concentrations. The standard error estimate for each experimentally determined binary diffusion

## MOLECULAR DIFFUSION COEFFICIENTS FOR THE

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#### SYSTEM ACETONE(1) - BENZENE(2) - METHANOL(3)

# AT 25° C

MOLE F	RACTION	I	DIFFUSION C	DEFFICIENTS	
×1	×2	D <sub>11</sub> ×10 <sup>5</sup> ,CM <sup>2</sup> /SEC.	D <sub>12</sub> ×10 <sup>5</sup> ,CM <sup>2</sup> /SEC.	D <sub>21</sub> ×10 <sup>5</sup> ,CM <sup>2</sup> /SEC.	D <sub>22</sub> x10 <sup>5</sup> ,CM <sup>2</sup> /SEC
0.350	0.302	3,819	0•420	-0.561	2.133
0.766	0.114	4.400	0•921	-0.684	2.680
0.553	0.193	4.472	0•962	-0.480	2.569
0.400	0.500	4.434	1.866	-0.816	1.668
0.299	0.150	3.192	0•277	-0.191	2.368
0.206	0.548	3.513	0.665	-0.602	1.948
0.102	0.795	3.502	1.204	-1.130	1.124
0.120	0.132	3.115	0.138	-0.227	2•235
0.150	0.298	3.050	0.150	-0.269	2.25

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#### MOLECULAR DIFFUSION COEFFICIENTS FOR THE

## SYSTEM ACETONE(1) - ETHANOL(2) - WATER(3)

# AT 25° C

MOLE F	RACTION		DIFFUSION C	DEFFICIENTS	
×l	× 2	D11×10 <sup>5</sup> ,CM <sup>2</sup> /SEC.	D <sub>12</sub> ×10 <sup>5</sup> ,CM <sup>2</sup> /SEC.	D <sub>21</sub> ×10 <sup>5</sup> , CM <sup>2</sup> /SEC.	D <sub>22</sub> ×10 <sup>5</sup> , CM <sup>2</sup> /SEC
0.100	0.100	2.608	-0.166	-1.881	0.634
0.100	0.400	0.567	-0.328	0•646	1.336

## MOLECULAR DIFFUSION COEFFICIENTS FOR THE

## SYSTEM ACETONE-BENZENE

# AT 25° C

MASS FRACTION Acetone			MOLE FRACTION Acetone			DIFFUSION COEFFICIENT	
INI	TIAL	AVERAGE	INI	TIAL	AVERAGE	D <sub>AB</sub> ×10 <sup>5</sup> , CM <sup>2</sup> /SEC.	
ω '	ω"	ω	×'	×"	x		
0.0000	0.0010	0.0005	0.0000	0.0013	0.0007	3.0368	
0.1986	0.2000	0.1993	0.2500	0.2516	0.2508	2.7448	
0.4233	0.4242	0.4237	0.4968	0.4972	0.4972	3.1354	
0.6875	0.6881	0.6878	0•7474	0.7479	0.7476	4.1367	
1.0000	0.9980	0•9990	1.0000	0.9985	0.9992	4.2778	

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## MOLECULAR DIFFUSION COEFFICIENTS FOR THE

#### SYSTEM ACETONE-METHANOL

# AT 25° C

MASS FRACTION Acetone			MOLE FRACTION Acetone			DIFFUSION COEFFICIENT
INI	TIAL	AVERAGE	INI	TIAL	AVERAGE	DAB X10 <sup>5</sup> , CM <sup>2</sup> /SEC.
ω '	ω"	ω	x'	×"	x	
0.0000	0.0099	0.0049	0.0000	0.0054	0.0027	2.6009
0.3766	0.3796	0.3781	0.2500	0.2524	0.2512	3.4104
0.6493	0.6502	0•6498	0.5053	0•5063	0.5058	3.6857
0.8433	0.8440	0.8437	0.7480	0.7491	0.7486	3.6817
1.0000	0.0099	0.9950	1.0000	0.9822	0.9911	4.7951

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## MOLECULAR DIFFUSION COEFFICIENTS FOR THE

## SYSTEM BENZENE-METHANOL

## AT 25° C

MASS FRACTION MOLE FRACTION BENZENE BENZENE			DN	DIFFUSION COEFFICIENT		
INI	TIAL	AVERAGE	INI	TIAL	AVERAGE	D <sub>AB</sub> ×10 <sup>5</sup> , CM <sup>2</sup> /SEC.
ω'	ω <sup>Ħ</sup>	ω	x '	<b>X</b> "	x	
0.0000	0.0010	0.0005	0.0000	0.0004	0.0002	2.4159
0.4483	0.4490	0.4486	0.2500	0.2506	0.2503	1.7888
0.7091	0.7100	0.7095	0.5000	0.5010	0.5005	1.0984
0.8797	0.8800	0.8798	0.7500	0.7505	0.7502	1.0210
1.0000	0.9990	0.9995	1.0000	0.9976	0•9988	3.6480

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### MOLECULAR DIFFUSION COEFFICIENTS FOR THE

#### SYSTEM ACETONE-WATER

# AT 25° C

MA	ACETONE	ON	MO	LE FRACTIO	л	DIFFUSION COEFFICIENT
INI	TIAL	AVERAGE	INI	TIAL	AVERAGE	D <sub>AB</sub> ×10 <sup>5</sup> , CM <sup>2</sup> /SEC.
ω '	ω"	ω	x '	×"	x	
0.0000	0.0066	0.0033	0.0000	0.0020	0.0010	1.3048
0.2210	0.2251	0.2231	0.0809	0.0826	0.0818	0•9131
0.5198	0.5246	0.5222	0.2513	0.2550	0.2532	0.7133
0.7619	0.7644	0.7632	0.4981	0.5016	0.4999	0.8000
1.0000	0.9920	0.9960	1.0000	0.9748	0.9874	4.9610

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# MOLECULAR DIFFUSION COEFFICIENTS FOR THE

#### SYSTEM ETHANOL-WATER

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# AT 25° C

MASS FRACTION Ethanol			МС	ETHANOL	DIFFUSION COEFFICIENT	
INI	INITIAL AVERAGE		INI	INITIAL AVERAG		D <sub>AB</sub> ×10 <sup>5</sup> ,CM <sup>2</sup> /SEC.
ω "	ω"	ω	х'	×"	x	
0.000	0.0050	0.0025	0.0000	0.0020	0.0010	1.2038
0.5347	0.5393	0.5370	0.3102	0.3142	0.3122	0.3725
0.2105	0.2157	0.2131	0.0945	0.0971	0.0958	0.8670
0.07059	0.7086	0.7072	0•4843	0•4876	0.4860	0.4433
1.0000	0.9960	0.9980	1.0000	0.9899	0.9949	1.1812

## MOLECULAR DIFFUSION COEFFICIENTS FOR THE

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#### SYSTEM ACETONE-ETHANOL

# AT 25° C

MASS	MASS FRACTION Acetone			E FRACT	ION	DIFFUSION COEFFICIENT	STD. ERROR Error, <sup>8</sup>
INITIAL AVERAGE		INITIAL		AVERAGE	D <sub>AB</sub> ×10 <sup>5</sup> , CM <sup>2</sup> /SEC.		
ω *	ω "	ω	x '	x "	x		
0.0291	0.0476	0.0384	0.0232	0•0381	0.0307	0.6278	69.65
0.5000	0.5102	0.5051	0.4422	0.4523	0.4472	2.1312	7.67
1.0000	0.9709	0.9854	1.0000	0.9635	0.9818	2.3707	4.73

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coefficient was calculated. For the five binary systems: Acetone-Benzene, Acetone-Methanol, Benzene-Methanol, Acetone-Water, and Ethanol-Water, the standard errors were less than 1 percent. The large standard error estimates for the system Acetone-Ethanol, as given in Table 9, can be explained as follows: Due to the very small refractive index difference between Acetone and Ethanol, a relatively large concentration difference between the test solutions was required to permit the measurement of the diffusion coefficients. Use of a large concentration difference violates the basic assumptions made in the development of the data analysis technique, namely, no change of volume on mixing, and a linear relationship between the refractive index of the solution and its concentration.

However, it should be pointed out that the error contributed by the above sources does not exceed 10 percent. At infinite dilution of Acetone in Ethanol, an inversion in the refractive index gradient profile was observed. Thus, the measurement of binary diffusion coefficient at this limit was not possible. The measured diffusion coefficient at a concentration near this point yielded the isolated point with a standard error estimate equal to 69.65 percent. This indicated that in the neighborhood of the inversion point, the assumption of a linear relationship between the refractive index of the solution and its concentration was not valid. Lack of an adequate re-

fractive index difference between components of the system Acetone-Ethanol-Water imposed serious limitations on the measurement of the ternary diffusion coefficients. As a result, the diffusion coefficients for this system were measured at only two concentration levels. These diffusion coefficients are given in Table 3. Moreover, due to the possible effect of the observed inversion point in the reflactive index gradient profile of the system Acetone-Ethanol, on the refractive index gradient profile of this ternary system, the accuracy of these ternary measurements is guestionable.

#### Theoretical

The modified absolute rate theory developed in this work was tested against the experimental data for one of the two ternary systems studied, as well as three ternary systems from the literature (5,8,73). The proposed predictions were found to yield excellent results. Calculated diffusion coefficients and phenomenological coefficients were compared in Tables 10 through 17 with the above mentioned experimental data. The necessary thermodynamic factors were calculated through the use of the Wilson equation, a complete analysis of which is given in Appendix E. The Wilson Parameters were taken from Holmes and VanWinkle (44). The data on the system Toluene-Chlorobenzene-Bromobenzene were obtained by Burchard and Toor (5) at six concentration levels. These data were compared with cal-

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COMPARISON OF EXPERIMENTAL DIFFUSION COEFFICIENTS WITH THOSE CALCULATED FROM EQUATION 150 FOR SYSTEM\*TOLUENE(1) - CHLOROBENZENE(2) - BROMOBENZENE(3)

MOLE	FRACTION		DIFFUSION COEFFICIENTS						
×ı	×2	D11×10,50	CM <sup>2</sup> /SEC.	D <sub>12</sub> ×105	CM <sup>2</sup> /SEC.	D <sub>21</sub> ×105	CM <sup>2</sup> /SEC.	D22×10,50	M <sup>2</sup> /SEC
		EXPT.	CALC.	EXPT.	CALC.	EXPT.	CALC.	EXPT.	CALC.
0.250	0.500	1.848	1.821	-0.063	-0.018	-0.052	-0.071	1.797	1.752
0.260	0.030	1.570	1.611	-0.077	-0.031	-0.012	-0.006	1.606	1.578
0.700	0.150	2.330	2.274	-0.432	-0.650	0.132	0.114	2.971	3.237
0-150	0.700	1.961	2.199	0.013	-0.185	-0.149	-0.308	1.929	2.072
0.450	0.250	2.006	1.883	-0.020	-0.041	-0.198	-0.051	1.890	1.842
0.180	0.280	1.774	1.655	-0.037	-0.018	0.003	-0.047	1.518	1.592

AT 29.6°C

\*Data of Burchard and Toor (5)

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COMPARISON OF EXPERIMENTAL PHENOMENOLOGICAL COEFFICIENTS WITH THOSE CALCULATED FROM EQUATION 150 FOR SYSTEM\* TOLUENE(1) - CHLOROBENZENE(2) - BROMOBENZENE(3)

MOLE FRACTION			CAL COEFFICIENTS	ENTS			
×ı	×2	L <sub>12XR</sub>	FX10 <sup>5</sup>	L <sub>21</sub> ×F	L <sub>21</sub> XRTX10 <sup>5</sup>		
		EXPT.	CALC.	EXPT.	CALC.		
0.250 0	0.500	-2.3836	-2.2467	-2.2652	-2.2457		
0.260 0	0.030	-0.1450	-0.1356	-0.1480	-0.1356		
0.700 0	0.150	-2.0482	-2.1217	-2.1746	-2.1217		
0.150 0	0.700	-1.7774	-1.8555	-1.9430	-1.8555		
0.450 0	0.250	-2.2119	-2.1168	-2.5021	-2.1168		
0.180 0	0.280	-0.9613	-0.8661	-0.7580	-0.8661		

AT 29.6°C

\*Data of Burchard and Toor (5).

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COMPARISON OF EXPERIMENTAL DIFFUSION COEFFICIENTS WITH THOSE CALCULATED FROM EQUATION 150 FOR SYSTEM\*METHANOL(1) - ISD-BUTANOL(2) - N-PROPANOL(3)

MOLE	FRACTION		DIFFUSION COEFFICIENTS						
×ı	×2	D11×10,	CM <sup>2</sup> /SEC.	D12×10, CM <sup>2</sup> /SEC.		D <sub>21</sub> ×10 <sup>5</sup> cm <sup>2</sup> /SEC.		D <sub>22</sub> ×10 <sup>5</sup> cm <sup>2</sup> /sec	
		EXPT.	CALC.	EXPT.	CALC.	EXPT.	CALC.	EXPT.	CALC.
0.460	0.240	1.039	1.135	0.032	0.057	-0.023	-0.026	0.875	0.960
0.250	0.100	0.909	0.991	0.030	0.049	-0.009	-0.003	0.721	0.778
0.270	0.570	0.765	0.859	0.027	-0.001	-0.039	-0.065	0.624	0.688
0.820	0.070	1.505	1.651	0.211	0.182	-0.004	-0.013	1.383	1.494

\*Data of Shuck and Toor (73).

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COMPARISON OF EXPERIMENTAL PHENOMENOLOGICAL COEFFICIENTS WITH THOSE CALCULATED

FROM EQUATION 150 FOR SYSTEM\*METHANOL(1) - ISO-BUTANOL(2) - N-PROPANOL(3)

MOLE FRACTION		PHENOMENOLOGICAL COEFFICIENTS						
×ı	×2	L <sub>12</sub> XR	TX10 <sup>5</sup>	L <sub>21</sub> ×RTX10 <sup>5</sup>				
		EXPT.	CALC.	EXPT.	CALC.			
0.460	0.240	-1.7071	-1.8178	-1.6489	-1.8178			
0.250	0 • 1 0 0	-0.2866	-0.2911	-0.2902	-0.2911			
0.270	0.570	-1.0250	-1.2033	-1.0146	-1.2033			
0.820	0.070	-3.0492	-3.4082	-3.0806	-3.4082			

AT 30° C

\*Data of Shuck and Toor (73).

COMPARISON OF EXPERIMENTAL DIFFUSION COEFFICIENTS WITH THOSE CALCULATED FROM EQUATION 150 FOR SYSTEM\*ACETONE(1) - BENZENE(2) - CARBON TETRACHLORIDE(3)

MOLE F	LE FRACTION $x_1 = x_2 = D_{11} \times 10^5 \text{ cm}^2/\text{SEC}$		DIFFUSION COEFFICIENTS D12×10,7cm <sup>2</sup> /sec. D21×10,7cm <sup>2</sup> /sec.				D <sub>22</sub> ×10 <sup>5</sup> cm <sup>2</sup> /sec		
-	-	EXPT.	CALC.	EXPT.	CALC.	EXPT.	CALC.	EXPT.	CALC.
0.300	0.350	1.887	1.657	-0.213	-0.320	-0.037	-0.045	2.225	2.189
0.150	0.150	1.598	1.480	-0.058	-0.153	-0.083	-0.089	1.812	1.713
0.150	0.700	1.853	1.818	0.049	-0.008	-0.068	-0.071	1.841	1.750
0.700	0.150	2.132	2.068	0.051	-0.062	-0.071	-0.038	2.062	2.070

AT 25° C

\*Data of Cullinan and Toor (8).

COMPARISON OF EXPERIMENTAL PHENOMENOLOGICAL COEFFICIENTS WITH THOSE CALCULATED FROM EQUATION 150 FOR SYSTEM\*ACETONE(1) - BENZENE(2) - CARBON TETRACHLORIDE(3)

MOLE FRACTION		PHENOMENOLOGICAL COEFFICIENTS							
×ı	×2	L <sub>12</sub> xR	тх 1 о <sup>5</sup>	L <sub>21</sub> ×RTX10 <sup>5</sup>					
		EXPT.	CALC.	EXPT.	CALC.				
0.300	0•350	-2.8909	-2.8897	-2.8899	-2.8897				
0.150	0.150	-0.3001	-0.4184	-0.4192	-0.4184				
0.150	0.700	-2.2140	-2.9549	-2.4898	-2.9549				
0.700	0.150	-4.5528	-4.8149	-4.2940	-4.8149				

AT	<b>2</b> 5°	С
AT	25	С

\*Data of Cullinan and Toor (8).

#### COMPARISON OF EXPERIMENTAL DIFFUSION COEFFICIENTS WITH THOSE CALCULATED

FROM EQUATION 150 FOR SYSTEM ACETONE(1) - BENZENE(2) - METHANOL(3)

MOLE F	MOLE FRACTION				DIFFUSION COEFFICIENTS				
×	×_2	D11×105	CM <sup>2</sup> /SEC.	D12×105	CM <sup>2</sup> /SEC.	D21×105	CM <sup>2</sup> /SEC.	D22×10,	CM <sup>2</sup> /SEC
-	_	EXPT.	CALC.	EXPT.	CALC.	EXPT.	CALC.	EXPT.	CALC.
0.350	0.302	3.819	3.874	0.420	0.647	-0.561	-0.474	2.133	2.417
0.766	0•114	4.400	4.404	0•921	0.635	-0.684	-0.408	2.680	3.234
0.553	0.193	4.472	4.249	0.962	0.784	-0.480	-0.448	2.569	2.784
0.400	0.500	4.434	4.779	1.866	1.856	-0.816	-1.435	1.668	1.282
0.299	0.150	3.192	3.451	0.277	0.264	-0.191	-0.185	2.368	2.663
0.206	0.548	3.513	3.792	0.665	0.779	-0.602	-0.819	1.948	1.772
0.102	0.795	3.502	3.874	1.204	1.086	-1.130	-1.529	1.124	0.741
0.120	0•132	3.115	2.942	0.138	0.055	-0.227	-0.110	2.235	2.466
0.150	0.298	3.050	3.175	0.150	0.186	-0.269	-0.273	2.250	2.337

АТ 25<sup>0</sup> С

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## TABLE 17

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COMPARISON OF EXPERIMENTAL PHENOMENOLOGICAL COEFFICIENTS WITH THOSE CALCULATED

FROM EQUATION 150 FOR SYSTEM ACETONE(1) - BENZENE(2) - METHANOL(3)

MOLE FRACTION		PHENOMENOLOGICAL COEFFICIENTS				
×1 ×2		L <sub>12</sub> ×RTX10 <sup>5</sup>		L <sub>21</sub> ×RTX10 <sup>5</sup>		
		EXPT.	CALC.	EXPT.	CALC.	
0.350	0.302	-6.9902	-6.5269	-6.1909	-6•5269	
0.766	0.144	-5.3852	-5.7798	-5.5550	-5.7798	
0.553	0.193	-7.0901	-7.0037	-6.6668	-7.0037	
0•400	0.500	-7.6970	-8.7309	-7.7073	-8.7309	
0.299	0.150	-3.5750	-3.9319	-3.5703	-3.9319	
0.206	0.548	-4.8543	-5.0880	-4•9345	-5.0880	
.102	0.795	-2.1364	-2.7789	-2.7414	-2.7789	
.120	0.132	-1.7099	-1.7537	-1.8190	-1.7537	
.150	0.298	-3.2135	-3.2710	-3.1593	-3.2710	

AT 25° C

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culated values from theory in Tables 10 and 11. The average deviation between the calculated and the experimental main diffusion coefficients was 4 percent. Since, the cross-term diffusion coefficients are relatively small, reporting a percentage deviation may be misleading. However, in 10 out of 12 cases the calculated values reproduced the correct sign on the cross-term diffusion coefficients. Moreover, considering the experimental errors involved the predicted values were excellent. The phenomenological coefficients were calculated assuming the activity of a given component in the mixture to be equal to its mole fraction. It is observed that the phenomenological coefficients satisfy the ORR within the limits of experimental error. The results of comparing the data of Shuck and Toor (73) on the system Methanol-Isobutanoln-propanol with the calculated values are given in Tables 12 and 13. It was assumed that the activities could be taken to be equal to the mole fractions. The average deviation of 8 percent for the main diffusion coefficients was obtained. The calculated values of the cross-term diffusion coefficients reproduced the proper signs except for an isolated point. For this system, the ORR were also satisfied within the limits of experimental error. Cullinan and Toor (8) reported the data on the system Acetone-Benzene-Carbon tetrachloride at 4 concentration levels. In the calculation of thermodynamic terms, the Wilson equa-

tion was used to calculate activity coefficients. Tables 14 and 15 provide a comparison of calculated values and the experimental data. The average deviation between the calculated values and data for the main diffusion coefficients was 4 percent. In 6 out of 8 cases the calculated values of cross-term diffusion coefficients reproduced the proper signs. The diffusional behavior of the system Acetone-Benzene-Methanol was experimentally studied in the present work; and the data was used to test the theory. Again, the Wilson equation was used to calculate the activity coefficients. The results of comparing calculated values with data are given in tables 16 and 17. The calculated values of the main diffusion coefficients deviate from data by an average of 11 percent. The calculated cross-term diffusion coefficients reproduce the proper sign in all the cases. As it was mentioned earlier, the accuracy of the data on the system Acetone-Ethanol-Water was questionable. Therefore, no attempt was made to compare these data with calculated values from the theory.

In summary, for the four ternary systems tested the modified absolute rate theory predicted the main diffusion coefficients with an average deviation from data of 7.5 percent.

## CHAPTER VI

### CONCLUSIONS

The modified absolute rate theory developed in this work is capable of accurately predicting multicomponent diffusion and phenomenological coefficients from selfdiffusion and infinite dilution binary diffusion coefficients. This eliminates the time-consuming techniques now available for obtaining ternary diffusion coefficients.

Experimental data obtained in this study was used to test the Onsager Reciprocal Relations (ORR). The validity of the ORR was confirmed within the limits of experimental error. Moreover, it demonstrates the validity and applicability of the absolute rate theory.

Also, it can be concluded that the birefringent interferometer yields accurate ternary diffusion coefficients.

### CHAPTER VII

### FUTURE WORK

#### Theoretical

The modified absolute rate theory developed in this work yielded excellent results. However, it was found that the average deviation of calculated values from data increased by increasing the degree of nonideality of the system. One of the areas open for future work is to obtain improved version of this theory to predict multicomponent diffusion coefficients with better consistency and to eliminate the assumption of constant partial molar volumes. Extensive theoretical work on the prediction of self-diffusion and infinite dilution binary diffusion coefficients from the molecular parameters is in order.

### Experimental

There is still urgent need for binary diffusion coefficients at infinite dilution as well as further ternary data. The birefringent interferometer proved to produce these data with a high degree of accuracy. However, it was found that a simple modification can further improve the accuracy attainable. By replacing the lens  $L_4$  by a longer focal length lens, a dual purpose can be accom-

plished. This modification will increase the number of fringes considerably, which in turn will reduce the fringe width and provide better accuracy in measurement of the fringes. At the same time, it will yield an interference pattern which approximates the optical path gradient more closely (in general the interference patterns represent a difference quotient). In a preliminary trial using a lens of 400mm f/l the number of fringes increased from 7 to 22. It is recommended that the lens  $L_4$  be replaced by a lens of 300mm f/l.

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## NOMENCLATURE

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A AB	Energy of interaction
<sup>a</sup> i,j	Parameter, equation (45)
a <sub>A</sub>	Activity of species A
a	Distance between equilibrium positions
в <mark>ху</mark> ік	Parameter, equation (11)
с <sub>д</sub>	Concentration of species A
D <sub>AB</sub>	Binary diffusivity
Ðij	Multicomponent diffusivity
Dxc ij	Multicomponent diffusivity
	Binary diffusivity at infinite dilution
D <sub>AA</sub>	Ternary diffusion coefficient, equations (71a and 72a)
D <sub>AB</sub>	Ternary diffusion coefficient, equations (71b and 72b)
D <sub>BA</sub>	Ternary diffusion coefficient, equations (71c and 72c)
D <sub>BB</sub>	Ternary diffusion coefficient, equations (71d and 72d)
D <sub>BB</sub>	Self diffusion coefficient
D¢C ij	Ternary diffusion coefficient, equation (150)
EO	Activation energy
<sup>E</sup> d,AB	Activation energy for diffusion
<sup>Е</sup> п, В	Activation energy for viscosity
F	Partition function of the normal state

F≠	Partition function of the activated state
<u>F</u> <sub>K</sub>	External force
<sup>F</sup> i,r	Resisting force per molecule of species i
F <sub>ij</sub>	Friction coefficient, equation (88)
fi	Coefficient, equation (68)
G <mark>с'с</mark> кј	Parameter, equation (13)
∆G <sup>≠</sup>	Gibbs free energy of formation
<sup>∆G</sup> io	Free energy barrier for diffusion of species i in a homogeneous mixture
∆G <sup>O</sup> ij	Activation energy for infinite dilution of species i in j
н	Transmission coefficient
<sup>H</sup> i	Parameter, equation (67a)
h	Planck's Constant
JA	Diffusional flux of species A
J <sup>xc</sup> i	Diffusional flux of species i in a mixture rela- tive to molar average velocity
<u>J</u> ω s	Entropy flux relative to mass average velocity
$\overline{\mathbf{J}}_{\mathbf{m}}^{\mathbf{d}}$	Multicomponent heat flux relative to mass average velocity
k	Hydrodynamic parameter
$\mathtt{L}_{\mathtt{i}\mathtt{i}}^{\mathtt{vc}}$	Phenomenological coefficient, equation (97)
L <sup>VC</sup> ij	Phenomenological coefficient, equation (98)
LlC ii	Phenomenological coefficient, equation (116)
L <sub>1</sub>	Parameter, equation (163b)
<sup>L</sup> 2	Parameter, equation (163c)
L <sup>O</sup> 1	Parameter, equation (175a)
$L_1^1$	Parameter, equation (175b)
L <sub>B</sub> ,L	Latent heat of vaporizations

<sup>μ</sup>Β,<sup>μ</sup>ω

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M.	Molar mass of species i
M	Magnification factor
N	Avogadro's number
N <sup>O</sup> 1	Parameter, equation (176c)
$N_{1}^{1}$	Parameter, equation (176d)
n	Refractive index
Р	equilibrium pressure
Q <sub>ij</sub>	Parameter, equation (67b)
R	Gas constant
Ri	Refractive index derivative, equation (161)
r <sub>A</sub>	Radius of spherical particle A
S	Entropy per unit mass
Т	Absolute temperature
t	Time
U	Velocity
U <sub>i</sub>	Velocity of species i
U	Internal energy
$\overline{v}_{i}$	Partial molar volume of species i
V <sub>f,AB</sub>	Free volume of a molecule A surrounded by mole- cules B
V <sub>f,BB</sub>	Free volume of a molecule B surrounded by mole cules B
×i	Concentration fraction of species i
Yi	Parameter, equation (34)
αi	Refractive index fraction, equations (162a and 162b)
<sup>α</sup> i,j	Parameters, equation (45)
β	Coefficient of sliding friction

- ...

δ <sub>i</sub>	Kronecker delta
ζ	Viscous resistance per molecule
<sup>n</sup> B	Viscosity of species B
<sup>n</sup> AB	Viscosity of mixture AB
<sup>n</sup> 1′ <sup>n</sup> 2	Similarity variables, equation (159c)
θ <sub>A</sub>	Parameter, equation (65a)
к	Boltzman's constant
۴ı	Parameter, equation (67c)
<sup>ĸ</sup> 2	Parameter, equation (67d)
к	Thermal conductivity
<sup>ĸ</sup> io	Parameter, equation (99)
<sup>ĸ</sup> ij	Parameter, equation (100)
۴ı	Parameter, equation (169)
<sup>ĸ</sup> 2	Parameter, equation (170)
$^{\lambda}$ ib	Distance between molecules in $i^{-th}$ coordinate direction
<sup>λ</sup> ι' <sup>λ</sup> 2	Eigenvalues, equations (159a and 159b)
<sup>μ</sup> κ	Chemical potential of species ĸ
μ <sub>ij</sub>	Chemical potential derivatives, equation (41)
<u>π</u>	Pressure tensor
$\nu_{i}^{\pm}$	Frequencies of jumps of species i, equation (109)
ρ	Mass density
σ	Resistance coefficient
σ	Rate of entropy production
τA	Parameter, equation (65b)
<sup>¢</sup> i	Volume fraction
x	Empirical number of nearest neighbors
ωĸ	Mass fraction of component $\kappa$

### APPENDIX A

## SOLUTION OF DIFFERENTIAL EQUATIONS

The differential equations may be written in matrix notation as

$$\frac{\partial \underline{C}}{\partial t} = \underline{\underline{D}} \quad \frac{\partial^2 \underline{C}}{\partial x^2} \tag{A-1}$$

where  $\underline{C}$  is concentration vector and  $\underline{D}$  is matrix of diffusion coefficients. Initial and boundary conditions are

$$\underline{C} = \underline{\overline{C}} + \frac{\Delta \underline{C}}{2} \quad \text{for } X > 0, t = 0 \qquad (A-2a)$$

$$\underline{C} = \underline{\overline{C}} - \frac{\Delta \underline{C}}{2} \quad \text{for } X < 0, t = 0 \qquad (A-2b)$$

$$\underline{C} \rightarrow \underline{\overline{C}} + \frac{\Delta \underline{C}}{2} \quad \text{for} \quad X \rightarrow \infty, \ t > 0 \qquad (A-2c)$$

$$\underline{C} \rightarrow \overline{\underline{C}} - \frac{\Delta \underline{C}}{2}$$
 for  $X \rightarrow -\infty$ ,  $t > 0$  (A-2d)

Define

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$$\underline{C} = \underline{M} \quad \underline{\hat{C}} \tag{A-3}$$

where  $\underline{M}$  is the modal matrix of the diffusivity matrix  $\underline{D}$ . Substituting <u>C</u> from equation (A-3) into equation (A-1) results in

$$\underline{\underline{M}} \quad \frac{\partial \hat{\underline{C}}}{\partial t} = \underline{\underline{D}} \quad \underline{\underline{M}} \quad \frac{\partial^2 \underline{\underline{C}}}{\partial X^2}$$
 (A-4)

Multiplication of both sides of equation (A-4) by  $\underline{M}^{-1}$ , the inverse matrix of  $\underline{M}$  leads to

$$\underline{\underline{M}}^{-1} \underline{\underline{M}} \frac{\partial \hat{\underline{C}}}{\partial t} = [\underline{\underline{M}}^{-1} \underline{\underline{D}} \underline{\underline{M}}] \frac{\partial^2 \hat{\underline{C}}}{\partial X^2}$$
 (A-5)

The quantity in the bracket is a diagonalized matrix, the non-zero elements  $\lambda_{i}$  of which are the eigenvalues of the diffusivity matrix  $\underline{D}$  and  $\underline{M}^{-1}\underline{M}$  is the identity matrix. Therefore, equation (A-5) can be rewritten as

$$\frac{\partial \hat{C}_{1}}{\partial t} = \lambda_{1} \frac{\partial^{2} \hat{C}_{1}}{\partial x^{2}}$$

$$\frac{\partial \hat{C}_{2}}{\partial t} = \lambda_{2} \frac{\partial^{2} \hat{C}_{2}}{\partial x^{2}}$$
(A-6)

Define

$$n_1 = \frac{X}{2\sqrt{\lambda_1 t}}$$
,  $n_2 = \frac{X}{2\sqrt{\lambda_2 t}}$  (A-7)

Using similarity transformations (A-7) in equations (A-6), results in

$$-2\eta_{1} \frac{d\hat{C}_{1}}{d\eta_{1}} = \frac{d^{2}\hat{C}_{1}}{d\eta_{1}^{2}}$$
 (A-8a)

$$-2\eta_2 \frac{d\hat{C}_2}{d\eta_2} = \frac{d^2\hat{C}_2}{d\eta_2^2}$$
 (A-8b)

Equations (A-8) can be integrated to give

$$\frac{\hat{C}_{1}(n_{1}) - \hat{C}_{1}(-\infty)}{\hat{C}_{1}(\infty) - \hat{C}_{1}(-\infty)} = \frac{1}{2} \{1 + \operatorname{erf}(n_{1})\}$$

$$\frac{\hat{C}_{2}(n_{2}) - \hat{C}_{2}(-\infty)}{\hat{C}_{2}(\infty) - \hat{C}_{2}(-\infty)} = \frac{1}{2} \{1 + \operatorname{erf}(n_{2})\}$$
(A-9)

Rearranging equations (A-9) results in

$$\hat{C}_{1}(n_{1}) = \frac{1}{2}\{\hat{C}_{1}(\infty) + \hat{C}_{1}(-\infty)\} + \frac{1}{2}\{\hat{C}_{1}(\infty) - \hat{C}_{1}(-\infty)\}\operatorname{erf}(n_{1}) \quad (A-10a)$$

$$\hat{C}_{2}(n_{2}) = \frac{1}{2}\{\hat{C}_{2}(\infty) + C_{2}(-\infty)\} + \frac{1}{2}\{\hat{C}_{2}(\infty) - \hat{C}_{2}(-\infty)\}\operatorname{erf}(n_{2}) \quad (A-10b)$$

Equation (A-3) may be solved for  $\underline{C}$  to give

$$\hat{\underline{C}} = \underline{\underline{M}}^{-1}\underline{\underline{C}}$$
 (A-11)

Matrix  $\underline{M}^{-1}$  may be obtained as follows:

# Calculation of eigenvalues

The eigenvalues  $\lambda_1$  and  $\lambda_2$  are the roots of the polynomial determinant of the diffusivity matrix and may be obtained as follows

$$\begin{vmatrix} D_{11}^{-\lambda} & D_{12} \\ D_{21} & D_{22}^{-\lambda} \end{vmatrix} = 0$$
  
$$(D_{11}^{-\lambda}) (D_{22}^{-\lambda}) - D_{12}^{-\lambda} D_{21} = 0$$
  
$$\lambda^{2} - (D_{11}^{+\lambda} D_{22}^{-\lambda}) + |D| = 0 \qquad (A-12)$$

where |D| is the determinant of the diffusivity matrix <u>D</u>. The two eigenvalues may be obtained by solving the quadratic equation (A-12). These are:

$$\lambda_{1} = \frac{1}{2} (D_{11} + D_{22}) + [(D_{11} + D_{22})^{2} - 4|D|]^{\frac{1}{2}}$$
 (A-13a)

$$\lambda_{2} = \frac{1}{2} \{ (D_{11} + D_{22}) - [(D_{11} + D_{22})^{2} - 4 |D|]^{\frac{1}{2}} \}$$
 (A-13b)

From equations (A-13), it is evident that

$$\lambda_1 + \lambda_2 = D_{11} + D_{22}$$
 (A-14a)

$$\lambda_1 \lambda_2 = |D| = D_{11} D_{22} - D_{12} D_{21}$$
 (A-14b)

# Calculation of Eigenvectors

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To obtain the eigenvectors of <u>D</u> that correspond to eigenvalues  $\lambda_1$  and  $\lambda_2$ , the following eigenvector equations are used:

$$D_{11}X_{1} + D_{12}X_{2} = \lambda X_{1}$$
 (A-15a)  
$$D_{21}X_{1} + D_{22}X_{2} = \lambda X_{2}$$
 (A-15b)

The eigenvector corresponding to  $\lambda_1$  can be obtained from equation (A-15a) as

$$D_{11}M_{11} + D_{12}M_{21} = \lambda_1M_{11}$$
  
setting M<sub>11</sub>=1, there results M<sub>21</sub> =  $\frac{\lambda_1 - D_{11}}{D_{12}}$ 

The eigenvector corresponding to  $\lambda_2$  may be obtained in a similar way. The result is

$$M_{12} = 1$$
 ,  $M_{22} = \frac{\lambda_2^{-D}_{11}}{D_{12}}$  .

Therefore the modal matrix  $\underline{M}$  of the diffusivity matrix  $\underline{D}$  is

$$\underline{\underline{M}} = \begin{vmatrix} 1 & 1 \\ \frac{\lambda_{1} - D_{11}}{D_{12}} & \frac{\lambda_{2} - D_{11}}{D_{12}} \end{vmatrix}$$
(A-16)

The matrix  $\underline{\underline{M}}^{-1}$  is the inverse of modal matrix  $\underline{\underline{M}}$  and is found to be

$$\underline{\underline{M}}^{-1} = \begin{vmatrix} \frac{\lambda_2^{-D} \underline{11}}{\lambda_2^{-\lambda} \underline{1}} & \frac{-D_{\underline{12}}}{\lambda_2^{-\lambda} \underline{1}} \\ \frac{-(\lambda_1^{-D} \underline{11})}{\lambda_2^{-\lambda} \underline{1}} & \frac{D_{\underline{12}}}{\lambda_2^{-\lambda} \underline{1}} \end{vmatrix}$$
(A-17)

Substitution of  $\underline{M}^{-1}$  from equation (A-17) into equation (A-11) leads to

$$\hat{C}_{1} = \frac{\lambda_{2}^{-D} 1}{\lambda_{2}^{-\lambda_{1}}} C_{1} - \frac{D_{12}}{\lambda_{2}^{-\lambda_{1}}} C_{2}$$
 (A-18a)

$$\hat{C}_{2} = -\frac{\lambda_{1}^{-D} 1}{\lambda_{2}^{-\lambda_{1}}} C_{1} + \frac{D_{12}}{\lambda_{2}^{-\lambda_{1}}} C_{2}$$
 (A-18b)

The boundary conditions (A-2) may be written in terms of similarity variables  $n_1$  and  $n_2$  as

$$C_i = \overline{C}_i + \frac{\Delta C_i}{2}$$
 for  $n_i = \infty$  (A-19a)

$$C_i = \overline{C}_i - \frac{\Delta C_i}{2}$$
 for  $n_i = -\infty$  (A-19b)

Combining equations (A-18) and (A-19) results in

$$\hat{C}_{1}(\infty) = \left(\frac{\lambda 2^{-D} 1 1}{\lambda 2^{-\lambda} 1}\right) \left(\overline{C}_{1} + \frac{\Delta C_{1}}{2}\right) - \frac{D_{12}}{\lambda 2^{-\lambda} 1} \left(\overline{C}_{2} + \frac{\Delta C_{2}}{2}\right) \quad (A-20a)$$

$$\hat{C}_{1}(-\infty) = \left(\frac{\lambda 2^{-D} \mathbf{1} \mathbf{1}}{\lambda 2^{-\lambda} \mathbf{1}}\right) \left(\overline{C}_{1} - \frac{\Delta C_{1}}{2}\right) - \frac{D_{12}}{\lambda 2^{-\lambda} \mathbf{1}} \left(\overline{C}_{2} - \frac{\Delta C_{2}}{2}\right) \quad (A-20b)$$

$$\hat{C}_{2}(\infty) = -\frac{\lambda_{1}-D_{11}}{\lambda_{2}-\lambda_{1}} \left(\overline{C}_{1} + \frac{\Delta C_{1}}{2}\right) + \frac{D_{12}}{\lambda_{2}-\lambda_{1}} \left(\overline{C}_{2} + \frac{\Delta C_{2}}{2}\right) \quad (A-20c)$$

$$\hat{C}_{2}(-\infty) = -\frac{\lambda_{1}^{-D}11}{\lambda_{2}^{-\lambda_{1}}} \left(\overline{C}_{1} - \frac{\Delta C_{1}}{2}\right) + \frac{D_{12}}{\lambda_{2}^{-\lambda_{1}}} \left(\overline{C}_{2} - \frac{\Delta C_{2}}{2}\right) \quad (A-20d)$$

From equations (A-20) it is evident that

$$\hat{C}_{1}(\infty) + \hat{C}_{1}(-\infty) = 2\left[\left(\frac{\lambda_{2}^{-D}11}{\lambda_{2}^{-\lambda}1}\right)\overline{C}_{1} - \frac{D_{12}}{\lambda_{2}^{-\lambda}1}\overline{C}_{2}\right] \qquad (A-21a)$$

$$\hat{C}_{1}(\infty) - \hat{C}_{1}(-\infty) = 2\left[\left(\frac{\lambda_{2}^{-D}11}{\lambda_{2}^{-\lambda_{1}}}\right)\frac{\Delta C_{1}}{2} - \frac{D_{12}}{\lambda_{2}^{-\lambda_{1}}}\frac{\Delta C_{2}}{2}\right]$$
 (A-21b)

$$\hat{C}_{2}(\infty) + \hat{C}_{2}(-\infty) = 2\left[-\frac{\lambda_{1}^{-D}1}{\lambda_{2}^{-\lambda_{1}}}\overline{C}_{1} - \frac{D_{12}}{\lambda_{2}^{-\lambda_{1}}}\overline{C}_{2}\right] \quad (A-21c)$$

$$\hat{C}_{2}(\infty) - \hat{C}_{2}(-\infty) = 2\left[-\frac{\lambda_{1}-D_{11}}{\lambda_{2}-\lambda_{1}}\frac{\Delta C_{1}}{2} + \frac{D_{12}}{\lambda_{2}-\lambda_{1}}\frac{\Delta C_{2}}{2}\right]$$
 (A-21d)

Equations (A-21) may be inserted into equations (A-10) to give

$$\hat{C}_{1}(n_{1}) = \left[ \left( \frac{\lambda_{2}^{-D} \mathbf{1} \mathbf{1}}{\lambda_{2}^{-\lambda_{1}}} \right) \overline{C}_{1} - \frac{D_{12}}{\lambda_{2}^{-\lambda_{1}}} \overline{C}_{2} \right]$$

$$+ \left[ \left( \frac{\lambda_{2}^{-D} \mathbf{1} \mathbf{1}}{\lambda_{2}^{-\lambda_{1}}} \right) \frac{\Delta C_{1}}{2} - \frac{D_{12}}{\lambda_{2}^{-\lambda_{1}}} \frac{\Delta C_{2}}{2} \right] \operatorname{erf}(n_{1}) \qquad (A-22a)$$

$$\hat{C}_{2}(n_{2}) = \left[ - \left( \frac{\lambda_{1}^{-D} \mathbf{1} \mathbf{1}}{\lambda_{2}^{-\lambda_{1}}} \right) \overline{C}_{1} + \frac{D_{12}}{\lambda_{2}^{-\lambda_{1}}} \overline{C}_{2} \right]$$

$$+ \left[ - \left( \frac{\lambda_{1}^{-D} \mathbf{1} \mathbf{1}}{\lambda_{2}^{-\lambda_{1}}} \right) \frac{\Delta C_{1}}{2} + \frac{D_{12}}{\lambda_{2}^{-\lambda_{1}}} \frac{\Delta C_{2}}{2} \right] \operatorname{erf}(n_{2}) \qquad (A-22b)$$

Substitution of  $\hat{C}_1(n_1)$  and  $\hat{C}_2(n_2)$  from equations (A-18) into equations (A-22) leads to

$$\frac{\lambda_{2}^{-D} 1}{\lambda_{2}^{-\lambda_{1}}} C_{1}(n_{1}) - \frac{D_{12}}{\lambda_{2}^{-\lambda_{1}}} C_{2}(n_{2}) = \left[ \left( \frac{\lambda_{2}^{-D} 1}{\lambda_{2}^{-\lambda_{1}}} \right) \overline{C}_{1} - \frac{D_{12}}{\lambda_{2}^{-\lambda_{1}}} \overline{C}_{2} \right]$$

$$+ \left[ \left( \frac{\lambda_{2}^{-D} 1}{\lambda_{2}^{-\lambda_{1}}} \right) \frac{\Delta C_{1}}{2} - \frac{D_{12}}{\lambda_{2}^{-\lambda_{1}}} \frac{\Delta C_{2}}{2} \right] \operatorname{erf}(n_{1})$$
(A-23a)

$$-\left(\frac{\lambda_{1}-D_{11}}{\lambda_{2}-\lambda_{1}}\right)C_{1}(n_{1}) + \frac{D_{12}}{\lambda_{2}-\lambda_{1}}C_{2}(n_{2}) = \left[-\left(\frac{\lambda_{1}-D_{11}}{\lambda_{2}-\lambda_{1}}\right)\overline{C}_{1} + \frac{D_{12}}{\lambda_{2}-\lambda_{1}}C_{2}\right] + \left[-\left(\frac{\lambda_{1}-D_{11}}{\lambda_{2}-\lambda_{1}}\right)\frac{\Delta C_{1}}{2} + \frac{D_{12}}{\lambda_{2}-\lambda_{1}}\frac{\Delta C_{2}}{2}\right]erf(n_{2})$$
 (A-23b)

For the sake of simplicity  $C_1(n_1)$ ,  $C_2(n_2)$  will be written as  $C_1$ ,  $C_2$  respectively and equations (A-23) will be rearranged to give

$$\begin{pmatrix} \lambda_{2}^{-D}\underline{11} \\ \lambda_{2}^{-\lambda}\underline{1} \end{pmatrix} (C_{1}^{-}\overline{C}_{1}) - \frac{D_{12}}{\lambda_{2}^{-\lambda}\underline{1}} (C_{2}^{-}\overline{C}_{2}) = \\ \left[ \begin{pmatrix} \lambda_{2}^{-D}\underline{11} \\ \lambda_{2}^{-\lambda}\underline{1} \end{pmatrix} \begin{pmatrix} \Delta C_{1} \\ - \end{pmatrix} - \frac{D_{12}}{\lambda_{2}^{-\lambda}\underline{1}} \begin{pmatrix} \Delta C_{2} \\ -\lambda_{2}^{-\lambda}\underline{1} \end{pmatrix} \begin{pmatrix} \Delta C_{1} \\ -\lambda_{2}^{-\lambda}\underline{1} \end{pmatrix} (C_{1}^{-}\overline{C}_{1}) + \frac{D_{12}}{\lambda_{2}^{-\lambda}\underline{1}} (C_{2}^{-}\overline{C}_{2}) = \\ \left[ - \begin{pmatrix} \lambda_{1}^{-D}\underline{11} \\ \lambda_{2}^{-\lambda}\underline{1} \end{pmatrix} \begin{pmatrix} \Delta C_{1} \\ -\lambda_{2}^{-\lambda}\underline{1} \end{pmatrix} \begin{pmatrix} \Delta C_{1} \\ -\lambda_{2}^{-\lambda}\underline{1} \end{pmatrix} \begin{pmatrix} \Delta C_{1} \\ -\lambda_{2}^{-\lambda}\underline{1} \end{pmatrix} \begin{pmatrix} \Delta C_{2} \\ -\lambda_{2}^{-\lambda}\underline{1} \end{pmatrix} (A-24b) \right]$$

Equations (A-24) may be solved for  $(C_1 - \overline{C}_1)$  and  $(C_2 - \overline{C}_2)$  as

$$\begin{split} \mathrm{C}_{1}-\overline{\mathrm{C}}_{1} &= \frac{1}{2} \{ \left( \frac{\lambda_{2}^{-\mathrm{D}} 11}{\lambda_{2}^{-\lambda_{1}}} \right) \Delta \mathrm{C}_{1} - \frac{\mathrm{D}_{12}}{\lambda_{2}^{-\lambda_{1}}} \Delta \mathrm{C}_{2} \} \mathrm{erf}(\mathrm{n}_{1}) \\ &+ \frac{1}{2} \{ - \left( \frac{\lambda_{1}^{-\mathrm{D}} 11}{\lambda_{2}^{-\lambda_{1}}} \right) \Delta \mathrm{C}_{1} + \frac{\mathrm{D}_{12}}{\lambda_{2}^{-\lambda_{1}}} \Delta \mathrm{C}_{2} \} \mathrm{erf}(\mathrm{n}_{2}) \quad (\mathrm{A-25a}) \\ \mathrm{C}_{2}-\overline{\mathrm{C}}_{2} &= \frac{1}{2} \{ \frac{(\lambda_{2}^{-\mathrm{D}} 11)(\lambda_{1}^{-\mathrm{D}} 11)}{\mathrm{D}_{12}(\lambda_{2}^{-\lambda_{1}})} \Delta \mathrm{C}_{1} - \frac{\lambda_{1}^{-\mathrm{D}} 11}{\lambda_{2}^{-\lambda_{1}}} \Delta \mathrm{C}_{2} \} \mathrm{erf}(\mathrm{n}_{1}) \\ &+ \frac{1}{2} \{ - \frac{(\lambda_{2}^{-\mathrm{D}} 11)(\lambda_{1}^{-\mathrm{D}} 11)}{\mathrm{D}_{12}(\lambda_{2}^{-\lambda_{1}})} \Delta \mathrm{C}_{1} + \frac{\lambda_{2}^{-\mathrm{D}} 11}{\lambda_{2}^{-\lambda_{1}}} \Delta \mathrm{C}_{2} \} \mathrm{erf}(\mathrm{n}_{2}) \end{split}$$

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(A-25b)

Equations (A-25) are the desired solutions to equations (A-1).

### APPENDIX B

### NON-LINEAR LEAST SQUARES

The general theory of least squares involves the minimization of the sum of residual squares. For a function of the following form:

$$y = f(C_j, X_{\kappa})$$
(B-1)

where  $X_{\kappa}$ 's are independent variables and  $C_{j}$ 's are the parameters of the model, the least square criterion takes the form

$$R = \sum_{i=1}^{n} [y_{i} - f(C_{j}, X_{\kappa})_{i}]^{2} = Minimum \quad (B-2)$$

where n = no. of data points.

To determine the parameters of the equation (B-1), the equation (B-2) is differentiated with respect to each parameter and the resultant equation is set equal to zero. This produces a set of simultaneous equations, called normal equations. If the model is linear, the normal equations are solved in a straight forward manner. In the non-linear case, the parameters are determined through an iterative process. The first step in the Gauss-Newton method used in the following developments is to expand the model by a Taylor series about some initial guesses for the parameters and truncation of the series after the second term. The expanded form of the model is then used in the normal equations and corrections to the parameters are obtained by solving the normal equations. These corrections are added to the old values of the parameters and a new iteration is started. This process continues until convergence is achieved.

Equation (172) may be rewritten in the following form

$$f = C_1 \exp\left(\frac{-X^2}{4C_2(t+C_4)}\right) + (1-C_1) \exp\left(\frac{-X^2}{4C_3(t+C_4)}\right)$$
(B-3)

where  $C_1 = \kappa_1$ ,  $C_2 = \lambda_1$ ,  $C_3 = \lambda_2$ , and  $C_4 = t_c$ . A Taylor series expansion, trunctated after the second term, of the equation (B-3) gives:

$$\mathbf{f} = \mathbf{f}^{\star} + \sum_{j=1}^{4} \left( \frac{\partial \mathbf{f}}{\partial C_{j}} \right)_{C_{\kappa \neq j}}^{\star} \Delta C_{j} \qquad (B-4)$$

where superscript "\*" indicates that the function is evaluated at current values of  $C_j$ 's.

To generate the normal equations, equation (B-2) is differentiated with respect to each parameter and set equal to zero.

$$-\frac{1}{2}\left(\frac{\partial R}{\partial C_{\kappa}}\right)_{\ell \neq \kappa} = \sum_{i=1}^{n} (y_{i} - f_{i}) \left(\frac{\partial f_{i}}{\partial C_{\kappa}}\right)_{\ell \neq \kappa} = 0 \quad \kappa = 1, 2, \dots 4 \quad (B-5)$$

Inserting equation (B-4) into equation (B-5) one obtains

$$\sum_{i=1}^{n} [y_i - f_i^* - \sum_{j=1}^{4} (\frac{\partial f_i}{\partial C_j})^* \Delta C_j] (\frac{\partial f_i}{\partial C_\kappa})^* = 0 \quad (B-6)$$

$$\kappa = 1, 2, \dots 4$$

Equation (B-6), after rearrangement becomes

$$\sum_{j=1}^{4} \sum_{i=1}^{n} \left(\frac{\partial fi}{\partial C_{\kappa}}\right)^{*} \left(\frac{\partial fi}{\partial C_{j}}\right)^{*} \Delta C_{j} = \sum_{i=1}^{n} \left(y_{i} - f_{i}^{*}\right) \left(\frac{\partial fi}{\partial C_{\kappa}}\right)^{*}$$
(B-7)

This system of four equations in four unknowns can be represented in matrix notation as

$$\underline{\mathbf{A}} \land \underline{\mathbf{C}} = \underline{\mathbf{B}} \tag{B-8}$$

where

. \*

$$\underline{\mathbf{A}} = \begin{bmatrix} \mathbf{a}_{\kappa j} \end{bmatrix}_{4:4} \tag{B-9}$$

$$\mathbf{a}_{\kappa j} = \sum_{i=1}^{n} \left(\frac{\partial fi}{\partial C_{\kappa}}\right)^{*} \left(\frac{\partial fi}{\partial C_{j}}\right)^{*}$$
(B-10)

 $\Delta \underline{C} = [\Delta C_j]_{4:1}$  is a column matrix

$$\underline{B} = [B_{\kappa}]_{4:1} \text{ is a column matrix}$$
$$B_{\kappa} = \sum_{i=1}^{n} (y_{i} - f_{i}^{*}) \left(\frac{\partial fi}{\partial C_{\kappa}}\right)^{*}$$
(B-11)

Thus, the coefficients expressed by equations (B-10) and (B-11) may be computed and solutions for parameters  $\Delta C_j$  may be obtained.

### APPENDIX C

### EVALUATION OF THE RATIO OF REFRACTIVE

#### INDEX DERIVATIVES

Equation (162) may be written for two diffusion runs at the same average concentration as

$$(\Delta n)_{I} = R_{1}(\Delta C_{1})_{I} + R_{2}(\Delta C_{2})_{I} \qquad (C-la)$$

$$(\Delta n)_{II} = R_1 (\Delta C_1)_{II} + R_2 (\Delta C_2)_{II} \qquad (C-lb)$$

where I and II refer to diffusion runs one and two respectively. The quantities  $(\Delta n)_{I}$  and  $(\Delta n)_{II}$  are related to the area under optical path gradient profiles by

$$A_{T} = \alpha (\Delta n)_{T} \qquad (C-3a)$$

$$A_{II} = \alpha (\Delta n)_{II} \qquad (C-3b)$$

Dividing equation (C-3a) by equation (C-3b), results in

$$\frac{A_{I}}{A_{II}} = \frac{(\Delta n)_{I}}{(\Delta n)_{II}}$$
(C-4)

Substitution of  $(\Delta n)_{I}$  and  $(\Delta n)_{II}$  from equations (C-la) and (C-lb) leads to

$$\frac{A_{I}}{A_{II}} = \frac{R_{1}(\Delta C_{1})_{I} + R_{2}(\Delta C_{2})_{I}}{R_{1}(\Delta C_{1})_{II} + R_{2}(\Delta C_{2})_{II}}$$
(C-5)

Equation (C-5) may be rewritten as

$$\frac{A_{I}}{A_{II}} = \frac{\frac{R_{I}}{R_{2}} (\Delta C_{1})_{I} + (\Delta C_{2})_{I}}{\frac{R_{I}}{R_{2}} (\Delta C_{1})_{II} + (\Delta C_{2})_{II}}$$
(C-6)

Equation (C-6) can be solved to give the expression for  $R_1/R_2$  in terms of C's and A's as

$$\frac{R_{1}}{R_{2}} = \frac{(\Delta C_{2})_{I} - (A_{I}/A_{II})(\Delta C_{2})_{II}}{(A_{I}/A_{II})(\Delta C_{1})_{II} - (\Delta C_{1})_{I}}$$
(C-7)

As it was mentioned earlier,  $A_I$  and  $A_{II}$  are the area under optical path gradient profiles and can be measured directly from the interference patterns produced by the birefringent interferometer used in this study.

## APPENDIX D

# CALCULATION OF DIFFUSION COEFFICIENTS BY

## AREA MOMENT METHOD

The optical path gradient profile produced by the birefringent interferometer used in this study is given by equation (152); it is repeated here for convenience.

$$\left(\frac{\partial Z}{\partial X}\right)_{t} = \frac{\alpha \Delta n}{2\sqrt{\pi t}} \left[ L_{1}/\sqrt{\lambda_{1}} \exp\left(-\frac{X^{2}}{4\lambda_{1}t}\right) + L_{2}/\sqrt{\lambda_{2}} \exp\left(-\frac{X^{2}}{4\lambda_{2}t}\right) \right] \quad (D-1)$$

where

$$L_{1} = \frac{R_{1}}{\Delta n} \left\{ \frac{\lambda_{2}^{-\lambda_{1}}}{\lambda_{2}^{-\lambda_{1}}} \Delta C_{1} - \frac{D_{12}}{\lambda_{2}^{-\lambda_{1}}} \Delta C_{2} + \frac{R_{2}}{\Delta n} \left\{ \frac{(\lambda_{2}^{-D} 11)(\lambda_{1}^{-D} 11)}{D_{12}(\lambda_{2}^{-\lambda_{1}})} \Delta C_{1} - \frac{\lambda_{1}^{-D} 11}{\lambda_{2}^{-\lambda_{1}}} \Delta C_{2} \right\}$$
(D-2a)

$$L_2 = 1 - L_1$$
 (D-2b)

$$\lambda_{1} = \frac{1}{2} \{ (D_{11} + D_{22}) + [ (D_{11} + D_{22})^{2} - 4 | D | ]^{\frac{1}{2}} \}$$
 (D-2c)

$$\lambda_{2} = \frac{1}{2} \{ (D_{11} + D_{22}) - [(D_{11} + D_{22})^{2} - 4 |D|]^{\frac{1}{2}} \}$$
 (D-2d)

The maximum of optical path gradient is

$$\left[\left(\frac{\partial Z}{\partial X}\right)_{t \max}^{2} = \frac{\alpha \Delta n}{2\sqrt{\pi t}} \left[L_{1}^{2}/\sqrt{\lambda_{1}} + L_{2}^{2}/\sqrt{\lambda_{2}}\right] \qquad (D-3)$$

The area under optical path gradient profile can be obtained from equation (D-1) as

$$A = 2 \int_0^\infty \frac{\alpha \Delta n}{2\sqrt{\pi t}} \left[ L_1 / \sqrt{\lambda_1} \exp\left(\frac{-X^2}{4\lambda_1 t}\right) + L_2 / \sqrt{\lambda_2} \exp\left(\frac{-X^2}{4\lambda_2 t}\right) \right] dX$$
$$A = \alpha \Delta n \left( L_1 + L_2 \right) = \alpha \Delta n \qquad (D-4)$$

The reduced height-area ratio is defined by

$$D_{A} \equiv \frac{A^{2}}{4\pi t \left[ \left( \frac{\partial Z}{\partial X} \right)_{t} \right]_{max}^{2}}$$
 (D-5)

Inserting equations (D-3) and (D-4) into equation (D-5) results in

$$D_{A} = \frac{(\alpha \Delta n)^{2}}{4\pi t \left(\frac{\alpha \Delta n}{2\sqrt{\pi t}}\right)^{2} \left[L_{1}/\sqrt{\lambda_{1}} + L_{2}/\sqrt{\lambda_{2}}\right]^{2}} = \frac{1}{\left[L_{1}/\sqrt{\lambda_{1}} + L_{2}/\sqrt{\lambda_{2}}\right]^{2}} (D-6)$$

The following relation, may be obtained from equation (D-6)

$$\frac{1}{\sqrt{D_A}} = L_1 / \sqrt{\lambda_1} + L_2 / \sqrt{\lambda_2}$$
 (D-7)

The second moment of the optical path gradient profile may be calculated as follows:

$$m_{2} = 2 \int_{0}^{\infty} X^{2} \frac{\alpha \Delta n}{2\sqrt{\pi t}} [L_{1}/\sqrt{\lambda_{1}} \exp\left(\frac{-X^{2}}{4\lambda_{1}t}\right) + L_{2}/\sqrt{\lambda_{2}} \exp\left(\frac{-X^{2}}{4\lambda_{2}t}\right)] dx \qquad (D-8)$$

Integration by parts of the equation (D-8) leads to

$$m_2 = 2\alpha\Delta t (L_1\lambda_1 + L_2\lambda_2)$$
 (D-9)

.

The reduced second moment is defined by

$$D_{2m} \equiv \frac{m_2}{2At} \qquad (D-10)$$

Substitution of  $m_2$  and A (from equations (D-9) and (D-4) into equation (D-10) results in

$$D_{2m} = \frac{2\alpha \Delta nt (L_1^{\lambda} + L_2^{\lambda})}{2\alpha \Delta nt} = L_1^{\lambda} + L_2^{\lambda}$$
(D-11)

Utilizing equations (D-2) and recalling that

$$\alpha_{1} = R_{1} \frac{\Delta C_{1}}{\Delta n} \qquad (D-12a)$$

$$\alpha_2 = R_2 \frac{\Delta C_2}{\Delta n} \qquad (D-12b)$$

$$\alpha_2 = 1 - \alpha_1 \tag{D-12c}$$

equation (D-7) becomes

$$\frac{1}{\sqrt{D_A}} = I_A + S_A^{\alpha} 1 \qquad (D-13)$$

where

$$I_{A} = \frac{1}{\sqrt{\lambda_{1}\lambda_{2}} (\sqrt{\lambda_{1}} + \sqrt{\lambda_{2}})} [D_{11} - \frac{R_{1}}{R_{2}} D_{12} + \sqrt{\lambda_{1}\lambda_{2}}] \quad (D-14a)$$

$$S_{A} = \frac{1}{\sqrt{\lambda_{1}\lambda_{2}} (\sqrt{\lambda_{1}} + \sqrt{\lambda_{2}})} [D_{22} - D_{11} + \frac{R_{1}}{R_{2}} D_{12} - \frac{R_{2}}{R_{1}} D_{21}] (D-14b)$$

Thus, a slope of  $1/\sqrt{D_A}$  versus  $\alpha_1$  should yield a straight line with stop  $S_A$  and intercept  $I_A$  at  $\alpha=0$ . At  $\alpha=1$  the value of  $1/\sqrt{D_A}$  is the sum of  $I_A$  and  $S_A$ , and is denoted by  $L_A$ . That is,

$$L_{A} = I_{A} + S_{A} = \frac{1}{\sqrt{\lambda_{1}\lambda_{2}} (\sqrt{\lambda_{1}} + \sqrt{\lambda_{2}})} [D_{22} - \frac{R_{2}}{R_{1}} D_{21} + \sqrt{\lambda_{1}\lambda_{2}}] (D-15)$$

Combining equations (D-2) and (D-11) results in

$$D_{2m} = \frac{R_1}{\Delta n} \{ -(\lambda_2 - D_{11}) \Delta C_1 + D_{12} \Delta C_2 \}$$

+ 
$$\frac{R_2}{\Delta n} \{ D_{21} \Delta C_1 + (\lambda_1 - D_{11}) \Delta C_2 \} + \lambda_2$$
 (D-16)

Making use of equations (D-12), equation (D-16) becomes

$$D_{2m} = -(\lambda_2 - D_{11})\alpha_1 + \frac{R_1}{R_2} D_{12}\alpha_2 + \frac{R_2}{R_1} D_{21}\alpha_1 + (\lambda_1 - D_{11})\alpha_2 + \lambda_2 \quad (D-17)$$
  
Equation (D-17) can be rearranged to give

$$D_{2m} = [D_{11} - D_{22} - \frac{R_1}{R_2} D_{12} + \frac{R_2}{R_1} D_{21}]\alpha_1 + \frac{R_1}{R_2} D_{12} + D_{22} (D-18)$$

From equation (D-18) it is evident that a plot of  $D_{2m}$ versus  $\alpha_1$  produces a straight line with slope  $S_{2m}$  and intercept  $I_{2m}$  at  $\alpha_1=0$ . These are given by

$$s_{2m} = D_{11} - D_{22} - \frac{R_1}{R_2} D_{12} + \frac{R_2}{R_1} D_{21}$$
 (D-19a)

$$I_{2m} = D_{22} + \frac{R_1}{R_2} D_{12}$$
 (D-19b)

The value of  $D_{2m}$  at  $\alpha$ =1 is denoted by  $L_{2m}$  and is given by

$$L_{2m} = I_{2m} + S_{2m} = D_{11} + \frac{R_2}{R_1} D_{21}$$
 (D-20)

Dividing equation (D-19a) by equation (D-14b), results in

$$\frac{s_{2m}}{s_A} = -\sqrt{\lambda_1 \lambda_2} \left(\sqrt{\lambda_1} + \sqrt{\lambda_2}\right) \qquad (D-21)$$

Both sides of equation (D-21) may be squared to give

$$\left(\frac{s_{2m}}{s_{A}}\right)^{2} = \lambda_{1}\lambda_{2}\left(\lambda_{1} + \lambda_{2} + 2\sqrt{\lambda_{1}\lambda_{2}}\right) \qquad (D-22)$$

Recalling that  $\lambda_1 \lambda_2 = |D|$  and  $\lambda_1 + \lambda_2 = D_{11} + D_{22}$ , equation (D-22) takes the form

$$\left(\frac{s_{2m}}{s_{A}}\right)^{2} = |D| (D_{11} + D_{22} + 2\sqrt{|D|})$$
 (D-23)

Equation (D-14a) may be multiplied by equation (D-21) to give

$$I_{A} \frac{S_{2m}}{S_{A}} = -D_{11} + \frac{R_{1}}{R_{2}} D_{12} - \sqrt{|D|}$$
 (D-24)

Combining equation (D-24) with equation (D-19b) results in

$$D_{11} + D_{22} = I_{2m} - I_A (\frac{S_{2m}}{S_A}) - \sqrt{|D|}$$
 (D-25)

Substitution of  $D_{11}+D_{22}$  from equation (D-25) into equation (D-23) leads to

$$(\sqrt{DT})^{3} + [I_{2m} - I_{A}(\frac{S_{2m}}{S_{A}})(\sqrt{DT})^{2} - (\frac{S_{2m}}{S_{A}})^{2} = 0$$
 (D-26)

The quantity  $\sqrt{|D|}$  is the root of the cubic equation (D-26) and can be determined numerically by a digital computer. Multiplying equations (D-19b) and (D-20) by D<sub>11</sub> and D<sub>22</sub> respectively and adding together, one obtains

$$I_{2m}D_{11} + L_{2m}D_{22} = 2D_{11}D_{22} + \frac{R_1}{R_2}D_{11}D_{12} + \frac{R_2}{R_1}D_{21}D_{22}$$
 (D-27)

Equation (D-19b) may be multiplied by equation (D-20) to give

$$I_{2m}L_{2m} = D_{11}D_{22} + D_{12}D_{21} + \frac{R_1}{R_2} D_{11}D_{12} + \frac{R_2}{R_1} D_{21}D_{22} \quad (D-28)$$

Combining equations (D-27) and (D-28), and recalling the form of |D|, results in

$$I_{2m}D_{11} + L_{2m}D_{22} = I_{2m}L_{2m} + |D|$$
 (D-29)

The value of |D| is known from equation (D-26), therefore  $D_{11}$  and  $D_{22}$  can be obtained from equations (D-25) and (D-29). These are

$$D_{11} = - \frac{|D| + L_{2m} \sqrt{|D|} + L_{2m} L_{2m} S_{2m}}{S_{2m}}$$
(D-30a)

$$D_{22} = \frac{|D| + I_{2m} \sqrt{|D|} + I_{2m} L_A S_{2m} S_A}{S_{2m}}$$
(D-30b)

Substitution of values obtained for  $D_{11}$  and  $D_{22}$  from the above expressions into equations (D-19b) and (D-20) yields the values of  $D_{12}$  and  $D_{21}$  respectively.

### APPENDIX E

### DETERMINATION OF CHEMICAL POTENTIAL DERIVATIVES

The chemical potential derivatives are defined as

$$\mu_{ij} = \begin{pmatrix} \partial \mu_{i} \\ \partial C_{j} \end{pmatrix}_{C_{\kappa \neq j, N}}$$
(E-1)

The chemical potential of component i may be expressed as

$$\mu_{i} = \mu_{i}^{O} + RT \ln a_{i} \qquad (E-2)$$

where  $\mu_i^0$  is a function of temperature T, and pressure p, and  $a_i$  is the activity of species i. The activity of component i can be expressed as

$$a_i = x_i \gamma_i \qquad (E-3)$$

where  $x_i$  is the mole fraction and  $\gamma_i$  is the activity coefficients of component i respectively. Substitution of equation (E-3) into equation (E-2) results in

$$\mu_{i} = \mu_{i}^{O} + RT(\ln x_{i} + \ln \gamma_{i}) \qquad (E-4)$$

Utilizing equation (E-4), equation (E-1) takes the form

$$\mu_{ij} = RT\left(\frac{\partial \ln x_{i}}{\partial C_{j}}\right) + RT\left(\frac{\partial \ln \gamma_{i}}{\partial C_{j}}\right) (E-5)$$

$$(E-5)$$

It follows for a ternary system that

$$c = c_1 + c_2 + c_3$$
 (E-6)

$$C_1 \overline{V}_1 + C_2 \overline{V}_2 + C_3 \overline{V}_3 = 1$$
 (E-7)

Making use of equation (E-6) and equation (E-7), and assuming that partial molar volumes are constant, the first term on the right hand side of equation (E-5) can be obtained. This is

$$\operatorname{RT}\left(\frac{\partial \ln x_{i}}{\partial C_{j}}\right)_{C_{\kappa \neq j},3} = \frac{\operatorname{RT}}{C} \left[\delta_{ij} - x_{i}\left(1 - \frac{V_{j}}{V_{3}}\right)\right] \quad (E-8)$$

In the evaluation of the activity coefficient derivatives appearing in equation (E-5) the following expression proposed by Wilson (87) for the molar excess free energy,  $g^E$ , is utilized,

$$\frac{g^{E}}{RT} = -\sum_{i=1}^{n} x_{i} \ln \left[\sum_{j=1}^{n} A_{ij} x_{j}\right]$$
(E-9)

where

$$\Lambda_{ij} \equiv \frac{V_j}{V_i} \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right)$$
 (E-10)

where  $V_i$  are the pure component liquid molar volumes and  $(\lambda_{ij}-\lambda_{ii})$  are empirically determined energy terms between i-j, and i-i pairs. These are referred to as the Wilson parameters.

The resulting equations for the activity coefficients in a ternary system are

$$ln\gamma_{i} = l - ln\left[\sum_{j=1}^{3} x_{j} \wedge_{ij}\right] - \sum_{\kappa=1}^{3} \frac{x_{\kappa} \wedge_{\kappa i}}{\sum_{j=1}^{3} x_{j} \wedge_{\kappa j}}$$
(E-11)

Making use of the identity

$$\frac{\partial f}{\partial x} = \sum_{j} \left( \frac{\partial f}{\partial y_{j}} \right)_{\substack{y_{i \neq j} \\ i \neq j}} \left( \frac{\partial y_{j}}{\partial x_{i}} \right)_{\substack{k \neq i}}$$
(E-12)

where

$$f = f(y_1, y_2)$$
 (E-13)

i

and

$$y_{i} = y_{i}(x_{1}, x_{2})$$
 (E-14)

The second term in the right hand side of equation (E-5) can be expressed as

$$\operatorname{RT}\left(\frac{\partial \ell n \gamma_{\mathbf{i}}}{\partial C_{\mathbf{j}}}\right)_{C_{\kappa \neq \mathbf{j},3}} = \sum_{\ell=1}^{2} \left(\frac{\partial \ell n \gamma_{\mathbf{i}}}{\partial \mathbf{x}_{\ell}}\right)_{\mathbf{x}_{m \neq \ell}} \left(\frac{\partial \mathbf{x}_{\ell}}{\partial C_{\mathbf{j}}}\right)_{C_{\kappa \neq \mathbf{j},3}}$$
(E-15)

Differentiation of equation (E-11) yields

$$\begin{pmatrix} \frac{\partial \ln \gamma_{i}}{\partial \mathbf{x}_{l}} \end{pmatrix}_{\mathbf{x}_{m \neq l}, 3} = - \frac{\bigwedge_{il} - \bigwedge_{i3}}{\sum_{i=1}^{3} \mathbf{x}_{j} \wedge_{ij}} - \frac{\bigwedge_{li}}{\sum_{j=1}^{3} \mathbf{x}_{j} \wedge_{lj}} + \frac{\bigwedge_{3i}}{\sum_{j=1}^{2} \mathbf{x}_{j} \wedge_{3j}} + \frac{\bigwedge_{i=1}^{3} \frac{\mathbf{x}_{k} \wedge_{ki} (\bigwedge_{k} - \bigwedge_{k3})}{\sum_{j=1}^{3} \mathbf{x}_{j} \wedge_{kj}^{2}} + \frac{\bigwedge_{k=1}^{3} \frac{\mathbf{x}_{k} \wedge_{ki} (\bigwedge_{k} - \bigwedge_{k3})}{\left(\sum_{j=1}^{3} \mathbf{x}_{j} \wedge_{kj}\right)^{2}}$$
(E-16)

Therefore, equations (E-5, E-8, E-15, E-16) provide the necessary expressions for the determination of chemical potential derivatives.
APPENDIX F

COMPUTER PROGRAMS

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GAUSS-NEWTON NONLINEAR LEAST SQUARES PROGRAM
     FOR TERNARY DATA REDUCTION
     NDS IS THE NUMBER OF DATA SETS
     NRUN IS THE NUMBER OF RUNS PER DATA SET
     NNEG IS THE NUMBER OF PHOTOGRAPHS PER RUN
     NMPN IS THE NUMBER MEASUREMENTS PER PHOTOGRAPH
     YMI, YMF ARE THE MEASURED COORDINATES OF THE CELL WIDTH
     ON EACH PHOTOGRAPH
     TNEG IS THE MEASURED TIME CORRESPONDING TO EACH PHOTOGRAPH
     AL IS THE REFRACTIVE INDEX FRACTION OF COMPONENT 1
     RA IS THE RATIO OF THE REFRACTIVE INDEX DERIVATIVES
     DIMENSION AL(5), RL(5), YI(30), XI(30), XF(30), CM(4,5), D(2,2)
     COMMON X(60),Y(60),T(60),C(4)
     NJ=2
     NI=5
     READ (NJ, 99) NDS
99
     FORMAT(12)
     00 1 I=1.NDS
     READ(NJ,100)NRUN
     FORMAT(12)
100
     DO 2 J=1, NRUN
     N=0
     READ(NJ, 101)NNEG
101
     FORMAT(12)
     DO 3 K=1,NNEG
     READ (NJ. 102) YMI, YMF, TNEG, NMPN
102
     FORMAT(3F10.0,I2)
     READ(NJ,103)(YI(L),XI(L),XF(L),L=1,NMPN)
103 FORMAT(3F10.0)
     NM2=NMPN-2
     DD 4 L=1.NM2
     N=N+1
     LP1=L+1
     X(N) = 635*(XF(LP1)-XI(LP1))/(2**(YMF-YMI))
     X(N) = -(X(N) * * 2)/4.
     Y(N) = (YI(LP1) - YI(1)) / (YI(NMPN) - YI(1))
     T(N) = TNEG
4
     CONTINUE
3
     READ(NJ, 104)(C(L), L=1, 4)
104
     FORMAT(F10.0,2E10.4,F10.0)
     CALL LSQ(N)
     DO 5 M=1.4
5
     CM(M,J) = C(M)
2
     CONTINUE
     READ(NJ,105)(AL(JJ),JJ=1,NRUN)
105
     FORMAT(F10.0)
     DO 6 JJ=1.NRUN
6
     RL(JJ)=CM(1,JJ)*SORT(CM(2,JJ))/((1,JJ))*SORT
    1(CM(3,JJ))+CM(1,JJ)*SQRT(CM(2,JJ)))
     CALL UNIQ(AL, RL, NRUN, RL10, RL11)
     RN10=CM(2,1)+RL10*(CM(3,1)-CM(2,1))
     RN11=CM(3,1)-RL11*(CM(3,1)-CM(2,1))
```

D(1,1)=(CM(2,1)\*CM(3,1)-RN10\*RN11)/(CM(2,1)+CM(3,1)-RN10 1-RN11) D(2,2)=CM(2,1)+CM(3,1)-D(1,1) READ(NJ,106)RA 106 FORMAT(F10.0) D(1.2)=(D(1.1)-RN10)/RA D(2.1)=(-D(1.1)+RN11)\*RA wRITE(NI.107)((D(K,J),J=1.2),K=1.2) 107 FORMAT(10X,4F10.4) 1 CONTINUE CALL EXIT END

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1+(1.-C(1))*(-X(K)/(C(3)*(C(4)+T(K))**2))* EX
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COMMON X (6)
DO 11 J=1.)
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                                                                                                  NE=4
                                                                                                                                                          DC
                                                                                                                                                                                         DO
                                                                                                                                                                                                                                                                                        DER(I,K)=(-X(K)/(C(3)**2*(C(4)+T(K)))*EXP(XX2(K))*(1
                                                                                                                                                                                                                                                                                                           DER([+K)=C(1)*(-X(K)/(C(2)**2*(C(4)+T(K))))*
                                                                                                                                                                                                                                                                                                                                          XX1(K)=X(K)/(C(2)*(C(4)+T(K)))
XX2(K)=X(K)/(C(3)*(C(4)+T(K)))
GO TO (1.2.3.4).1
                                                                                                                                                                                                                                                                                                                                                                                σ
                                                                                                                                                                                                                                                                                                                                                                                                                         A(I.J)=0.0
CONTINUE
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                                                                                                                                                 DEL(K)=Y(K)-C(1)*
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GO TO 99
C(1)=C(1)+COEF(1)
CONTINUE
                           C(I) = C(I) + • 1 * COEF(I)
                                                          CALL
                                                                                                                                                                     CONT I NUE
                                                                                                                                                                             A(L,M)=A(L,M)+DER(M,I)+DER(L,
                                                                                                                                                                                                                                                   CONT I NUE
                                      IF(ABS(C(I))-
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                                                                                                                                                                                                                                                              EXP(XX2(K))
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                NONL INE AR
                                                                                                                                                                                                                                                                      EXP(XX1(K))
                                                                                                                                                                                                                                                                                                              EXP(XX1(K))
                                                                                                                                                                                                                                                                                                                                                                                                                                                                          DEL(60
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                MODE
                                                                                                                                                                                                                                                                                          1
                                                                                                                                                                                                                                                                                           1
                                                                                                                                                                                                                                                                                                                                                                                                                                                                           ũ
```

0

ONVERGENCE

CHECK

DO 111 I=1,4 IF(ABS(COEF(I))-.01\*ABS(C(I)))122.133.133 133 I=4 GO TO 222 122 CONTINUE 111 CONTINUE RETURN

END

<del>..</del> .

-

```
SUBROUTINE GJR FOR SOLUTION OF SIMULTANEOUS LINEAR
    ALGEBRAIC EQUATIONS
    S IS THE AUGMENTED MATRIX OF COEFFICIENTS
    NE IS THE NUMBER OF EQUATIONS
    COEF IS THE SOLUTION VECTOR
    IDENT IS AN INTEGER VECTOR
    SUBROUTINE GJR(S,NE,COEF)
    DIMENSION IDENT(4), COEF(4), S(4,5)
    NE1=NE+1
    DO 50 I=1.NE
    IDENT(I) = I
 50 CONTINUE
    BEGIN MAIN CALCULATION STEP
    DO 20 NS=1.NE
    G=0.0
    JMARK=NS
    IMARK=NS
    DO 18 I=NS.NE
    DO 18 J=NS.NE
                           . .
    TEST= ABS(S(1,J))
    IF(TEST-G)18,18,24
 24 G=TEST
     IMARK=I
     JMARK=J
 18 CONTINUE
     INTERCHANGE ROWS AND COLUMNS TO GET LARGEST ELEMENT ON DIAGONAL
    DO 12 J=1,NE1
    BA=S(IMARK.J)
     S(IMARK, J) = S(NS, J)
 12 S(NS, J)=BA
     DO 19 I=1.NE
    BA=S(I, JMARK)
     S(I, JMARK)=S(I,NS)
 19 S(I,NS)=BA
     IT=IDENT(NS)
     IDENT(NS)=IDENT(JMARK)
     IDENT(JMARK)=IT
     END OF EXCHANGE PROCESS
     BEGIN GAUSS-JORDAN OPERATION ON MATRIX ELEMENTS
     DO 20 I=1.NE
     IF(I-NS)1600.1500.1600
1500 GO TO 20
1600 AM=S(I.NS)/S(NS.NS)
     DO 20 J=NS,NE1
     S(I,J)=S(I,J)-AM*S(NS,J)
 20 CONTINUE
```

END OF GAUSS-JORDAN PROCEDURE BEGIN CALCULATING RESULTS

DO 126 I=1.NE ID=IDENT(I) 126 COEF(ID)=S(I.NE1)/S(I.I)

> RETURN END

•

```
SUBROUTINE UNIQ(AL, RL, NRUN, RL10, RL11)
     DIMENSION AL(5), RL(5), DRL(5), DAL(5)
     XBAR=0.0
     YBAR=0.0
     DO 1 I=1.NRUN
     YBAR=YBAR+RL(I)
     XBAR=XBAR+AL(I)
     CONTINUE
1
     F N=NRUN
     XBAR=XBAR/FN
     YBAR=YBAR/FN
     DO 2 I=1, NRUN
     DAL(I)=AL(I)-XBAR
     DRL(I)=RL(I)-YBAR
2
     CONTINUE
     SQX=0.0
     SQY=0.0
     SQXY=0.0
     DO 3 I=1.NRUN
     SQX=SQX+DAL(I)*DAL(I)
     SQY=SQY+DRL(I)*DRL(I)
     SQXY=SQXY+DAL(I) *DRL(I)
3
     CONTINUE
     B1=SQXY/SQX
     B0=YBAR-B1 *XBAR
     RL10=B0
     RL11=80+81
     RETURN
     END
```

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а <sup>с</sup>

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AREA-MOMENT PROGRAM FOR TERNARY DATA REDUCTION
    TM IS THE MEASURED TIME CORRESPONDING TO EACH PHOTOGRAPH.
    G IS THE MAXIMUM REFRACTIVE INDEX GRADIENT.
    A IS THE AREA UNDER THE REFRACTIVE INDEX GRADIENT CURVE.
     AL IS THE REFRACTIVE INDEX FRACTION OF COMPONENT 1.
    TE IS THE TIME CORRECTION
    H IS THE SQUARE ROOT OF DETERMINANT OF DIFFUSIVITIES
    REAL I2M.L2M.IA.LA
    DIMENSION TM(10),G(10),A(10),SM(10),AL(10),TE(10)
    1,X(10),Y(10),DA(5),D2M(5),C(4),Q(4),E(4),POL(4),D(2,2)
     WRITE(5,119)
119
    FORMAT(1H1)
    K=0
7
     READ(2,10) INDEX, N
10
    FORMAT(11,12)
     IF(INDEX)30,20,30
20
     READ(2,100)(TM(I),G(I),A(I),SM(I),I=1,N)
100 FORMAT(4F10.0)
     K = K + 1
     DO 1 I=1,N
     Y(I) = .5 + SM(I) / A(I)
1
    CONTINUE
     CALCULATION OF TE, DA, D2M
     CALL UNIQU (TM, Y, N, B1, B0, XBAR, YBAR)
     D2M(K)=B1
     TE(K)=80/81
     XBAR=0.0
     DO 2 I=1.N
     X(I)=((A(I)/G(I))**2)/(4.*3.1416*(TM(I)+TE(K)))
     XBAR=XBAR+X(I)
2
     CONTINUE
     FN=N
     XBAR=XBAR/FN
     DA(K)=XBAR
     GO TO 7
      READ(2,1000)R .L
30
1000
     FORMAT( F10.6.11)
     READ(2,999)(AL(I), I=1,L)
999
     FORMAT(2F10.0)
     00 3 I=1.L
     X(I) = 1.07 SQRT(DA(I))
3
     CONTINUE
     CALCULATION OF SA, IA, LA
    1
     CALL UNIQU(AL,X,L,B1,B0,XBAR,YBAR)
     SA=B1
     IA=80
     LA=SA+IA
```

CALCULATION OF S2M, 12M, L2M CALL UNIQU (AL, D2M, L, B1, BD, XBAR, YBAR) S2M=B1 I2M=80 L2M=S2M+12M CALCULATION OF COEFFICIENTS OF THE CUBIC EQUATION C(1) = -(S2M/SA) + (S2M/SA)C(2) = 0.0C(3) = 12M - IA + S2M/SAC(4) = 1. WRITE(5,101)(C(I),I=1,4) 101 FORMAT(//,15X,4F10.5) CALCULATION OF H CALL POLRT(C,POL,3,Q,E,IR) DO 3333 M=1.3 IF(Q(M))3333,3333,80 80 H=Q(M) CALCULATION OF THE DIFFUSION COEFFICIETS D(1,1) = -(H + H + L2M + H + L2M + IA + S2M / SA) / S2MD(2,2)=(H\*H+I2M\*H+I2M\*LA\*S2M/SA)/S2M D(2.1)=(L2M-D(1.1))\*RD(1,2)=(12M-D(2,2))/RWRITE(5,178)R, AL(1), AL(2), SA, IA, LA, S2M, I2M, L2M 178 FORMAT(10X.9F10.5) WRITE(5,177)(DA(1),D2M(1),TE(1),I=1,L) FORMAT(15X,3F15.8) 177 WRITE(5,93)H FORMAT(//,15X,F15.7) 93 WRITE(5,206) 206 FORMAT(15X, THESE ARE THE DIFFUSION COEFFICIENTS) WRITE(5,207)((D(I,J),J=1,2),I=1,2) 207 FORMAT(15X,2E20.8) 3333 CONTINUE CALL EXIT END

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SUBROUTINE UNIQU (X,Y,N,B1,BU,XBAR,YBAR) DIMENSION X(10), Y(10), DX(10), DY(10) XBAR=0.0 YBAR=0.0 DO 1 I=1.N YBAR=YBAR+Y(I) XHAR=XBAR+X(I) CONTINUE FN=N XBAR=XBAR/FN YBAR=YBAR/FN DO 2 I=1.N DX(I) = X(I) - XBARDY(I) = Y(I) - YBARCONTINUE UMSQX=0.0 UMSQY=0.0 UMDXY=0.0 00 3 I=1.N UMSQX = UMSQX+DX(1) \* DX(1)UMSQY= UMSQY+DY(I)\*DY(I) UMDXY= UMDXY+DX(I)\*DY(I) CONTINUE E1= UMDXY/ UMSQX BO=YBAR-B1\*XBAR

LINEAR REGRESSION SUBROUTINE

RETURN END

1

2

3

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```
GAUSS-NEWTON NONLINEAR LEAST SQUARES PROGRAM
    FOR BINARY DATA REDUCTION
    DIMENSION DATA(36), TIME(36), THETA(36), DI(36), DF(36), DA(36)
   1DB(36),ETA(36),AM(9),BM(3),LL(3),MM(3),CM(3),STD(9),DCI(36)
   1.TITLE(80)
    N=2
    M=5
 69 READ(N,49)KSET
 49 FORMAT(13)
    DO 700 L=1.KSET
    WRITE(M,1030)
1030 FORMAR(1H1)
    READ INPUT INFORMATION AND CONVERT DATA
    READ(N.1) (TITLE(1), I=1.80)
   1 FORMAT(80A1)
     WRITE(M,2)(TITLE(I), I=1,80)
   STORE=0.
     READ(N,619)NP,A0,B0,TI.SCALE
 619 FORMAT(12,E16.8,2F10.5,F12.4)
     DO 604 I=1.NP
 604 READ(N.605)TIME(I).DI(I).DF(I)
 605 FORMAT(3F12.4)
     DO 606 [=1,NP
 606 DATA(I)=((DF(I)-DI(I))*0.2500*2.54/SCALE)**2
     BEGIN REGRESSION CALCULATION
     A=AO
     8=80
     C = TI
     ITER=1
  10 DO 5 I=1,NP
     DC=A
     DELT=B
     DTI=C
     TERM=(DTI+DELT)/(TIME(1)+DELT)
     SLOG=ALOG(TERM)
     THETA(1)=8*DC*(TIME(1)+DELT)*(1*SLOG)
     ETA(I)=DATA(I)-THETA(I)
     DA(I) = (TIME(I) + DELT) * (1 + SLOG) * 8.
     DB(I)=8.*DC*(SLOG+1./TERM)
   5 DCI(I)=8. #DC#((TIME(I)+DELT)/(DTI+DELT))
    FORM SUMS FOR NORMAL EQUATIONS
     SUMAE=0.
     SUMAA=0.
     SUMAB=0.
     SUMAG=0.
     SUMBE=0.
```

```
SUMBB=0.
   SUMBG=0.
   SUMGE=0.
   SUMGG=0.
   SUMS0=0.
   DO 7 I=1.NP
   SUMSQ=SUMSQ+ETA(I) *ETA(I)
   SUMAE=SUMAE+DA(I)*ETA(I)
   SUMBB=SUMBB+DB(I)*DB(I)
   SUMAA=SUMAA+DA(I)*DA(I)
   SUMAB=SUMAB+DA(I)*DB(I)
   SUMAG=SUMAG+DA(I)*DCI(I)
   SUMBE=SUMBE+DB(I)*ETA(I)
   SUMBG=SUMBG+DB(I)*DCI(I)
   SUMGE=SUMGE+ETA(I) *DCI(I)
 7 SUMGG=SUMGG+DCI(I)*DCI(I)
   AM(1)=SUMAA
   AM(2)=SUMAB
   AM(3)=SUMAG
   AM(4) = SUMAB
   AM(5)=SUMBB
   AM(6) = SUMBG
   AM(7)=SUMAG
   AM(8)=SUMBG
   AM(9)=SUMGG
   BM(1)=SUMAE
                          -
                              •
   BM(2)=SUMBE
   BM(3)=SUMGE
  CALL NORMAL EQUATION MATRIX INVERSION SUBPROGRAM
    CALL MINV(AM, 3, DET, LL, MM)
    CALL GMPRD(AM, BM, CM, 3, 3, 1)
   DELA=CM(1)
   ·DELB=CM(2)
   DELC=CM(3)
    DELI=ABS((STORE-SUMSQ)/SUMSQ)
   STORE=SUMSQ
   CHECK FUR CONVERGENCE
    IF(DELI-0.0001)999,999,110
110 IF(ITER-I0)113,113,999
113 A=DELA+A
    B=DEL8+8
    C=DELC+C
    ITER=ITER+1
    GO TO 10
   CALCULATE STATISTICS
999 NPM2=NP-2
    DNP=NPM2
    FAC=SUMSQ/DNP
```

- 22

SXY=SORT(FAC) DO 13 I=1.9.4 13 STD(1)=SQRT(AM(1)\*FAC) PRINT OUTPUT WRITE(M, 201) 201 FORMAT(1H0,7X,7HEXPMTAL,16X,5HCALCD,13X,10HDIFFERENCE, 114X,4HTIME) DO 204 I=1.NP 204 WRITE(M,202)DATA(I),THETA(I),ETA(I),TIME(I) 202 FORMAT(3X,E16.8.5X,E16.8.5X,E16.8.5X,F10.2) WRITE(M, 336) ITER 336 FORMAT(9X,12HITERATION = ,I3,///) WRITE(M.206) 206 FORMAT(3X,21HDIFFUSION COEFFICIENT,5X,9HZERD TIME,5X,11HSU 1M SQUARES, 5X, 9HSTD ERROR, 19X, 2HTI) WRITE(M.9)A.B.SUMSQ.SXY.C 9 FORMAT(3X,E16.8,8X,F10.2,5X,E16.8,5X,E16.8,5X,F10.3,///) WRITE(M.207) 207 FORMAT(5X,14HSTD ERROR OF D,5X,15HSTD ERROR OF T0,5X,15HS 1TD ERROR OF TI) wRITE(M,208)STD(1),STD(5),STD(9) 208 FORMAT(5X,E16.8,5X,E16.8,5X,E16.8) 700 CONTINUE 51 CALL EXIT

END

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THIS PROGRAM CALCULATES TERNARY DIFFUSION COEFFICIENTS
     AND PHENOMENOLOGICAL COEFFICIENTS FOR IDEAL SYSTEMS
     DI(1.1), DI(2.2), DI(3.3) ARE THE SELF DIFFUSION COEFFICIENTS
     DI(I,J) ARE THE BINARY DIFFUSION COEFFICIENTS AT INFINITE
     DILUTION
     V(I) ARE MOLAR VOLUMES
     DE(I.J) ARE THE EXPERIMENTAL DIFFUSION COEFFICIENTS
     DC(I,J) ARE THE CALCULATED DIFFUSION COEFFICIENTS
     DIMENSION DI(3,3),V(3),X(3),DE(2,2),C(3),TC(2,2),F(2,2),
    1DC(2,2),TITLE(80),TITL(80),A(2,2),AL(2,2)
     READ(2,99)((DI(I,J), J=1,3), I=1,3)
99
     FORMAT(9F8.0)
     READ(2,100)(V(I),I=1,3)
100
     FORMAT(3F10.0)
     WRITE(5,107)
107
     FORMAT(1H1)
     READ(2,105)(TITLE(I), I=1,80)
     READ(2,105)(TITL (1),1=1,80)
     FORMAT(80A1)
105
     WRITE(5,106)(TITLE(I), I=1,80)
     WRITE(5,106)(TITL (1), I=1,80)
106
     FORMAT(10X,80AI)
     READ(2.189)N
189
     FORMAT(12)
     DO 1 JI=1.N
     READ(2,101)(X(I),I=1,2)
101
     FORMAT(2F10.0)
     READ(2,102)((DE(1,J),J=1,2),1=1,2)
102
     FORMAT(4F10.0)
     X(3) = 1 - X(2) - X(1)
     VT = V(3)
     DO 2 I=1.2
2
     VT = VT + X(I) * (V(I) - V(3))
     DO 3 I=1,3
3
     C(I) = X(I) / VT
     TC(1,1) = (VT/X(1)) - VT + (1 - (V(1)/V(3)))
     TC(1,2) = -VT * (1 - (V(2)/V(3)))
     TC(2,1) = -VT + (1 - (V(1)/V(3)))
     TC(2,2)=(VT/X(2))-VT*(1-(V(2)/V(3)))
     XL1=DI(1,1)**X(1)*DI(1,2)**X(2)*DI(1,3)**X(3)
     XL2=DI(2,1)**X(1)*D1(2,2)**X(2)*DI(2,3)**X(3)
     XL3=DI(3,1)**X(1)*DI(3,2)**X(2)*DI(3,3)**X(3)
     C1PV1 = (1 - C(1) + V(1)) + C(1)
     C2PV2=(1 - C(2) + V(2)) + C(2)
     C12V2=C(1)*C(2)*V(2)
     C12V3=C(1)*C(2)*V(3)
     C12V1=C(1)*C(2)*V(1)
     C22V3=C(2)**2*V(3)
     C11V3=C(1)**2*V(3)
     F(1,1)=C1PV1*XL1+C11V3*XL3
     F(2,2)=C2PV2*XL2+C22V3*XL3
     F(1,2)=-C12V2*XL2+C12V3*XL3
```

```
S.
                                                                                                                                                                                                                                                                                                                                                     4
                                                                                                                                                                      N
                                                                                                                                                                                                                  NN
                                                                                                                                                                                                                                                  N
                        118
1
                                                         111
                                                                                                                                                                      4
                                                                                                                                                                                                                   - N
                                                                                                                                                                                                                                                  ير)
                                                                                                                                                                                                                                                         ,1.2
,...,J)=0.0
,0 5 1=1.2
D0 5 J=1.2
D0 5 K=1.2
DC(1.J)=DC(1.J
D0 21 1=1.2
D0 21 J=1.7
A(1.J)=7
                                                                                                                                                                                                    DO 21 J=1.2
A(I.J)=0.0
IF(I-J)22.23.22
AL(I.J)=1.+(C(J)*V(I))/(C(3)*V(3))
GO TO 21
AL(I.J)=(C(J)*V(I))/(C(3)*V(3))
CONTINUE
DO 24 I=1.2
                                                                                                  1*A(2.1))
EL21=(A(2.2)*DE(2.1
1*A(2.1))
CL12=(A(1.1)*DC(1.2
1*A(2.1))
                                                                             CL21=(A(2.2)*DC(2.1)-A(1.2)*DC(2.2))/(A(1.
1*A(2.1))
                                                                                                                                                        UD 24 J=1.2
UD 24 K=1.2
A(I.J)=A(I.J)+AL(J.K)*TC(K.I)
EL12=(A(1.I)*DE(1.2)-A(2.I)*DE(1.1))/(A(1.I)*A(2.
                                                                                                                                                                                                                                                                                                                                                                         00
wRITE(5.111)(X(K).K=1.2).((DE(I.J).DC(I.J).J=1.2).FORMAT(2X.2F6.3.4(F10.3.3X.F7.3.2X))
wRITE(5.118)X(1).X(2).EL12.CL12.EL21.CL21
FORMAT(6X.2F5.2.4E18.5)
CONTINUE
CALL EXIT
END
                                                                                                                                                                                                                                                                                                                                                                                     -m
                                                                                                                                                                                                                                                                                                                                                                                     2
                                                                                                                                                                                2 2 2
2 4 4
                                                                                                                                                                                                                                                                                                                                                                            ₽
                                                                                                                                                                                                                                                                                                                                                                                     ٠
                                                                                                                                                                                                                                                                                                                                                                                      1
                                                                                                                                                                                                                                                                                                                                                               I=1•2
J=1•2
                                                                                                                                                                               I=1.2
J=1.2
K=1.2
                                                                                                                                                                                                                                                                                                                                                                                      II.
                                                                                                                                                                                                                                                                                                                                                                                      .
                                                                                                                                                                                                                                                                                                                                                                                     ò
                                                                                                                                                                                                                                                                                                                                                                                     12V1 *XL1+C12V3*XL3
                                                                                                                                                                                                                                                                                                         J)+F
                                                                                                                                                                                                                                                                                                         (I.K) *TC(K.J)
                                                                                                                2)-A(2
                                                                                                                                     1)-A(1.2)*DE(2
                                                                                                                .1)*DC(1.1))/(A(1.1)*A(2.2)-
                                                                                                                                     •2))/(A(1•1)*A(2
                                                                                          1)*A(2.
                                                                                                                                     .
                                                                                                                                                             2)-
                                                                                          2)-A(1.2)
                                                                                                                                      2)-A(1
                                                                                                                A(1,2)
                                                                                                                                                             A(1.
                                                                                                                                      ٠
                                                                                                                                      N
                                                                                                                                                             N
                                                                                                                                                             -
```

THIS PROGRAM CALCULATES TERNARY DIFFUSION COEFFICIENTS AND PHENOMENOLOGICAL COEFFICIENTS FOR NONIDEAL SYSTEMS USING WILSON PARAMETERS DI(1,1), DI(2,2), DI(3,3) ARE THE SELF DIFFUSION COEFFICIENTS A(I,J) ARE WILSON PARAMETERS DI(I,J) ARE THE BINARY DIFFUSION COEFFICIENTS AT INFINITE DILUTION V(I) ARE MOLAR VOLUMES DE(I,J) ARE THE EXPERIMENTAL DIFFUSION COEFFICIENTS DC(1,J) ARE THE CALCULATED DIFFUSION CDEFFICIENTS DIMENSION DI(3.3), V(3), X(3), DE(2.2), C(3), TC(2.2), F(2.2). 1DC(2,2),TITLE(80),TITL(80),A(3,3),GAM(2,2),A1(3),X1(2,2), 1Y(2,2),AL(2,2) READ(2,99)((A(I,J),J=1,3),I=1,3) READ(2,99)((DI(I,J),J=1,3),I=1,3) 99 FORMAT(9F8.0) READ(2,100)(V(I),I=1,3)FURMAT(3F10.0) 100 READ(2,95)R,T 95 FORMAT(2F10.0 WRITE(5,107) 107 FORMAT(1H1) READ(2,105)(TITLE(I),I=1,80) READ(2,105)(TITL (1), I=1,80) FURMAT(80A1) 105 WRITE(5,106)(TITLE(I), I=1,80) WRITE(5,106)(TITL (1),1=1,80) 106 FORMAT(10X,80A1) DO 6 I=1.3 DO 6 J=1.3 IF(I-J)7,8,7 8 A(I,J)=1. GO TO 6 7 A(I,J)=(V(I)/V(J))\*EXP(-A(I,J)/(R\*T))CONTINUE 6 READ(2,189)N FORMAT(12) 189 DO 1 JI=1.N READ(2,104)(X(I),I=1,2)101 FORMAT(2F10.0) READ(2,102)((DE(I,J),J=1,2),I=1,2)

```
([·3))/A1([))-(A(L.])/A1(())
                                                                                                                                                D 39 K=1.3
D 39 K=1.3
GAM(1.L)=GAM(I.L)+X(K)*A(K.I)*(A(K.L)-A(K.3))/(A1(K)**2)
D 13 1=1.2
D 13 J=1.2
IF(I-J)14.15.14
X1(I.J)=VT*(1.-X(I)*(1.-V(J)/V(3)))
G T 0 13
X1(I.J)=VT*X(I)*(1.-V(J)/V(3))*(-1.)
CONTINUE
                                                                                                                                                                                                                                                                                            =TC(I,J)+GAM(I,K)*X1(K,J)
                                                                                           DD 11 J=1.2
GAM(1.J)=0.0
DD 12 I=1.2
UD 12 L=1.2
GAM(1.L)=GAM(1.L)-((A(I.L)-A (1
1+A(3.1)/A1(3)
UD 39 I=1.2
UD 39 I=1.2
                                                                            (1 * 1) = 41 ( 1) + X ( I ) * 4( 1 * 1)
                             ~
                     DD 2 I=1.2
VT=VT+X(I)*(V(I)-V(3)
DD 29 I=1.3
AT(4F10.0)
=1.-X(2)-X(1)
                                                                                                                                                                                                                                                                                       •19
                                          C(I)=X(I)/VT
DO 9 I=1•3
Al(I)=0•0
                                                                                                                                                                                                                                                                                      02.01(L
                                                                                                                                                                                                                                                                      J=1.2
                                                               10 I=1,3
10 J=1,3
                                                                                                                                                                                                                      I=1,2
J=1,2
J=0,0
                                                                                                                                              L=1,2
                                                                                                                                                                                                                                                   J=1,2
                                                                                     I=1,2
J=1,2
                                                                                                                                                                                                                                                          =1,2
                                                                                                                                                                                                                                           1=1,2
                                                                                                                                                                                                                                                                                J=1.2
                                                                                                                                                                                                                      00 16 I=1.
                                                                                                                                                                                                                                   I • J) =0•
                                                                                                                                                                                                                                                                 י
רי
                                                                                                                                                                                                                                                          ¥
MAT(
              VT=V(3)
                                                                                                                                               39
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                                                                                                                                                   AL(I.J)=1.+(C(J)*V(I))/(C(3)*V(3))
GQ TO 21
AL(I.J)= (C(J)*V(I))/(C(3)*V(3))
CONTINUE
DO 24 I=1.2
DO 24 J=1.2
DO 24 K=1.2
DO 24 K=1.2
Y(I.J)=Y(I.J)+AL(J.K)*TC(K.I)
EL12=(A(1.1)*DE(1.2)-A(2.1)*DE(1.1))
                                                                                                                                                                                                                                                                       DO 21 J=1,2
Y(I,J)=0.0
IF(I-J)22,23,22
                                                                                                                               1*A(2.1))
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                                                                                                         CL12=(A(1.1)
1*A(2.1))
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      I=1.2

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DO 5 J=1.2
DC(I.J)=DC(I.J)+F(I.K)*TC(K.J)
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wRITE(5,111)(X(K)+K=1.2).((DE(I.J).DC(I.J)
FORMAT(2X.2F6.3.4(F10.3.3X.F7.3.2X))
wRITE(5.118)X(1).X(2).EL12.CL12.EL21.CL21
FORMAT(6X.2F5.2.4E18.5)
CONTINUE
CALL EXIT
END
                                                                                             CL21=(A(2.2)*DC(2.1)-A(1.2)*DC(2.2))/(A(1.1)*A(2.
                                                                                                                                            EL21=(A(2,2
                                                                                                                                                                                                                                                                                                                                                                                                        (1,1)=C1PV1*XL1+C11V3*XL3
(2,2)=C2PV2*XL2+C22V3*XL3
(1,2)=-C12V2*XL2+C12V3*XL3
(2,1)=-C12V1*XL1+C12V3*XL3
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#### TABLE 18.

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#### PHYSICAL PROPERTIES OF THE PURE COMPONENTS.

Component	Molecular _weight	Temperature <u>°C</u>	Molar Volume cc/mole
Acetone	58.08	25	73.99
Benzene	78.11	25	89.4
Carbon- Tetrachloride	153.84	25	97.12
Methanol	32.04	25 30	40.42 40.85
Ethanol	46.07	25	58.09
Water	18.016	25	18.07
Chlorobenzene	112.56	29.6	106.0
Bromobenzene	157.02	29.6	102.8
Toluene	92.13	29.6	107.4
n-Propanol	60.09	30	76.0
Isobutanol	74.12	30	94.0

### TABLE 19.

# BINARY DIFFUSION DATA AT INFINITE DILUTION.

Binary system	Temperature	D <sup>0</sup> ij×10 <sup>5</sup>
<u>(i dilute in j)</u>	°C	$cm^2/sec$
Acetone-Benzene Acetone-Methanol Benzene-Methanol Benzene-Acetone Methanol-Acetone Methanol-Benzene Toluene-Chlorobenzene Toluene-Bromobenzene Chlorobenzene-Toluene Chlorobenzene-Toluene Bromobenzene-Toluene Bromobenzene-Chlorobenzene Methanol - n-Propanol Methanol-Isobutanol n-Propanol - Methanol n-Propanol - Isobutanol Isobutanol-methanol Isobutanol - n-Propanol Acetone-Carbon tetrachloride Benzene-Carbon tetrachloride Carbon tetrachloride-Acetone Carbon tetrachloride-Benzene Acetone-Water Ethanol-Water Water-Acetone	25 25 25 25 25 29.6 $^{a}$ 29.6 $^{a}$ 29.6 $^{a}$ 29.6 $^{a}$ 29.6 $^{a}$ 30 $^{b}$ 30 $^{b}$ 25 $^{c}$ 25 $^$	3.0368 2.6009 2.4159 4.2778 4.7951 3.6480 1.41 2.36 1.36 2.27 1.76 .804 .587 1.966 .398 1.838 .584 1.70 1.38 3.57 1.90 1.3048 1.2038 4.9610 1.1812

<sup>a</sup>Burchard and Toor (5) <sup>b</sup>Shuck and Toor (73) <sup>C</sup>Cullinan and Toor (8)

# SELF DIFFUSION DATA.

	Temperature	D <sup>o</sup> x10 <sup>5</sup>
Component	°C	cm <sup>2</sup> /sec
Acetone	25	4.77#
Benzene	25	2.16*
Carbon tetrachlor:	ide 25	1.32#
Methanol	25	2.27*
Methanol	30	2.46*
Ethanol	25	1.02*
Chlorobenzene	29.6	1.79#
Bromobenzene	29.6	1.23#
Toluene	29.6	2.60#
n-Propanol	30	.736*
Isobutanol	30	.48*

\*Reference (47)

#Reference (48)

### TABLE 21.

# WILSON PARAMETERS\*

	Temper- ature	$\lambda$ 12 <sup>-<math>\lambda</math></sup> 11	$^{\lambda}$ 12 <sup>-<math>\lambda</math></sup> 22
System	<u>°C</u>	cal/g.mol.	<pre>cal/g.mol.</pre>
Acetone-Benzene	25	494.92	-167.91
Acetone-Mathanol	25	-214.95	664.08
Acetone-Carbon tetrachloride	25	651.76	-12.67
Benzene-Carbon tetrachloride	25	-103.41	204.82
Benzene-Methanol	25	153.86	1620.36

\*Reference (44).