

TRACER AND MUTUAL DIFFUSION
IN ISOTHERMAL LIQUID SYSTEMS
WITH SPECIFIC ASSOCIATION

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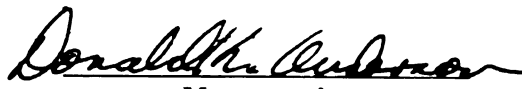
TRACER AND MUTUAL DIFFUSION IN ISOTHERMAL
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ABSTRACT

TRACER AND MUTUAL DIFFUSION IN ISOTHERMAL LIQUID SYSTEMS WITH SPECIFIC ASSOCIATION

by Guy B. Wirth

A theoretical and experimental study was made to investigate the effects of specific association on mutual and tracer diffusion. The Hartley and Crank (1) intrinsic diffusion approach was used to describe the diffusion mechanism from which equations were derived which relate the mutual and tracer diffusivities to the thermodynamic and molecular properties of the systems of interest.

For associated systems, it is necessary to consider diffusion of clusters as well as the individual molecules. A general chemical model, suggested by Nikolskii (2), was used to calculate the concentration of these clusters and the solution activities.

Three types of associated systems were studied:

- (a) binary mixtures of A and B where A associates to form a dimer cluster and B remains inert
- (b) binary mixtures of A and B where A associates with B to form a bimolecular cluster
- (c) ternary mixtures of A, B and C where A associates with B as in (b) and C remains inert.

A Mach-Zehnder diffusimeter was used to measure the mutual diffusion coefficients. Tracer diffusion coefficients were determined by a modified capillary method, developed to minimize errors inherent in previous capillary studies using Carbon-14 tracers. The accuracy of the capillary method was found to be $\pm 2\%$.

Data were collected for six systems at 25°C:

- (1) benzene-carbon tetrachloride--an example of a nonassociating system
- (2) chloroform - carbon tetrachloride--an example of a nonassociating system
- (3) methyl ethyl ketone-carbon tetrachloride--a type (a) associated system
- (4) acetic acid - carbon tetrachloride--a type (a) associated system
- (5) ether-chloroform--a type (b) associated system
- (6) ether-chloroform - carbon tetrachloride--a type (c) associated system.

These data agree well with values predicted by the equations derived in this work. Deviations can be attributed to the inability of the models to take into account nonideal behavior as well as inaccuracy in the experimental values of diffusion coefficients and activities.

¹G. S. Hartley and J. Crank, Trans. Faraday Soc., 45, 801 (1949).

²S. S. Nikol'skii, Theoreticheskaya i Eksperimental'naya Khimiya, 2 (3), 343 (1966).

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INTRODUCTION

Interest in liquid diffusion had been maintained for over a century. Since the diffusion process is one of the fundamental aspects of liquid behavior which must be described by a liquid state theory, diffusion rates have been useful in testing such theories. The importance of understanding diffusion has also increased as more basic consideration is being given to various mass transfer processes where liquid diffusion is one of the important factors.

In the usual sense, diffusion of mass refers to the dissipation of a chemical concentration gradient by molecular transfer with no overall mass flow caused by forces external to the diffusion system. Thus, if two miscible liquids, containing the same components but having different concentrations, are placed together, the molecules of the components will diffuse from the higher to lower concentration until the solution is uniform. This diffusion process results from the thermal energy of the molecules which gives rise to their Brownian movement.

Fick (28) was one of the first to mathematically describe diffusion. By analogy to conductive heat transfer, he deduced that the rate of transfer of a material

was proportional to its concentration gradient at constant temperature and pressure. That is:

$$\bar{J} = -D \nabla C \quad (1)$$

where $\bar{J}$ is the flux (i.e., the rate of transfer) of material across a reference plane of unit area and ∇C is the three dimensional concentration gradient. The constant of proportionality, D , is called the diffusion coefficient and was first thought to be constant for each system at constant temperature and pressure. But, it is now known to be a function of concentration. Equation (1) is usually simplified to the one-dimensional form given by equation (2) because of the difficulty in obtaining measurements for diffusion in more than one direction.

$$J = -D \frac{\partial C}{\partial z} . \quad (2)$$

Either equation (1) or (2) is used to define the diffusion coefficient.

Tracer diffusion is different than ordinary diffusion in that it is observed when there are no chemical concentration gradients present. To better visualize this, consider a solution of uniform chemical composition in which part of the molecules of one component is labelled. If there is a higher concentration of labelled molecules in one region of this solution than in another, measurable diffusion of these labelled molecules will take place even though the solution is chemically uniform. The flux of

labelled molecules is measured in the laboratory. Frequently this labelling is accomplished with a radioactive tracer, from which the name tracer diffusion is derived. As in ordinary diffusion, the tracer diffusion coefficient is defined by equation (2). For example, denoting the labelled component by *, the defining relation is:

$$J^* = -D^* \frac{\partial C^*}{\partial z} \quad (3)$$

where D^* is the tracer diffusion coefficient. Like the ordinary diffusion coefficient, it also is a function of concentration.

Studies have been published recently concerning the concentration dependence of the diffusion coefficients in nonideal solutions in which nonideality is caused by association of the molecules. In an associated mixture, two or more molecules may cluster together and diffuse through solution as a unit instead of as single molecules.

In this study, relationships between tracer and ordinary diffusion coefficients are derived for systems where the molecules associate to form simple clusters of two molecules. Experimental measurements of the diffusion coefficients were used to verify these relationships.

BACKGROUND

Intrinsic Diffusion

For a system to be at equilibrium at constant temperature and pressure, the chemical potential must be uniform throughout the system. For example, a system having two phases will be in equilibrium only if the chemical potential of each species is the same in both phases. If the chemical potentials of a component are not equal in both phases, there will be a spontaneous migration or, properly, diffusion of that component from the phase of high potential to the phase of lower potential. This diffusion will continue until the chemical potentials, but not necessarily the concentrations, are equal in both phases.

The diffusion process will also occur within a single phase. The molecules will diffuse from a region of high concentration and high potential to a region of low concentration and low potential until the concentration and the chemical potential are uniform. The rate of approach to equilibrium will depend upon the difference in chemical potential gradient. Therefore, it is reasonable to state that the chemical potential gradient

is the quantity which drives the system to equilibrium, that is, it is the driving force for diffusion.

$$[\text{driving force for diffusion}] = - \frac{\partial \mu_i}{\partial z} \quad (4)$$

A nonuniform chemical potential can be thought to exert a force on a molecule which causes the molecule of the i -th component to move with a velocity, v_{im} , with respect to the surrounding medium. A molecule moving in this fashion is said to be undergoing intrinsic diffusion.

As this molecule diffuses, momentum transfer to the surrounding medium results in a resisting drag force which is exerted on the molecule in a direction, opposite to that of the velocity v_{im} . If the molecule is spherical and if the surrounding medium is assumed to be a continuum, Stokes' law applies and

$$[\text{resisting force for diffusion}] = -6\pi r_i \eta v_{im} \quad (5)$$

where r_i is the molecular radius and η is the viscosity of the surrounding medium. When the molecule diffuses with a constant velocity (i.e., it experiences no acceleration), the sum of the resisting force and the driving force for diffusion must be zero.¹ From equations (4)

¹For a more exact description of nonsteady-state diffusion, a term associated with the acceleration of the molecule should be included. Although such terms may be important in some cases, they become negligible for the small chemical potential gradients encountered in experiments designed to measure diffusion coefficients (42).

and (5) this sum is

$$-\frac{\partial \mu_i}{\partial z} - N6\pi r_i \eta v_{im} = 0 \quad (6)$$

where N is Avrogrado's number. Solving this equation for v_{im} and then multiplying by C_i , the concentration of the i -th component in moles/volume, yields:

$$C_i v_{im} = \frac{C_i}{6\pi r_i \eta N} \frac{\partial \mu_i}{\partial z} \quad (7)$$

Note the $C_i v_{im}$ is the molar flux of i . And, since v_{im} is the velocity relative to the medium, $C_i v_{im}$ will be the molar flux relative to the medium, J_{im} . Hence,

$$J_{im} = \frac{C_i}{6\pi r_i \eta N} \frac{\partial \mu_i}{\partial z} \quad (8)$$

From thermodynamics,

$$\mu_i - \mu_{i0} = NkT \ln A_i \quad (9)$$

where A_i is the activity of i and μ_{i0} is the chemical potential of i in the standard state--a function of temperature and pressure only. Using equation (9), one can rewrite equation (8) as

$$J_{im} = - \left[\frac{kT}{6\pi r_i \eta} \frac{\partial \ln A_i}{\partial \ln C_i} \right] \frac{\partial C_i}{\partial z} \quad (10)$$

Comparing this equation to equation (2), one can see that the bracketed term corresponds to a diffusion coefficient. Since the flux, J_{im} , is with respect to the medium, the diffusion coefficient is defined with respect to the

medium.

$$D_{im} = \frac{kT}{6\pi r_i \eta} \frac{\partial \ln A_i}{\partial \ln C_i} \quad (11)$$

In dilute solution, the activity of the solute is proportional to its mole fraction. Further, its mole fraction is

$$x_i = \frac{C_i}{C_{\text{solvent}}} \quad (12)$$

so that

$$\frac{\partial \ln A_i}{\partial \ln C_i} = 1. \quad (13)$$

Thus, equation (11) can be written as

$$D_{im} = \frac{kT}{6\pi r_i \eta} . \quad (14)$$

This equation, known as the Stokes - Einstein equation, was derived independently by Einstein (24) and Sutherland (64). It has found application in the diffusion of colloidal particles and macromolecules in low molecular weight solvents.

However, if the radius of the diffusing molecule is smaller than the molecules of the solvent, the molecule can no longer be considered to diffuse through a continuum. Rather, the medium must be viewed as containing particles of finite size. Also, most molecules are not spherical and their shape will effect their mobility. Thus, the resisting force for diffusion may not be given by Stokes' law.

The idea that the diffusion coefficient is inversely proportional to viscosity is an old one. In 1858 Wiedemann (68) observed that for a given solute in a series of solvents, the product $D\eta$ varied less than D alone. In view of this observation, it may be assumed that, even where Stokes' law is not obeyed, the resistance to diffusion can be separated into a product of viscosity and a parameter, f , which depends very little on viscosity (33). Now, the resisting force for diffusion is:

$$[\text{resisting force for diffusion}] = -f_i \eta v_{im} \quad (15)$$

where f_i is a friction coefficient. This friction coefficient will, in general, be concentration dependent and also dependent upon the size and shape of the molecule. By calculating f_i for several solutes in one solvent, Anderson (1) found that it is approximately proportional to the square of molecular radius. Bidlack (7) confirmed Anderson's findings and also concluded that f_i depends upon molecular shape, but only for very unsymmetrical molecules. In any case, equation (15) will be accepted as the resisting force.

Again, one can sum the driving and resisting forces for diffusion to obtain:

$$-\frac{\partial u_i}{\partial z} - f_i \eta v_{im} = 0. \quad (16)$$

From equation (16) it follows, as before, that:

$$D_{im} = \frac{kT}{f_i \eta} \frac{\partial \ln A_1}{\partial \ln C_i}. \quad (17)$$

This diffusion coefficient, which Hartley and Crank (33) called the intrinsic diffusion coefficient, will be used later in this work.

Intrinsic diffusion in liquids and solids may be clarified by identifying it with the widely known kinetic theory of diffusion developed by Eyring and co-workers (25, 26, 27, 39, 54, 62). According to this theory, the diffusing molecule spends most of its time oscillating within a "cage" of other molecules. At relatively infrequent intervals, such a molecule receives sufficient energy to break through the potential barrier which limits its motion and moves in a random direction into another "cage." This diffusion process thus consists of a series of activated, random jumps relative to the loose quasicrystalline lattice of the liquid or the better-defined lattice of the solid. The theoretical treatments of the above authors give the flux of the diffusing molecules with respect to the surrounding molecules. Diffusion coefficients calculated from this theory should be identified with intrinsic diffusion coefficients.

From the foregoing discussion, it can be said that the diffusion of molecules relative to their surroundings, i.e., relative to the surrounding medium, is one of the basic mechanisms for liquid and solid diffusion. Further, intrinsic diffusion is seen to occur because of the random motion of the molecules.

Planes of Reference

While Fick (28) extended the laws of heat conduction to the problem of diffusion in a simple manner, a complication arises in connection with diffusion. In a diffusing mixture, the velocity of the individual species, v_{ic} ,² are different and as a result, there is a bulk velocity of the fluid. This bulk velocity itself contributes to the overall flux of each species. To separate pure diffusive flux from the overall flux, it follows that the flux of a species should be measured relative to a plane which moves with the bulk velocity. There are several ways to define the bulk velocity so it is necessary to carefully specify the reference plane across which the flux is measured. Since the concept of the reference plane is basic to the definition of the diffusion coefficient, it is appropriate to discuss some of them. In this discussion, the following relations will be required:

$$\rho = \sum_{i=1}^C \rho_i \quad (18)$$

²The velocity, v_{ic} does not refer to the velocity of a particular molecule of the i -th component; rather it refers to the average velocity of the molecules in a small volume of the liquid. This velocity is a function of position and time.

and

$$1 = \sum_{i=1}^c c_i \bar{V}_i \quad (19)$$

where ρ is the density of the mixture (g/cc), ρ_i is the mass concentration of the i -th component (g/cc), $\bar{V}_i$ is the partial molal volume of the i -th component (cc/mole) and c is the total number components in the mixture.

Mass Fixed Reference Plane The mass fixed reference plane is defined as a plane through which there is no net transfer of mass. From this word definition, it follows that

$$\sum_{i=1}^c M_i J_{iM} = 0 \quad (20)$$

where J_{iM} is the molar flux of i relative to the mass fixed plane and M_i is the molecular weight of i .

The meaning of this reference plane may be clarified from the standpoint of experiment by determining its velocity and the flux J_{iM} in terms of fluxes relative to laboratory coordinates. The mass flux of the i -th component through the mass fixed plane is determined by the velocity of the component, v_{iM} , relative to that plane. That is,

$$M_i J_{iM} = \rho_i v_{iM}. \quad (21)$$

But, v_{iM} is the difference between the velocity of the i -th component relative to fixed coordinates and the

velocity of the mass fixed plane relative to fixed coordinates

$$v_{im} = v_{ic} - \bar{v}_{MC} \quad (22)$$

where $\bar{v}_{MC}$, the velocity of the mass fixed plane, is called the mass average velocity. Combining the last two equations yields:

$$M_i J_{iM} = \rho_i (v_{ic} - \bar{v}_{MC}). \quad (23)$$

Summing equation (23) over all species and combining the result with equation (20) gives:

$$\sum_{i=1}^c \rho_i (v_{ic} - \bar{v}_{MC}) = 0. \quad (24)$$

Or, after solving for $\bar{v}_{MC}$,

$$\bar{v}_{MC} = \sum_{i=1}^c \frac{\rho_i v_{ic}}{\rho}. \quad (25)$$

Identifying $\rho_i v_{ic}$ as the mass flux of i relative to fixed coordinates, one can see that the mass average velocity is the net flux of mass across a coordinate fixed plane divided by the solution density.

$$\bar{v}_{MC} = \sum_{i=1}^c \frac{M_i J_{iC}}{\rho} \quad (26)$$

Since both ρ and J_{iC} are functions of position and time, $\bar{v}_{MC}$ will also be so dependent.

To demonstrate the contribution of bulk flow to the overall flux of a component, expand equation (23) to

$$M_i J_{iM} = \rho_i v_{iC} - \rho_i \bar{v}_{MC} \quad (27)$$

or

$$M_i J_{iC} = M_i J_{iM} + \rho_i \bar{v}_{MC} \quad (28)$$

From this last result, one can see that the mass flux relative to the laboratory coordinates is the mass flux relative to the mass fixed plane plus a flux arising from the bulk motion.

Number Fixed Reference Plane The number fixed reference plane is defined as a plane through which there is no net flux of molecules; or, equivalently, a plane through which there is no net flux of moles. Therefore, this reference plane is also known as the molar fixed reference plane. From the definition of this plane, it follows that

$$\sum_{i=1}^c J_{iN} = 0 \quad (29)$$

where J_{iN} is the molar flux of the i -th component relative to the number fixed plane.

The relationship of this reference plane to experiment can be seen by noting that the flux

$$J_{iN} = C_i v_{iN} = C_i (v_{iC} - \bar{v}_{NC}) \quad (30)$$

where $\bar{v}_{NC}$, the velocity of the number fixed reference plane, is the number average velocity. Summing equation (30) over all components and combining the resulting equation with equation (29) yields:

$$\bar{v}_{NC} = \frac{\sum_{i=1}^c C_i v_{iC}}{\sum_{i=1}^c C_i} \quad (31)$$

Since $J_{iC} = C_i v_{iC}$,

$$\bar{v}_{NC} = \frac{\sum_{i=1}^c J_{iC}}{\sum_{i=1}^c C_i} . \quad (32)$$

Thus, the number average velocity, at a position in the fluid, is the net molar flux through a coordinate fixed plane at that position divided by the total molar concentration of the solution.

The effect of bulk motion can be seen by expanding equation (30) to

$$J_{iC} = J_{iN} + C_i \bar{v}_{NC} . \quad (33)$$

Again, the overall flux relative to a coordinate fixed plane is the flux relative to the number fixed plane plus

a term resulting from the bulk motion of the solution. (However, this bulk motion of the fluid is defined differently than in equation [28].)

Component Fixed Reference Plane The component fixed reference plane is defined as a plane through which there is no flux of one particular component. Usually, the reference component is taken as the solvent so this reference plane is often called the solvent fixed reference plane. From the definition,

$$J_{oo} = 0 \quad (34)$$

where the first subscript, o, designates the reference component and the second the component fixed reference plane. The flux of any other component, i, with respect to this reference plane is given by:

$$J_{io} = C_i v_{io} = C_i (v_{iC} - \bar{v}_{oC}) \quad (35)$$

where $\bar{v}_{oC}$ is the component average velocity. Writing this equation for the reference component, one obtains:

$$J_{oo} = C_o (v_{oC} - \bar{v}_{oC}). \quad (36)$$

Substituting equation (34) into equation (36) and solving for $\bar{v}_{oC}$ yields:

$$\bar{v}_{oC} = \frac{C_o v_{oC}}{C_o}. \quad (37)$$

Or, since $J_{OC} = C_O \bar{v}_{OC}$, this equation can be written as

$$\bar{v}_{OC} = \frac{J_{OC}}{C_O} \quad (38)$$

The component average velocity is simply the flux of the reference component across a coordinate fixed plane divided by the concentration of the reference component. To show this influence of bulk motion, equation (35) is rewritten as

$$J_{iC} = J_{iO} + C_i \bar{v}_{OC} \quad (39)$$

where the contribution to the overall flux of i by bulk motion is evident.

Volume Fixed Reference Plane The volume fixed reference plane is defined as a plane through which there is no net flux of volume. Noting that the volume flux of the i -th component relative to the volume fixed plane is $J_{iV} \bar{v}_i$, it follows from the definition that:

$$\sum_{i=1}^C J_{iV} \bar{v}_i = 0 \quad (40)$$

where J_{iV} is the molar flux relative to the volume fixed reference plane.

To show the relationship between this reference plane and the coordinate fixed plane, write the flux as:

$$J_{iV} = C_i v_{iV} = C_i (v_{iC} - \bar{v}_{VC}) \quad (41)$$

where $\bar{v}_{VC}$ is the volume average velocity. This equation can be rewritten as:

$$J_{iC} = J_{iV} + c_i \bar{v}_{VC} \quad (42)$$

where the contribution of bulk motion to the overall flux across a coordinate fixed plane is evident. Now, to obtain an expression for $\bar{v}_{VC}$, multiply equation (42) by $\bar{v}_i$ and sum over all components. The result is:

$$\sum_{i=1}^c J_{iC} \bar{v}_i = \sum_{i=1}^c J_{iV} \bar{v}_i + \bar{v}_{VC} \sum_{i=1}^c c_i \bar{v}_i \quad (43)$$

which, when combined with equation (19) and (40) gives:

$$\bar{v}_{VC} = \sum_{i=1}^c J_{iC} \bar{v}_i. \quad (44)$$

Thus, one sees that $\bar{v}_{VC}$ is the total volume flux across a coordinate fixed plane and as such, it will be zero when the total volume of the system is constant. In that case, equation (42) becomes:

$$J_{iC} = J_{iV} \quad (45)$$

and the coordinate fixed and volume fixed plane become identical. Experimentally, constant volume conditions can be maintained by having very small concentration differences in the system. Therefore, the volume fixed

plane has had wide application in the literature and will be used in this work to define diffusion coefficients.

For a binary system, two diffusion coefficients can be defined by the following equations:

$$J_{AV} = -D_{AV} \frac{\partial C_A}{\partial z} \quad (46)$$

$$J_{BV} = -D_{BV} \frac{\partial C_B}{\partial z} . \quad (47)$$

However, by using the fact that:

$$\bar{V}_A \partial C_A + \bar{V}_B \partial C_B = 0 \quad (48)$$

along with equation (40), it can be shown that:

$$D_{AV} = D_{BV} \equiv D_{AB} . \quad (49)$$

The coefficient, D_{AB} , is called the mutual diffusion coefficient and from this point on, it will imply that the volume fixed reference plane is used.

Medium Fixed Reference Plane In the discussion of the previous reference planes, the velocity of the various components were measured relative to the mass, number, component or volume average velocity. However, it was shown in the previous discussion of intrinsic diffusion that the velocity of a component relative to its surrounding medium is more significant. This is the velocity referred to in Stokes' law (equation [5]). Therefore, it is desirable to define a new reference plane

fixed with respect to the medium. (i.e., it has the same velocity as the medium.) Material would be transferred through such a plane by intrinsic diffusion only. Thus, the medium fixed reference plane is defined as a plane through which material is transferred by random molecular motion only.

The medium average velocity, $\bar{v}_{mC}$, can be written as:

$$\bar{v}_{mC} = v_{iC} - v_{im} \quad (50)$$

and the flux of the i-th component relative to the medium fixed plane is then:

$$J_{im} = C_i v_{im} = C_i \left(v_{iC} - \bar{v}_{mC} \right) \quad (51)$$

or, as before:

$$J_{iC} = J_{im} + C_i \bar{v}_{mC} \quad (52)$$

where $C_i \bar{v}_{mC}$ is a flux resulting from the bulk motion of the liquid. The kinetic theory discussed previously suggests a molecular mechanism for the bulk motion (33). Molecules do not always jump into "cages" which are large enough to accommodate them. They pass through an activated state of high potential energy to a new position which, although it has lower potential energy than the activated state, has higher energy than its original position. As a result, the new set of neighboring molecules is pushed slightly further apart to reduce potential

energy. The total effect over a large number of such processes is a small increase in hydrostatic pressure which is relieved by a bulk flow of the liquid.

Although this plane of reference is significant in terms of the molecular mechanism of diffusion, diffusion coefficients which are defined relative to it cannot be directly measured from experiment as can the mutual diffusion coefficient. However, the medium and volume fixed planes can be related in a useful way by multiplying equation (52) by $\bar{V}_i$ and summing over all components. Thus:

$$\sum_{i=1}^c J_{iC} \bar{V}_i = \sum_{i=1}^c J_{im} \bar{V}_i + \bar{v}_{mC} \sum_{i=1}^c c_i \bar{V}_i. \quad (53)$$

Combination of this equation with equation (19) and (44) gives the result:

$$\sum_{i=1}^c J_{im} \bar{V}_i = \bar{v}_{VC} - \bar{v}_{mC}. \quad (54)$$

The utility of the last equation will be seen in the next section. Hartley and Crank (33) were one of the first to formally discuss this plane of reference. However, they limited their work to constant volume systems in which $\bar{v}_{VC} = 0$.

Mutual Diffusion in Binary Systems

Recall that mutual diffusion refers to diffusion measured with respect to the volume fixed reference plane. The mutual diffusion coefficient, D_{AB} , is the coefficient usually calculated from diffusion experiments. From the point of view of interpreting diffusion coefficients in terms of molecular motions, D_{AB} appears to be complicated by the bulk motion of the liquid. On the other hand, intrinsic diffusion, i.e., diffusion with respect to the medium fixed reference plane, is not complicated by the bulk motion. Therefore, it is desirable to explore the relation between mutual and intrinsic diffusion. The basis for the following discussion is an important work by Hartley and Crank (33).

The flux of component A relative to the volume fixed reference plane is given by:

$$J_{AV} = C_A v_{AV} \quad (55)$$

or:

$$J_{AV} = C_A \left(v_{AC} - \bar{v}_{VC} \right). \quad (56)$$

To this equation, add and subtract $C_A \bar{v}_{mC}$. Thus,

$$J_{AV} = C_A \left(v_{AC} - \bar{v}_{mC} \right) - C_A \left(\bar{v}_{VC} - \bar{v}_{mC} \right). \quad (57)$$

But,

$$v_{Am} = v_{AC} - \bar{v}_{mC}. \quad (58)$$

So,

$$J_{AV} = J_{Am} - C_A \left(\bar{v}_{VC} - \bar{v}_{mC} \right). \quad (59)$$

At this point, use equation (54) with equation (59) to get:

$$J_{AV} = J_{Am} - C_A \left(J_{Am} \bar{v}_A + J_{Bm} \bar{v}_B \right). \quad (60)$$

From the definitions of the diffusion coefficients,

$$J_{AV} = -D_{AB} \frac{\partial C_A}{\partial z} \quad (61)$$

$$J_{Am} = -D_{Am} \frac{\partial C_A}{\partial z} \quad (62)$$

and,

$$J_{Bm} = -D_{Bm} \frac{\partial C_B}{\partial z}. \quad (63)$$

These last three equations are now combined with equation (60) to yield:

$$D_{AB} \frac{\partial C_A}{\partial z} = D_{Am} \frac{\partial C_A}{\partial z} - C_A \bar{v}_A D_{Bm} \frac{\partial C_A}{\partial z} - C_A \bar{v}_B D_{Bm} \frac{C_B}{z}. \quad (64)$$

Further, from equation (48),

$$\frac{\partial C_B}{\partial C_A} = \frac{\bar{v}_A}{\bar{v}_B}. \quad (65)$$

So, equation (64) becomes:

$$D_{AB} = D_{Am} \left(1 - C_A \bar{V}_A \right) + D_{Bm} C_A \bar{V}_A \quad (66)$$

which, when combined with equation (19), becomes:

$$D_{AB} = C_B \bar{V}_B D_{Am} + C_A \bar{V}_A D_{Bm}. \quad (67)$$

Equation (67) can be modified by substitution for D_{Am} and D_{Bm} from equation (17) to give:

$$D_{AB} = \frac{kT}{\eta} \left[\frac{1}{\bar{f}_A} \frac{\partial \ln A_A}{\partial \ln C_A} C_B \bar{V}_B + \frac{1}{\bar{f}_B} \frac{\partial \ln A_B}{\partial \ln C_B} C_A \bar{V}_A \right] \cdot \quad (68)$$

From the definition of mole fraction and equation (19), it can be shown that:

$$\frac{\partial \ln X_A}{\partial \ln C_A} = \frac{X_B}{C_B \bar{V}_B} \quad (69)$$

and:

$$\frac{\partial \ln X_B}{\partial \ln C_B} = \frac{X_A}{C_A \bar{V}_A} \quad (70)$$

Therefore, equation (68) can be rearranged to the well known Hartley-Crank equation (33):

$$D_{AB} = \frac{kT}{\eta} \left[\frac{X_B}{\bar{f}_A} + \frac{X_A}{\bar{f}_B} \right] \frac{\partial \ln A_A}{\partial \ln X_A} \cdot \quad (71)$$

The activity term, $\frac{\partial \ln A_A}{\partial \ln X_A}$, that can be factored out because the Gibbs-Duhem relation requires that $\frac{\partial \ln A_A}{\partial \ln X_A} = \frac{\partial \ln A_B}{\partial \ln X_B}$.

While Hartley and Crank (33) restricted their equation to systems having constant volume, no such restriction was necessary in the derivation presented here.

Tracer Diffusion

Tracer diffusion refers to diffusion in a chemically uniform mixture. It frequently is observed by labelling some of the molecules of one component with an isotopic form of one of their constituent atoms. Then a concentration gradient of labelled molecules is established while maintaining the total concentration at a constant value. After diffusion starts, the concentration gradient of labelled molecules will be dissipated by random molecular motion. The intrinsic flux of labelled molecules can be found by summing the driving and resisting forces to diffusion as done above. The result is:

$$J_{im}^* = - \left[\frac{kT}{nf_i^*} \frac{\partial \ln A_i^*}{\partial \ln C_i^*} \right] \frac{\partial C_i^*}{\partial z} \quad (72)$$

where superscript, *, indicates labelled molecules. Again, the term in the brackets is identified as the intrinsic diffusion coefficient, in this case, of the labelled molecules of the i-th component:

$$D_{im}^* = \frac{kT}{f_i^*} \frac{\partial \ln A_i^*}{\partial \ln C_i^*} . \quad (73)$$

Generally, the fact that a molecule is labelled does not change its physical properties appreciably.³ Therefore, it is reasonable to assume that the physical properties of the labelled and unlabelled molecules of the same component are identical so that $f_i^* = f_i$. The activity of the labelled species is:

$$A_i^* = \gamma_i^* X_i^* \quad (74)$$

where γ_i^* is the activity coefficient and is constant since the chemical concentration is uniform. Therefore, differentiation of equation (74) gives:

$$\frac{\partial \ln A_i^*}{\partial \ln X_i^*} = 1. \quad (75)$$

The concentration of labelled species in moles/cc, C_i^* , is related to its mole fraction, X_i^* , by:

$$C_i^* = \frac{X_i^*}{\sum_{i=1}^c X_i \bar{V}_i} . \quad (76)$$

³This is not a good assumption for molecules of low molecular weight like H_2 or even H_2O where the label can significantly change their molecular weight and size.

Because the chemical concentration is uniform, the denominator of equation (76) is constant and independent of X_i^* . Hence, equation (76) can be differentiated to yield:

$$\frac{\partial \ln X_i^*}{\partial \ln C_i^*} = 1. \quad (77)$$

Multiplication of equation (75) by equation (77) gives the result:

$$\frac{\partial \ln A_i^*}{\partial \ln C_i^*} = 1. \quad (78)$$

Thus, the intrinsic diffusion coefficient for the labelled molecules becomes:

$$D_{im}^* = \frac{kT}{\eta f_i}. \quad (79)$$

Another result of the uniform chemical concentration is that all the reference planes discussed previously are the same. That is, they all have the same velocity. This may be shown for the mass, number, component and volume fixed planes by substituting the relation, $J_{iC} = C_i v_{OC}$, into equations (26), (32), (38) and (44). Because v_{iC} must be zero for every component⁴ when all the chemical concentration gradients are zero, the resulting equations are readily simplified by using equations

⁴There are no external forces on the system which may cause convective flow, etc.

(18) and (19) and lead to:

$$\bar{v}_{MC} = \bar{v}_{NC} = \bar{v}_{OC} = \bar{v}_{VC} = 0. \quad (80)$$

It requires a slightly different argument to show that the medium average velocity, $\bar{v}_{mC}$, is the same as the other reference planes. Recall that

$$\bar{v}_{VC} - \bar{v}_{mC} = \sum_{i=1}^c J_{im} \bar{v}_i \quad (54)$$

and that the intrinsic flux

$$J_{im} = - D_{im} \frac{\partial C_i}{\partial z}. \quad (81)$$

Consider, for a moment, the components which are not labelled. Since their concentrations are uniform, it is apparent from equation (81) that their intrinsic fluxes are all zero. Therefore, the right side of equation (54) is the sum over the labelled and unlabelled i -th component. Thus,

$$\bar{v}_{VC} - \bar{v}_{mC} = J_{im}^* \bar{v}_i + J_{im}^u \bar{v}_i \quad (82)$$

where superscript, u , designates unlabelled i molecules. The overall concentration of the i -th component is the sum:

$$C_i = C_i^* + C_i^u \quad (83)$$

and is constant. Hence,

$$\frac{\partial C_i^*}{\partial z} = - \frac{\partial C_i^u}{\partial z} . \quad (84)$$

Also, the physical properties of the labelled and unlabelled molecules are the same so that $D_{im}^* = D_{im}^u$. Then, it follows from equation (81), (82) and (84) that:

$$\bar{v}_{mC} = \bar{v}_{VC} . \quad (85)$$

And finally, equations (80) and (85), taken together, show that

$$\bar{v}_{mC} = \bar{v}_{VC} = \bar{v}_{MC} = \bar{v}_{NC} = \bar{v}_{OC} = 0 . \quad (86)$$

Since all the reference planes are the same, the tracer diffusion coefficient in equation (3) can be defined with respect to any one of them. In particular, it can be defined with respect to the medium fixed reference plane. Then the tracer diffusion coefficient equals the intrinsic diffusion coefficient of the labelled molecules and from equation (79).

$$D_i^* = \frac{kT}{\eta f_i} . \quad (87)$$

For a binary mixture, the two tracer diffusion coefficients are:

$$D_A^* = \frac{kT}{\eta f_A} \quad (88)$$

and

$$D_B^* = \frac{kT}{\eta f_B} . \quad (89)$$

These last two expressions can be combined with equation (71) (the Hartley-Crank equation) to obtain a relationship between the mutual and tracer diffusion coefficients in binary mixtures.

$$D_{AB} = \left[X_A D_B^* + X_B D_A^* \right] \frac{\partial \ln A_A}{\partial \ln X_A} \quad (90)$$

Darken (16) first derived equation (90) and showed that it predicted the mutual diffusion coefficients in gold-silver alloys. Since that time, investigators have attempted to experimentally verify this equation but without great success. Their failures generally resulted from large experimental errors and, as will be pointed out later, a poor choice of systems.

The three diffusion coefficients in equation (90) are concentration dependent and are, in general, not equal. However, the limiting values of the mutual diffusion coefficient approach the tracer diffusion coefficient of the solute at each end of the concentration range. Thus,

$$\lim_{X_B \rightarrow 0} D_{AB} = D_B^* \quad (91)$$

and

$$\lim_{X_A \rightarrow 0} D_{AB} = D_A^* \quad (92)$$

as can readily be seen from equation (90).

Diffusion in Multicomponent Systems

The usual method of expressing diffusive fluxes in binary systems by means of a single mutual diffusion coefficient is simple and effective. In many practical cases, however, it is necessary to deal with diffusion processes occurring in multicomponent systems. A general description of these is, as would be expected, far from simple.

Gosting and co-workers suggested (5) and experimentally verified (23) that the fluxes J_{AV} and J_{BV} of solutes A and B in a solvent C may be described for the volume fixed plane of reference by the two equations:⁵

$$J_{AV} = - D_{AAV} \left(\frac{\partial C_A}{\partial z} \right)_{C_B, C_C} - D_{ABV} \left(\frac{\partial C_B}{\partial z} \right)_{C_A, C_C} \quad (93)$$

and

$$J_{BV} = - D_{BAV} \left(\frac{\partial C_A}{\partial z} \right)_{C_B, C_C} - D_{BBV} \left(\frac{\partial C_B}{\partial z} \right)_{C_A, C_C} \quad (94)$$

⁵For simplicity, the ensuing discussion will consider ternary systems. However, it can be extended to a c component system in a straight forward fashion (5).

where D_{AAV} and D_{BBV} are the main diffusion coefficients and D_{ABV} and D_{BAV} are the cross-term diffusion coefficients. The important thing to note here is that to describe mutual diffusion, more than one mutual diffusion coefficient must be defined. Thus, the relatively simple analysis which led to equation (71) for binary mixtures must be modified for multicomponent mixtures (41). However, mutual diffusion in multicomponent systems will not be considered in this work.

Tracer diffusion in multicomponent mixtures will be important here. The tracer diffusive flux of a component in a multicomponent mixture can still be expressed in terms of one tracer diffusion coefficient. This can be shown by applying equation (93) to the labelled molecules of, say, component A in a ternary mixture. Such a system can be thought of as a quaternary system of A^u , A^* , B and C. Recall that in the case of tracer diffusion, the concentration gradients of all the unlabelled components are zero and for the labelled component.

$$\left(\frac{\partial C_A^*}{\partial z} \right)_{C_B, C_C} = - \left(\frac{\partial C_A^u}{\partial z} \right)_{C_B, C_C} . \quad (95)$$

Hence, equation (93) reduces to

$$J_A^* = - \left(D_{AA}^{**} - D_{AA}^* \right) \frac{\partial C_A^*}{\partial z} \quad (96)$$

where D_{AA}^{**} is a main diffusion coefficient and D_{AA}^* is a cross term diffusion coefficient. In mutual diffusion, the cross term coefficients are an order of magnitude less than the main coefficients (23). While they have not been measured for tracer diffusion, one can see that the difference, $D_{AA}^{**} - D_{AA}^*$, can be identified as the tracer diffusion coefficient by comparing equation (96) to equation (3). Therefore, in a multicomponent system, there is only one tracer diffusion coefficient for each component. This is fortunate for it permits the analysis used to derive equation (87) to be used for a multicomponent system.

Thermodynamics of Solutions

The previous discussions have shown that the use of the chemical potential gradient as the driving force for diffusion intimately ties thermodynamics and solution ideality to the diffusion process. Therefore, a brief review of solution thermodynamics follows.

Ideal Solutions An ideal solution may be defined as a solution in which the various pure components involved do not experience any modification of properties other than that of dilution. Further, ideal solutions must obey Raoult's law throughout the range of concentration. Raoult's law states that the partial vapor pressure of any component is proportional to the mole fraction of that component.

$$p_k = p_k^* X_k \quad (97)$$

In terms of the interaction between molecules of a solution, an ideal solution is one in which the interaction between molecules of different substances in the mixture is the same as between the molecules in the pure component. The solvent in any binary solution, therefore, obeys Raoult's law in the limit as the concentration of the solute goes to zero.

Nonideal Solutions While the concept of the ideal solution is extremely useful, very few systems obey Raoult's law over the whole concentration range. The method usually adopted in dealing with nonideal solutions is to find a number, γ_k , which, when multiplied by the mole fraction of the particular species, makes applicable a relation having the form of Raoult's law. Thus,

$$p_k = p_k^* \gamma_k X_k \quad (98)$$

The number, γ_k , is the activity coefficient and is a function of composition. The quantity, $\gamma_k X_k$, is the activity of the k-th component.

The total pressure of a system is the sum of the partial pressures of all components, as shown in equation (99).

$$\pi = \sum_{k=1}^c p_k \gamma_k X_k \quad (99)$$

Unlike the ideal solution, the total pressure of a nonideal solution is not a linear function of mole fraction and negative as well as positive deviations from this relationship are observed.

In nonideal solutions, the intermolecular attractive energy between unlike molecules is different from that between like molecules. If the interaction between, say, A and B molecules is larger than either A - B or B - B interactions, the tendency of each of the molecules to escape from the liquid to the vapor phase is reduced and there are negative deviations from Raoult's law. Similarly, if the A - B interaction energy is smaller than either the A - A or B - B interaction energy, positive deviations result.

Molecular interactions have been accounted for in two ways; firstly, due to the effect of molecular sizes and nonspecific, nonbonding intermolecular forces and secondly, due to association.

In the first, molecules are thought to interact through van der Waal or London forces for example. Hildebrand, et al. (34, 35, 37), called attention to a particular class of these nonideal mixtures which Hildebrand (34) first called "regular solutions." As conceived by Hildebrand, these solutions differ from other nonideal solutions in that thermal energy still suffices to give nearly random molecular mixing. So, such solutions

are characterized by the absence of any specific interactions such as association and by equal sized molecules. Hildebrand and Scott (36) found, for regular binary solutions:

$$\frac{\partial \ln A_A}{\partial \ln X_A} = 1 - \frac{2B}{NkT} X_A X_B \quad (100)$$

and

$$\Delta H_{\text{mix}} = B X_A X_B \quad (101)$$

where B is a constant for a system. It is related to the difference in the energy of attraction of unlike molecules as compared with the mean of the energies for pairs of like molecules. Lewis and Randall (45) point out that equations (100) and (101) are in reasonable agreement with experimental data even if the component molecules are somewhat different in size.

The second model of solution nonideality considers the molecules to interact with relatively strong specific forces to form weakly bonded clusters of molecules. The individual molecules are thought to be in equilibrium with the clusters in the same way that reactants are in equilibrium with products in a conventional chemical reaction. Therefore, this approach is frequently called the chemical model of solution nonideality.

Chemical Model of Solution Nonideality Dolezalek

(19) was the first to propose the chemical model. He was able to successfully apply the model to several nonideal systems. For example, he explained the nonideality of the ether-chloroform system by assuming that one ether molecule associates with one chloroform molecule to form a bimolecular cluster. Then, assuming ideal solution behavior for this mixture of the ether molecules, chloroform molecules and clusters, he predicted the total pressure of the system as a function of composition to within the experimental accuracy of the data--using only one arbitrary parameter the equilibrium constant, K , for dimerization.

Dolezalek's success was, in part, fortuitous because early proponents of the chemical model were hindered by limited knowledge of molecular interactions and, in particular, of hydrogen bonding. This ignorance precluded *á priori* decisions as to the nature of the clusters to be expected. Hildebrand and Scott (36) showed that application of the chemical model to any general system can lead to results which are obviously inconsistent with presently accepted theories. For example, deviations of the argon-nitrogen system were explained by Dolezalek (20) using the chemical model with the unlikely assumption that the argon molecules associate.

Hildebrand and Scott (36) further point out that in spite of such inconsistencies, the basic premises of the chemical model are still valid when independent verification of association can be found. Such information can come from other physical properties of solutions such as the absorption of light at frequencies attributable to the formation of hydrogen bonds, etc.

Dolezalek (19) derived the equations of the chemical model separately for each type of specific interaction. However, it is possible to arrive at generalized equations with the more basic approach suggested by Nikol'skii (52).

Consider a system in which there are different chemical species, some of which may be inert and do not associate at all while the remainder are at reaction equilibrium with respect to one another. Let P be the number of phases and r the number of independent reactions of the type

$$\sum_{j=1}^n v_{jk} Q_{jk} = 0 \quad k = 1, 2, \dots, r \quad (102)$$

where v_{jk} is the stoichiometric coefficient of the j -th species, in the k -th reactor. The coefficients v_{jk} will be taken as positive if the j -th species is produced in the k -th reaction and negative if it is destroyed by this

reaction. If the j -th species does not take part in the k -th reaction, then $v_{jk} = 0$. The r reactions will be independent if the rank of the $r \times n$ matrix composed of the coefficients v_{jk} is equal to the number of equations, r . That is, there are stoichiometric coefficients such that

$$G = \begin{vmatrix} v_{11} & v_{12} & \cdots & v_{1r} \\ v_{21} & v_{22} & \cdots & v_{2r} \\ \vdots & \vdots & \ddots & \vdots \\ v_{r1} & v_{r2} & \cdots & v_{rr} \end{vmatrix} \neq 0. \quad (103)$$

Since the state of the system is specified by P values of temperature, P values of pressure and $P \times (n-1)$ mole fractions, $P \times (n+1)$ variables must be specified to describe the system. But, there are $(P-1)$ equalities of temperature, $(P-1)$ equalities of pressure, $n \times (P-1)$ equalities of chemical potential of the n species between the P phases and r conditions of chemical reaction equilibrium shown in equation (104).

$$\sum_{j=1}^n v_{jk} \mu_j = 0 \quad k = 1, 2, \cdots, r \quad (104)$$

Thus, the total number of equations between the variables is $(n+2) \times (P-1) + r$. And, in terms of Gibbs' phase rule, the degrees of freedom are $n - r + 2 - P$.

Making the same analysis of a system in which no reaction occurs, the degrees of freedom are found to be $c + 2 - P$ where c is the number of components. By comparison of the two expressions, it is seen that $c = n - r$. In addition, Denbigh (18) has shown that in a reacting system, $n - r$ is the minimum number of substances which must be available in the laboratory to prepare the system. So, the number of components is:

$$c \equiv n - r. \quad (105)$$

For this study, then, the components will refer to the various substances weighed out in the laboratory to prepare the system and the species will refer to the entities present in solution after equilibrium is attained. The monomer of a component will refer to that species containing one molecule of the component.

Call the r species which initially are absent the basic species. They are formed upon mixing components whose monomers may be the residual $n - r$ species or only some of these as is the case when some components are inert. Designate the number of moles of components initially present by $M_1, \dots, M_{n-r}$. The moles of species existing at any time will be taken as $\tilde{m}_1, \dots, \tilde{m}_r$ for the basic species and $m_1, \dots, m_{n-r}$ for the remaining species.

As a result of the k -th reaction, the masses of species are changed according to the equation:

$$\frac{\Delta m_{k1}}{v_{k1}} = \frac{\Delta m_{k2}}{v_{k2}} = \dots = \frac{\Delta m_{kr}}{v_{kr}} = \delta_k \quad (106)$$

$$k = 1, \dots, r$$

where Δm_{kj} is the change in numbers of moles of the j -th species due to the k -th reaction. The total change in the number of moles of the j -th species is then

$$\Delta m_j = \sum_{k=1}^r v_{kj} \delta_k \quad j = 1, 2, \dots, n. \quad (107)$$

The number of moles of the j -th basic species is

$$\tilde{m}_j = \sum_{k=1}^r v_{kj} \delta_k \quad j = 1, 2, \dots, n. \quad (108)$$

and the number of moles of the remaining $n-r$ species is

$$M_j = m_j - \sum_{k=1}^r v_{kj} \delta_k \quad j = 1, 2, \dots, n-r. \quad (109)$$

Solution of equation (108) for δ_k yields:

$$\delta_k = \frac{\sum_{j=1}^r A_{kj} \tilde{m}_j}{G} \quad k = 1, 2, \dots, r \quad (110)$$

where A_{kj} is the algebraic complement of the element v_{kj} in the G determinant. Substitution of equation (110) into equation (107) gives:

$$M_j = m_j - \sum_{k=1}^r \alpha_{jk} \tilde{m}_k \quad j = 1, 2, \dots, n-r \quad (111)$$

where

$$\alpha_{jk} = \frac{\sum_{i=1}^r v_{ij} A_{ik}}{G} . \quad (112)$$

For the $n-r$ nonbasic species, $m_j = 0$ (There was non originally present.) and

$$m_j = - \sum_{k=1}^r \alpha_{jk} \tilde{m}_k \quad j = 1, 2, \dots, n-r \quad (113)$$

The mole fraction of the j -th component is defined as

$$x_j = \frac{M_j}{\sum_{j=1}^{n-r} M_j} \quad j = 1, 2, \dots, n-r \quad (114)$$

and the mole fraction of the k -th species as

$$x_j \equiv \frac{m_j}{\sum_{j=1}^n m_j} \quad j = 1, 2, \dots, n. \quad (115)$$

Equations (111), (114) and (115) can be solved simultaneously to yield:

$$x_j = \frac{x_j - \sum_{k=1}^r \alpha_{jk} \tilde{x}_k}{\sum_{j=1}^{n-r} \left(x_j - \sum_{k=1}^r \alpha_{jk} \tilde{x}_k \right)} \quad j = 1, 2, \dots, n-r \quad (116)$$

Again, the $\tilde{}$ indicates a basic species.

Nikol'skii (52) has shown that the activity of a component is equal to the activity of its monomer. Further, if the phase of interest is liquid and if the vapor above it can be regarded as an ideal gas mixture with no association occurring in it, then

$$A_j^c = A_j^n = \frac{p_j}{p_{j0}} \quad j = 1, 2, \dots, n-r \quad (117)$$

where the superscripts c and n indicate component and species respectively. The quantities p_j and p_{j0} are, respectively, the partial pressure of the j-th species above the mixture and above the pure component in its standard state. Since the gas mixture in equilibrium

with the liquid is assumed ideal, the activity of the j -th component relative to the pure component standard state is:

$$A_j^C = \frac{x_j p_j^n}{p_j^C} \quad j = 1, 2, \dots, n-r \quad (118)$$

where p_j^C is the vapor pressure of the pure j -th component and p_j^n that of the pure j -th monomer. The ratio, p_j^n/p_j^C , can be calculated from the fact that $A_j^C = 1$ when $x_j = 1$. Thus,

$$\frac{p_j^n}{p_j^C} = \frac{1}{x_{j0}} \quad (119)$$

where x_{j0} is the mole fraction of the j -th monomer at the standard state. The activity now can be written as:

$$A_j^C = \frac{x_j}{x_{j0}} \quad j = 1, 2, \dots, n-r \quad (120)$$

In addition to the above composition relations, there are the conditions of equilibrium:

$$K_k = \prod_{j=1}^n (x_j)^{v_{kj}} \quad k = 1, 2, \dots, r \quad (121)$$

where K_k is the equilibrium constant of the k -th reaction. This equilibrium constant varies with temperature according to the well-known van't Hoff equation:

$$\frac{\partial \ln K_k}{\partial \left(\frac{1}{T}\right)} = - \frac{\Delta H_{rk}}{R} \quad k = 1, 2, \dots, r. \quad (122)$$

The quantity ΔH_{rk} is the standard enthalpy change due to the k -th reaction. It will, in general, be a function of temperature, but usually this dependence is not great.

Another quantity which will prove useful is defined by the following equation:

$$x_j^0 = \frac{c_j}{n-r + \sum_{k=1}^r c_k} \quad j = 1, 2, \dots, n \quad (123)$$

where c_j is the concentration (moles/liter) of the j -th species and C_i that of the i -th component. This expression can be rewritten in terms of known quantities as:

$$x_j^0 = \frac{x_j}{\sum_{i=1}^{n-r} x_i - \sum_{i=1}^{n-r} \sum_{k=1}^r \alpha_{ik} x_k} \quad (124)$$

$$j = 1, 2, \dots, n.$$

The $n-r$ conditions of equation (116) and the r conditions of equation (121) permit the mole fractions of all n species to be determined as a function of the equilibrium constants and mole fractions of the components.

Then, via equation (120) the activities of the components can be related to the same quantities. The resulting expression for A_j^C can be used to calculate vapor pressures of associated solutions by assigning appropriate values to K_k . Alternately, K_k can be determined by finding the value such that equation (120) best fits the available activity data.

THEORY

Concentration Dependence of Diffusivities-- Associated Systems

There is evidence which indicates that equation (90) is valid in the case of metallic solid solutions (16, 59, 60) where movement of simple atoms is involved. However, data for associated liquid solutions have conflicted with this equation. The works of Babb and co-workers (32), Carman and Miller (12) and Hammond and Stokes (31) all indicate the conflict. These investigators gave the probable explanation when they pointed out that associated liquids can form hydrogen-bonded clusters and diffusion may involve movement of these clusters.

Further, they noted that the thermodynamic factor in equation (90) always over-corrects when applied to associated systems. In other words, positive deviations from Raoult's law corresponding to $\frac{\partial \ln A_A}{\partial \ln X_A} < 1$ lead to calculated values of D_{AB} which are too small and negative deviations corresponding to $\frac{\partial \ln A_A}{\partial \ln X_A} > 1$ lead to values which

are too large. Positive deviations can be correlated with a tendency to form clusters of one type of molecule and negative deviations suggest clusters consisting of different types of molecules. According to the chemical model, these clusters are in equilibrium and the concentration of each species can be calculated. Therefore, it is possible, in principle, to modify the derivation of equation (90) to take the association into account (1). In reality, the equations of the chemical model are not analytically soluble when clusters of five or more molecules exist in solution. The only readily soluble cases are for simple clusters of two molecules.

Three of these relatively simple types of association will be discussed below. The tracer diffusivity expressions for these three cases have been independently developed over the last three years by the author. However, Stokes (63) derived similar equations for type (a) and more recently, Carman (10, 11) published diffusion expressions for both types (a) and (b).

Type (a) A binary mixture of A and B where component A associates to form a dimer cluster and component B is inert.

Thermodynamic Relations--For this case, the following quantities can be specified by inspection:

$$c = 2, \quad (125)$$

$$r = 1, \quad (126)$$

$$n = 3 \quad (127)$$

$$v_{11} = -2 \quad (128)$$

$$\tilde{v}_{11} = 1 \quad (129)$$

and

$$v_{12} = 0. \quad (130)$$

Specification of these quantities permits equations (116), (120), (121) and (124) to be solved for the mole fractions of the species and the activities. The following equations result:

$$K = \frac{x_{11}}{x_1^2}, \quad (131)$$

$$x_1 = \frac{2X_A}{1+Y}, \quad (132)$$

$$x_2 = 1 - \frac{2X_A}{1+Y} - \frac{4KX_A^2}{(1+Y)^2}, \quad (133)$$

$$\tilde{x}_{11} = \frac{4KX_A^2}{(1+Y)^2}, \quad (134)$$

$$x_1^0 = \frac{2X_A (1+Y)}{(1+Y)^2 + 4KX_A^2}, \quad (135)$$

$$x_2^O = 1 - \frac{2X_A (1+Y)}{(1+Y)^2 + 4KX_A^2} \quad , \quad (136)$$

$$\tilde{x}_{11}^O = \frac{4KX_A}{(1+Y)^2 + 4KX_A^2} \quad , \quad (137)$$

$$A_A^C = \frac{X_A (1 + [1+4K]^{1/2})}{1+Y} \quad (138)$$

and

$$A_B^C = 1 - \frac{2X_A}{1+Y} - \frac{4KX_A^2}{(1+Y)^2} \quad (139)$$

where

$$Y = \left(1 - 4KX_A (X_A - Z) \right)^{1/2} \quad (140)$$

It is now possible to differentiate equation (138) to obtain:

$$\frac{\partial \ln A_A^C}{\partial \ln X_A} = \frac{1 + \frac{4KX_A}{1+Y}}{Y} \quad (141)$$

Differentiation of equation (139) with respect to X_B and comparison of the result with equation (141) demonstrates that $\frac{\partial \ln A_A^C}{\partial \ln X_A} = \frac{\partial \ln A_B^C}{\partial \ln X_B}$ as required by the Gibbs-Duhem relation.

Diffusion Relations--Recall that the total flux of a component is calculated by adding the effects of intrinsic diffusion and bulk motion. For component A,

the total flux is the sum of the contributions resulting from diffusion of monomers, dimers and bulk motion. That is,

$$J_{AV} = J_{1m} + 2\tilde{J}_{11m} + C_A \left(\bar{v}_{VC} - \bar{v}_{mC} \right) \quad (142)$$

where in this case J_{1m} and $\tilde{J}_{11m}$ are the intrinsic fluxes of monomers and dimers, respectively, and

$$\bar{v}_{VC} - \bar{v}_{mV} = - \left(J_{1m} \bar{v}_1 + J_{2m} \bar{v}_2 + \tilde{J}_{11m} \bar{v}_{11} \right). \quad (143)$$

As before,

$$J_{im} = - D_{im} \frac{\partial C_i}{\partial z} \quad (144)$$

and

$$J_{AV} = - D_{AB} \frac{\partial C_A}{\partial z}. \quad (145)$$

Now, by substituting equation (143), (144) and (145) into equation (142) and solving for the mutual diffusion coefficient, one obtains:

$$D_{AB} = D_{1m} \frac{\partial c_1}{\partial C_A} + 2 \tilde{D}_{11m} \frac{\partial \tilde{c}_{11}}{\partial C_A} - C_A \left(\bar{v}_1 D_{1m} \frac{\partial c_1}{\partial C_A} + \right. \\ \left. \tilde{v}_{11} \tilde{D}_{11m} \frac{\partial c_{11}}{\partial C_A} + \bar{v}_2 D_{2m} \frac{\partial c_2}{\partial C_A} \right). \quad (146)$$

The molar volume of the dimer, $\tilde{V}_{11}$, is assumed to be:

$$\tilde{V}_{11} = 2\bar{V}_A. \quad (147)$$

Substitution of equation (147) into equation (146) followed by rearrangement of terms yields:

$$D_{AB} = \left(D_{1m} \frac{\partial c_1}{\partial C_A} + 2\tilde{D}_{11m} \frac{\partial \tilde{c}_{11}}{\partial C_A} \right) \left(1 - C_A \bar{V}_A \right) + D_{2m} \frac{\partial c_2}{\partial C_A} C_A \bar{V}_B. \quad (148)$$

Now, the two relations, $C_A \bar{V}_A + C_B \bar{V}_B = 1$ and $dC_A/dC_B = -\bar{V}_B/\bar{V}_A$, are used to reduce equation (148) to:

$$D_{AB} = \left(D_{1m} \frac{\partial c_1}{\partial C_A} + 2\tilde{D}_{11m} \frac{\partial \tilde{c}_{11}}{\partial C_A} \right) C_B \bar{V}_B + D_{2m} \frac{\partial c_2}{\partial C_A} C_A \bar{V}_A. \quad (149)$$

Equation (17) is now combined with (149) to give:

$$D_{AB} = \frac{kT}{\eta} \left[\left(\frac{c_1}{\tilde{f}_1 C_A} \frac{\partial \ln x_1}{\partial \ln X_A} + \frac{2\tilde{c}_{11}}{\tilde{f}_{11} C_A} \frac{\partial \ln \tilde{x}_{11}}{\partial \ln X_A} \right) X_B + \frac{1}{\tilde{f}_2} \frac{\partial \ln x_2}{\partial \ln X_B} X_A \right]. \quad (150)$$

By differentiating equation (131) to get:

$$\frac{\partial \ln x_{11}}{\partial \ln X_A} = 2 \frac{\partial \ln x_1}{\partial \ln X_A} \quad (151)$$

and by using equation (120) in conjunction with the Gibbs-Duhem relation to give

$$\frac{\partial \ln x_1}{\partial \ln X_A} = \frac{\partial \ln A_A^C}{\partial \ln X_A} = \frac{\partial \ln A_B^C}{\partial \ln X_B} = \frac{\partial \ln x_2}{\partial \ln X_B}, \quad (152)$$

equation (150) may be written as:

$$D_{AB} = \frac{kT}{\eta} \left[\left(\frac{c_1}{f_1 c_A} + \frac{4\tilde{c}_{11}}{\tilde{f}_{11} c_A} \right) x_B + \frac{1}{f_2} x_A \right] \frac{\partial \ln A_A^C}{\partial \ln X_A}. \quad (153)$$

For ease of computation, it is useful to define psuedo mole fractions by equation (123). Thus, the final result is:

$$D_{AB} = \frac{kT}{\eta} \left[\left(\frac{x_1^o}{f_1} + \frac{4\tilde{x}_{11}^o}{\tilde{f}_{11}} \right) \frac{x_B}{x_A} + \frac{x_A}{f_2} \right] \frac{\partial \ln A_A^C}{\partial \ln X_A} \quad (154)$$

as first derived by Anderson (1).

Tracer diffusion is concerned with the flux of labelled molecules of one particular component. Therefore, there will be a mixture of dimer clusters containing one and two labels in addition to the labelled monomers. The total concentration of labelled A molecules is given by:

$$C_A^* = c_1^* + \tilde{c}_{11}^* + 2\tilde{c}_{11}^{**}. \quad (155)$$

Since there is no bulk flow in the case of tracer diffusion, an expression for the flux of labelled A molecules is obtained by adding the fluxes of the various labelled species:

$$J_A^* = J_{1m}^* + \tilde{J}_{1m}^* + 2\tilde{J}_{11m}^{**} \quad (156)$$

and as before,

$$D_A^* = D_{1m}^* \frac{\partial c_1^*}{\partial C_A^*} + \tilde{D}_{11m}^* \frac{\partial \tilde{c}_{11}^*}{\partial C_A^*} + 2\tilde{D}_{11m}^{**} \frac{\partial \tilde{c}_{11}^{**}}{\partial C_A^*}. \quad (157)$$

Assuming that a dimer containing two labelled molecules has the same friction coefficient as one containing one labelled molecule, $\tilde{D}_{11m}^{**} = \tilde{D}_{11m}^*$ and equation (157) becomes:

$$D_A^* = D_{1m}^* \frac{\partial c_1^*}{\partial C_A^*} + \tilde{D}_{11m}^* \left(\frac{\partial \tilde{c}_{11}^*}{\partial C_A^*} + 2 \frac{\partial \tilde{c}_{11}^{**}}{\partial C_A^*} \right). \quad (158)$$

From equation (155),

$$\frac{\partial \tilde{c}_{11}^*}{\partial C_A^*} + 2 \frac{\partial \tilde{c}_{11}^{**}}{\partial C_A^*} = 1 - \frac{\partial c_1^*}{\partial C_A^*} \quad (159)$$

so that:

$$D_A^* = \left(D_{1m}^* - \tilde{D}_{11m}^* \right) \frac{\partial c_1^*}{\partial C_A^*} + \tilde{D}_{11m}^* \quad (160)$$

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It is now assumed that the labelled A molecules are distributed such that the ratio of members of labelled monomers to the number of labelled A molecules will equal the ratio of the total number of monomers to the total number of A molecules. Of course, this is not an assumption if the labelled molecules are identical to the unlabelled molecules. In terms of concentrations, this equality is:

$$\frac{c_1^*}{C_A^*} = \frac{c_1}{C_A} . \quad (161)$$

Since the concentration is uniform throughout the solution, it is apparent that the latter ratio is constant. So,

$$\frac{\partial c_1^*}{\partial C_A} = \frac{c_1}{C_A} . \quad (162)$$

Equation (160) can now be written as:

$$D_A^* = \left(D_{1m}^* - \tilde{D}_{11m}^* \right) \frac{x_1^0}{X_A} + \tilde{D}_{11m}^* \quad (163)$$

when x_1^0 is defined by equation (123). Recalling that

$$D_{im}^* = \frac{kT}{\eta f_i} , \quad (79)$$

the final result is:

$$D_A^* = \frac{kT}{\eta} \left[\left(\frac{1}{\tilde{f}_1} - \frac{1}{\tilde{f}_{11}} \right) \frac{x_1^0}{x_A} + \frac{1}{\tilde{f}_{11}} \right] . \quad (164)$$

The inert component, B, diffuses only as monomers so one can write simply:

$$J_B^* = J_{2m}^* \quad (165)$$

from which

$$D_B^* = \frac{kT}{\eta} \frac{1}{\tilde{f}_2} . \quad (166)$$

A relatively simple relation between the tracer and mutual diffusion coefficients can be obtained by combining equations (154), (164), and (166). This relation is:

$$D_{AB} = \left[x_A D_B^* + x_B D_A^* + 2 \frac{kT}{\eta} \frac{x_{11}^0}{\tilde{f}_{11}} \frac{x_B}{x_A} \right] \frac{\partial \ln A_A^C}{\partial \ln x_A} . \quad (167)$$

Stokes (63) and later Carman (10, 11) derived equations very similar to this equation.

Type (b) A binary mixture of A and B where A associates with B to form bimolecular clusters.

Thermodynamic Relations--The principles involved in Type (b) are the same as in Type (a). To avoid needless repetition, many equations will be presented without

detailed explanation. The following quantities are the same as Type (a):

$$c = 2, \quad (168)$$

$$\text{and } r = 1, \quad (169)$$

$$n = 3. \quad (170)$$

But, the stoichiometric coefficients for Type (b) are:

$$v_{11} = -1, \quad (171)$$

$$\text{and } \tilde{v}_{11} = 1, \quad (172)$$

$$v_{12} = -1. \quad (173)$$

The equations of the chemical model can now be solved to get:

$$K = \frac{\tilde{x}_{12}}{x_1 x_2}, \quad (174)$$

$$x_1 = \frac{X_A - X_B + Z}{1 + Z}, \quad (175)$$

$$x_2 = \frac{X_B - X_A + Z}{1 + Z}, \quad (176)$$

$$\tilde{x}_{12} = \frac{1 - Z}{1 + Z}, \quad (177)$$

$$x_1^O = x_A - \frac{1 - z}{2} , \quad (178)$$

$$x_2^O = x_B - \frac{1 - z}{2} , \quad (179)$$

$$x_{12}^O = \frac{1 - z}{2} , \quad (180)$$

$$A_A^C = \frac{x_A - x_B + z}{1 + z} \quad (181)$$

and

$$A_B^C = \frac{x_B - x_A + z}{1 + z} \quad (182)$$

where

$$z = \left(1 - \frac{4Kx_A x_B}{K + 1} \right)^{1/2} . \quad (183)$$

Also, the following equation can be derived from equation (134):

$$\frac{\partial \ln A_A^C}{\partial \ln x_A} = \frac{1}{z} . \quad (184)$$

Equations (181) and (182) can be shown, by direct differentiation, to satisfy the Gibbs-Duhem relation.

Diffusion Relations--The total flux of component A is given by:

$$J_{AV} = J_{1m} + \tilde{J}_{12m} + c_A \left(\bar{v}_{VC} - \bar{v}_{mC} \right) \quad (185)$$

where J_{1m} and $\tilde{J}_{12m}$ are the intrinsic fluxes of the monomer and cluster, respectively, and

$$\bar{v}_{VC} - \bar{v}_{mC} = \bar{v}_1 J_{1m} + \left(\bar{v}_1 + \bar{v}_2 \right) \tilde{J}_{12m} + \bar{v}_2 J_{2m}. \quad (186)$$

The partial molar volume of the cluster has been approximated by:

$$\tilde{\bar{v}}_{12} \cong \bar{v}_1 + \bar{v}_2. \quad (187)$$

Proceeding by the same steps presented in Type (2), the mutual diffusion coefficient is found to be:

$$D_{AB} = \frac{kT}{\eta} \left[\frac{1}{\tilde{f}_1} \frac{x_1^0}{\bar{x}_A} x_B + \frac{1}{\tilde{f}_2} \frac{x_2^0}{\bar{x}_B} x_A + \right. \quad (188)$$

$$\left. \frac{1}{\tilde{f}_{12}} \frac{\tilde{x}_{12}}{\bar{x}_A \bar{x}_B} \left(x_B - x_A \right)^2 \right] \frac{\partial \ln A_A^C}{\partial \ln \bar{x}_A}.$$

Again, Anderson (1) was the first to derive this equation.

Tracer diffusion in this case is less complicated than in Type (a) because the dimer can carry only one label. Thus the total concentration of labelled A molecules is:

$$C_A^* = C_1^* + \tilde{c}_{12}^* \quad (189)$$

and the flux of these molecules is simply:

$$J_A^* = J_{lm}^* + \tilde{J}_{12}^*. \quad (190)$$

Again, the final result follows immediately by the process discussed for the Type (a) associated system:

$$D_A^* = \frac{kT}{\eta} \left[\left(\frac{1}{\tilde{f}_1} - \frac{1}{\tilde{f}_{12}} \right) \frac{x_1^0}{X_A} + \frac{1}{\tilde{f}_{12}} \right]. \quad (191)$$

The same process applied to component B yields:

$$D_B^* = \frac{kT}{\eta} \left[\left(\frac{1}{\tilde{f}_2} - \frac{1}{\tilde{f}_{12}} \right) \frac{x_2^0}{X_B} + \frac{1}{\tilde{f}_{12}} \right]. \quad (192)$$

Combination of equations (188), (191) and (192) gives:

$$D_{AB} = \left[X_A D_B^* + X_B D_A^* - 2 \frac{kT}{\eta} \frac{x_{12}^0}{\tilde{f}_{12}} \right] \frac{\partial \ln A_A^C}{\partial \ln X_A} \quad (193)$$

as also derived by Carman (10, 11).

Type (c) A ternary mixture of A, B and C where A associates with B and C is inert.

Thermodynamic Relations--Here there are three components, four species and one reaction. So,

$$c = 3, \quad (194)$$

$$n = 4, \quad (195)$$

$$r = 1, \quad (196)$$

$$v_{11} = -1, \quad (197)$$

$$\tilde{v}_{11} = 1 \quad (198)$$

$$v_{12} = -1 \quad (199)$$

and $v_{13} = 0. \quad (200)$

These conditions combined with equations (116), (120), (121) and (124) of the chemical model yield:

$$K = \frac{\tilde{x}_{12}}{x_1 x_2}, \quad (201)$$

$$x_1 = \frac{x_Z - x_B - \frac{x_C}{K+1} + U}{1 + \frac{Kx_C}{K+1} + U}, \quad (202)$$

$$x_2 = \frac{x_B - x_A - \frac{x_C}{K+1} + U}{1 + \frac{Kx_C}{K+1} + U}, \quad (203)$$

$$\tilde{x}_{12} = \frac{1 - 2x_C + \frac{x_C}{K+1} - U}{1 + \frac{Kx_C}{K+1} + U}, \quad (204)$$

$$x_3 = \frac{2x_C}{1 + \frac{Kx_C}{K+1} + U}, \quad (205)$$

$$x_1^O = x_A - \frac{1 - \frac{Kx_C}{K+1} - U}{2}, \quad (206)$$

$$x_2^O = x_B - \frac{1 - \frac{Kx_C}{K+1} - U}{2}, \quad (207)$$

$$\tilde{x}_{12} = \frac{1 - \frac{Kx_C}{K+1} - U}{2}, \quad (208)$$

$$x_3^C = x_C \quad (209)$$

$$A_A^C = \frac{x_A - x_B - \frac{x_C}{K+1} + U}{1 + \frac{Kx_C}{K+1} + U}, \quad (210)$$

$$A_B^C = \frac{x_B - x_A - \frac{x_C}{K+1} + U}{1 + \frac{Kx_C}{K+1} + U} \quad (211)$$

and

$$A_C^C = \frac{2x_C}{1 + \frac{Kx_C}{K+1} + U} \quad (212)$$

where

$$U = \left(1 - \frac{2Kx_C}{K+1} + \frac{K^2x_C^2}{(K+1)^2} - \frac{4Kx_Ax_B}{K+1} \right)^{1/2}. \quad (213)$$

Diffusion Relations--Recall that simple flow equations, such as equation (2), are not applicable to mutual diffusion in ternary systems. But, since there

are no concentration gradients of components in tracer diffusion, a single tracer diffusion coefficient still suffices to describe the process. Then, the intrinsic diffusion model can be applied to describe tracer diffusion as before.

In fact, the addition of the third inert component to a Type (b) associating system does not change the diffusion equations from the form of those in the previous case (Type [b]). The flux of labelled A molecules is still:

$$J_A^* = J_{1m}^* + \tilde{J}_{12m}^* \quad (214)$$

and the flux of labelled B and C molecules is:

$$J_B^* = J_{2m}^* + \tilde{J}_{12m}^* \quad (215)$$

and

$$J_C^* = J_{3m}^* \quad (216)$$

The counterpart of equation (76) for this ternary system is:

$$C_i^* = \frac{X_i^*}{X_A \bar{V}_A + X_B \bar{V}_B + X_C \bar{V}_C} \quad (217)$$

where the denominator is again independent of X_i^* . Hence,

$\frac{\partial \ln A_i^*}{\partial \ln C_i^*} = 1$ and equation (79) is valid as before.

Equations (214), (215) and (216) can now be simplified to:

$$D_A^* = \frac{kT}{\eta} \left[\left(\frac{1}{\tilde{f}_1} - \frac{1}{\tilde{f}_{12}} \right) \frac{x_1^0}{X_A} + \frac{1}{\tilde{f}_{12}} \right] \quad (218)$$

$$D_B^* = \frac{kT}{\eta} \left[\left(\frac{1}{\tilde{f}_2} - \frac{1}{\tilde{f}_{12}} \right) \frac{x_2^0}{X_B} + \frac{1}{\tilde{f}_{12}} \right] \quad (219)$$

and

$$D_C^* = \frac{kT}{\eta \tilde{f}_3} . \quad (220)$$

Although the form of these equations is the same as their counterparts in Type (b) [equations (191) and (192)], the composition variables are different because of the presence of the third component.

Selection of Systems

Usually, there are several systems which one might guess to associate in a given way, but few whose activity and spectroscopic data have been reported in the literature. Since these data are required to make firm decisions as to the exact nature of the association, the number of systems suitable for study is greatly reduced. Another factor to be considered is the availability of labelled material. Surprisingly, many common chemicals

are not available from commercial tracer suppliers. Thus, it is frequently a problem to find a system which can be studied. In this section the six systems that were investigated are presented along with evidence of their association behavior.

Chloroform (A) - Carbon Tetrachloride (B) The isothermal vapor-liquid equilibrium data by McGlashan, Prue and Sainsbury (49) coupled with the absence of a temperature effect on the heat of mixing of the system (13) indicates that chloroform - carbon tetrachloride mixtures are nonideal and nonassociative. Krishnaiah, et al. (44) concluded further that the system is regular. By fitting heat of mixing data (13) to equation (101) a value of B was determined with which the thermodynamic factor can be calculated from equation (100) as:

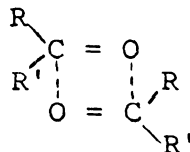
$$\frac{\partial \ln A_A^C}{\partial \ln X_A} = 1. - 0.74 X_A X_B. \quad (221)$$

Benzene (A) - Carbon Tetrachloride (B) Staveley and co-workers (61) report that this system behaves as a regular solution and as such is nonassociative. Lewis and Randall (45) fit the thermodynamic data by Staveley (61) to obtain the B factor in equation (101). Using their value:

$$\frac{\partial \ln A_A^C}{\partial \ln X_A} = 1. - 0.23 X_A X_B \quad (222)$$

Methyl Ethyl Ketone (A) - Carbon Tetrachloride (B)

Affsprung and co-workers (46) investigated self-association of ketones in carbon tetrachloride. Their results indicate that methyl ethyl ketone dimerizes in carbon tetrachloride. They proposed that the dimers are formed by dipole-dipole interactions of the type shown below.



Such antiparalled arrangements are feasible as long as the groups R and R' are small enough to permit the close approach of the two carbonyl groups. Such is the case for methyl ethyl ketone. This system is an example of a Type (a) associated system.

Equations (138) and (139) were fitted to the experimental activity data of Fowler and Norris (29) by finding the value of K which gave the best fit. A non-linear least square computer program was used to accomplish this task. The best value of K was found to be 5.62 which agrees closely with the value of 5.60 found by Anderson (1). Figure 1 is a plot which compares the results of equations (138) and (139) to the data. It can be seen that the equations predict the data very well.

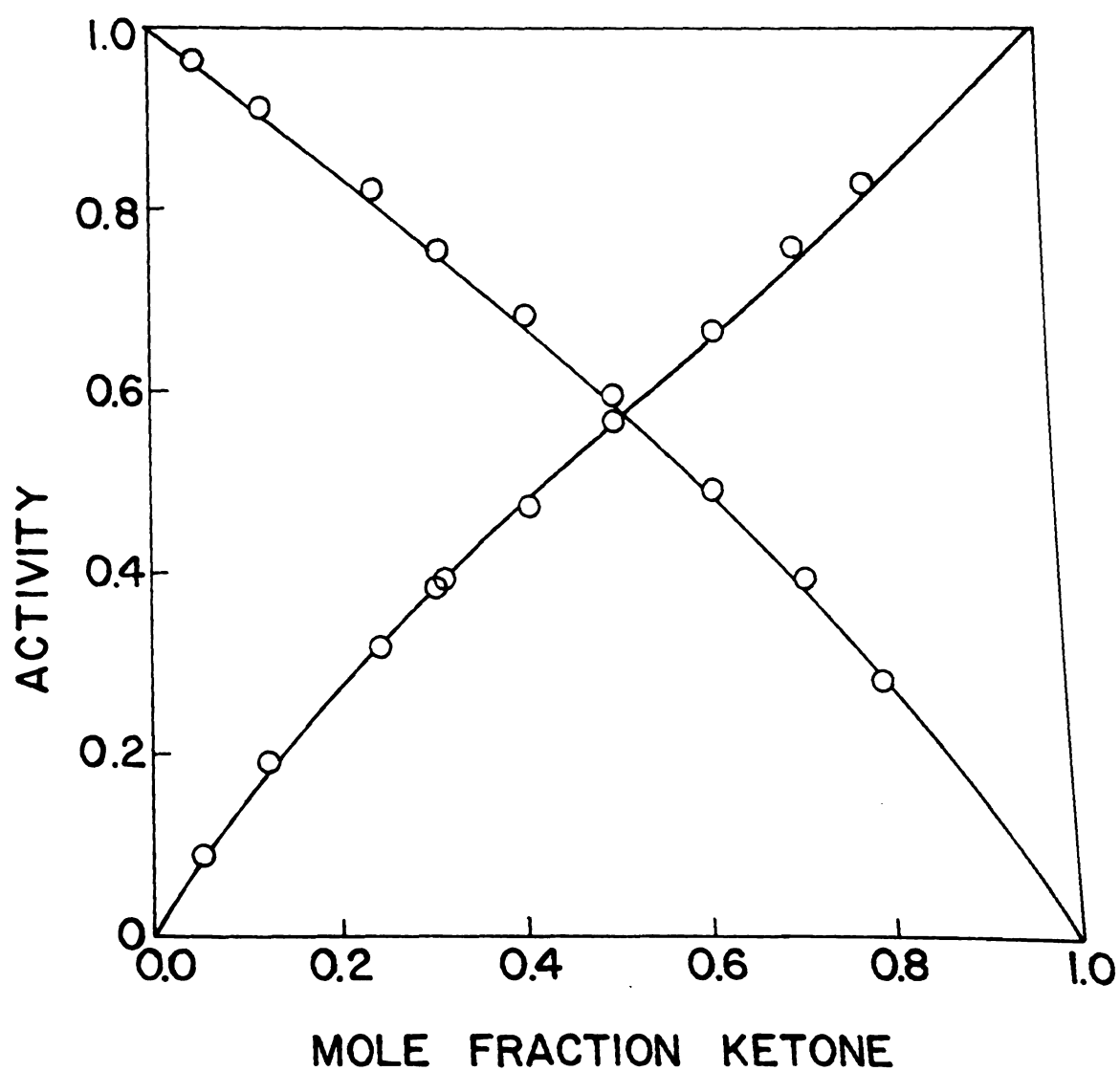
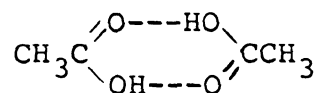


Figure 1. Activity as a Function of Mole Fraction for the Methyl Ethyl Ketone - Carbon Tetrachloride System. O Data, Reference (29); — Calculated from Equations (138) and (139).

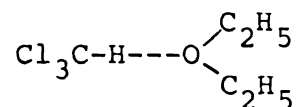
Acetic Acid (A) - Carbon Tetrachloride (B) There is a great deal of evidence which indicates that acetic acid strongly associates in solution. In fact, the association is so pronounced that in solutions concentrated in acetic acid, it "polymerizes" to very large clusters (53). Spectroscopic data of Barrow and Yerger (6) suggest that acetic acid associates to form only dimers when the concentration is below 0.01 mole fraction acetic acid. For these low concentrations, this binary mixture is an example of a Type (a) associated system. A schematic of an acid dimer is shown below.



Barrow (6), Davies (17) and Wenograd (67) determined the dimerization equilibrium constant for acetic acid in dilute solutions. Their values varied from 930 (mole fraction)⁻¹ by Barrow to 55,000 (mole fraction)⁻¹ by Davies. Hence, it is not possible to arrive at a meaningful value for K from the literature. Therefore, the equilibrium constant will be determined later from consideration of the diffusion data.

Ether (A) - Chloroform (B) Lord and co-workers (47) and Gerbier and Gerbier (30) studied this system using I. R. and Raman spectroscopic techniques,

respectively. Both investigations showed that the two components associate to form a bimolecular cluster as shown below.



This system is an example of a Type (b) associated system.

Given this specific association, other physical phenomena can be predicted. Since only total pressure versus composition data are available for this system, it is not possible to determine the equilibrium constant, K , from the activities of each component. But, it is possible to calculate the total pressure of the system by combining equations (99), (181) and (182) to obtain an expression for the total pressure in terms of mole fractions of the components and the equilibrium constant.

$$\pi = p_{\text{A}}^{\text{C}_\text{A}\text{C}} + p_{\text{B}}^{\text{C}_\text{A}\text{C}} \quad (223)$$

The best value of K was determined by fitting this equation to the total pressure data with the computer program shown in Appendix I. It can be seen from Figure 2 that equation (223) predicts the total pressure very well.

TOTAL VAPOR PRESSURE

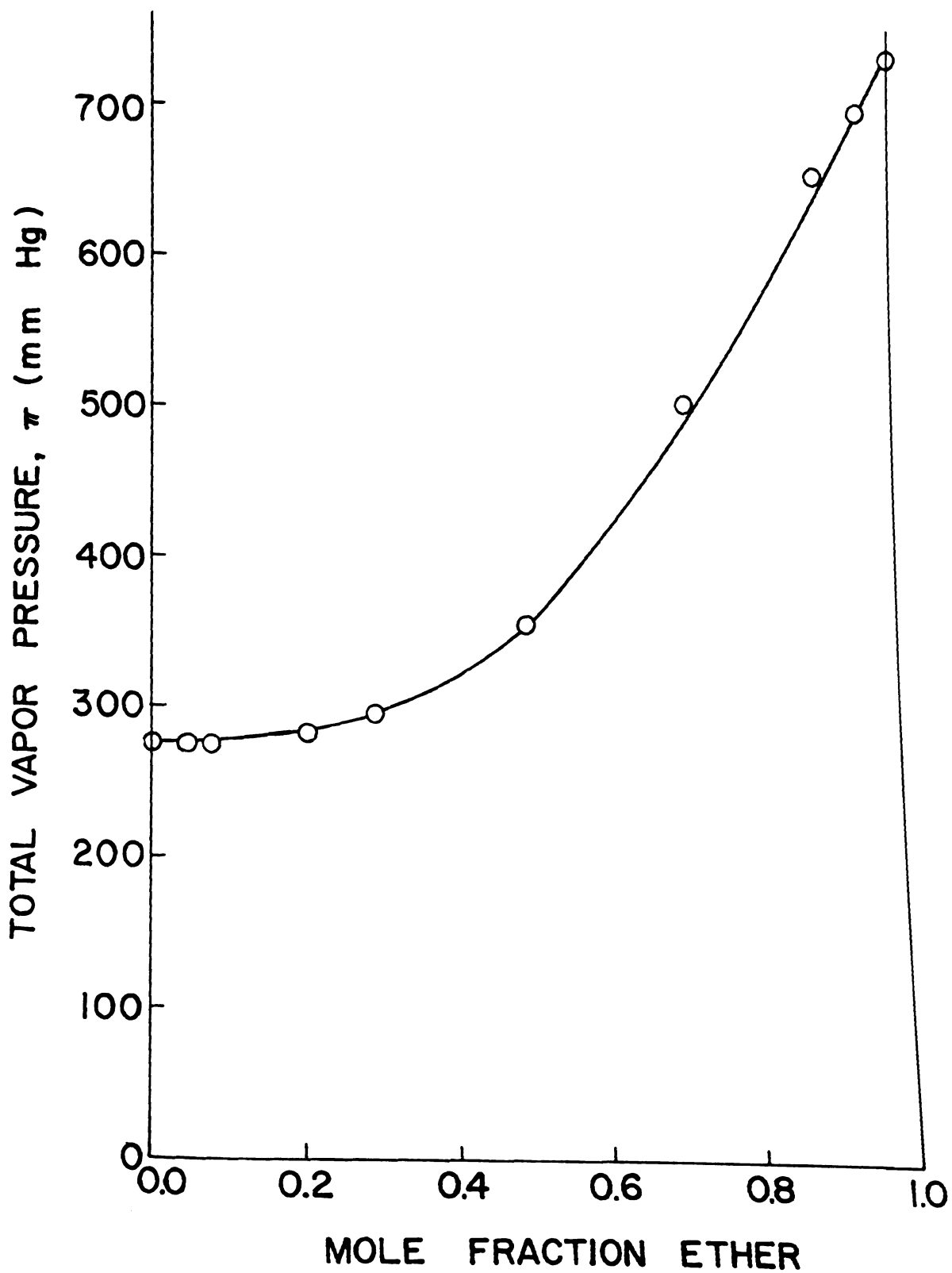


Figure 2. Total Pressure as a Function of Mole Fraction for the Ether - Chloroform System. O Data, Reference (22); — Calculated from Equation (223).

Several investigators (21, 22, 43, 50, 58) determined total pressure data at different temperatures. So, K was determined at various temperatures. Recalling that

$$\frac{\partial \ln K}{\partial (1/T)} = - \frac{\Delta H_R}{R} , \quad (122)$$

it is obvious that a plot of $\ln K$ versus $1/T$ should be a straight line with a slope of $-\frac{\Delta H_R}{R}$. Figure 3 is such a plot. From a least squares fit to the data, it is found that $\Delta H_R = 2.72$ (k cal/mole); a very reasonable hydrogen bond energy. Also from this fit, $K = 2.86$ (mole fraction)⁻¹ at 25°C. This is in fair agreement with the value of 2.73 (mole fraction)⁻¹ suggested by Anderson (1).

Anderson (1) showed that if the three species, ether monomer, chloroform monomer and cluster, mix ideally, the heat of mixing for the mixture is given by:

$$\Delta H_{\text{mix}} = \Delta H_R \tilde{x}_{12}^0. \quad (224)$$

Equation (180) and the value of ΔH_R found above were used with equation (224) to calculate ΔH_{mix} as a function of mole fraction. The results are compared to the data of Hirobe (38) on Figure 4. The agreement between the two is very good.

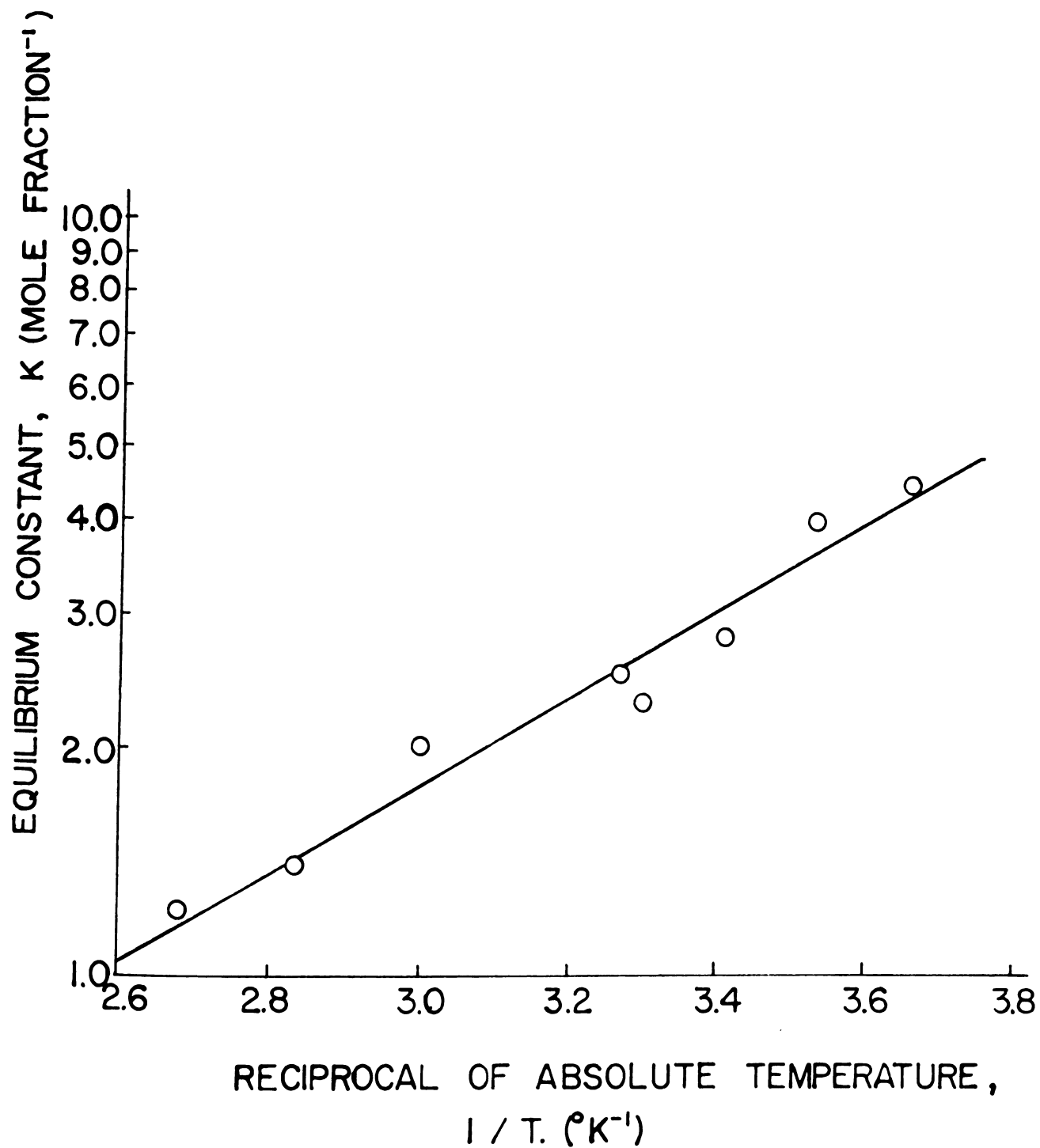


Figure 3. Logarithm K as a Function of $1/T$ for the Ether - Chloroform System. O Calculated from Data, References (21), (22), (43), (50), (58); _____ Least Square fit.

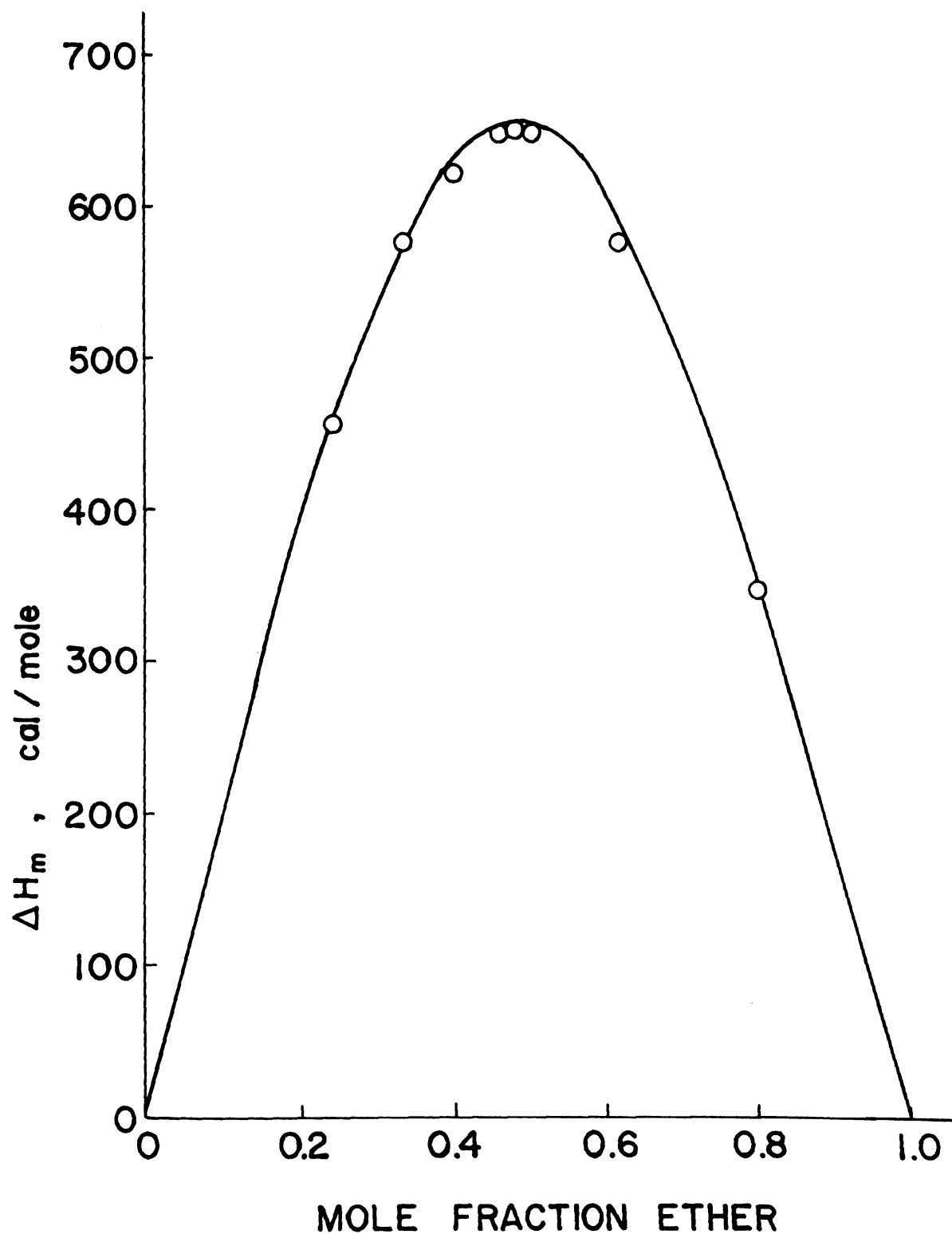


Figure 4. Heat of Mixing as a Function of Mole Fraction for the Ether - Chloroform System. O Data, Reference (38); — Calculated from Equation (224).

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

(C) To the author's knowledge, none of the physico-chemical properties of this system have been studied. However, one can speculate as to the association that should be observed. Notice that this ternary system can be formed by adding carbon tetrachloride to the binary ether-chloroform system. Assuming that the carbon tetrachloride is completely inert, its addition to a binary system should have no effect other than dilution. Then the nature of the ether-chloroform association should be the same as a Type (b) associating system, and the value of the equilibrium constant should not change from the value observed for the ether-chloroform mixtures, $2.86 \text{ (mole fraction)}^{-1}$.

EXPERIMENTAL METHOD

The open-end capillary method for measurement of tracer diffusion coefficients is one of the earliest and most widely used methods (4, 56, 66). The principle of this method is as follows. A capillary of known length, L , closed at one end, is filled with a solution of known concentration. Some of the molecules of one component are labelled with an isotopic form of one of the constituent atoms. The capillary is immersed in a solution of the same chemical concentration but which contains no labelled molecules. The volume of the unlabelled bulk solution is much larger than the labelled capillary solution. Therefore, the concentration of labelled molecules remains essentially zero in the bulk solution as they diffuse from the capillary. Natural convection, caused by slight temperature variations or mechanical vibrations, sweeps the labelled molecules from the neighborhood of the capillary mouth and maintains zero concentration at the mouth.

This process is described mathematically by the following differential equation and boundary conditions:

$$\frac{\partial C_i^*}{\partial \theta} = D_i^* \frac{\partial^2 C_i^*}{\partial z^2} \quad (a)$$

$$\frac{\partial C_i^*}{\partial z} = 0 \text{ at } z = 0, t > 0 \quad (b)$$

(225)

$$C_i^* = \text{at } z = L, t > 0 \quad (c)$$

$$C_i^* = C_{i0}^* \text{ at } \theta = 0, 0 < z < L \quad (d)$$

If measurements are made by the open-end method, there are two sources of error which may affect the diffusion coefficients (56):

- (1) The immersion effect--When a cell is immersed in the unlabelled bulk solution, there occurs a mixing of the capillary solution and the bulk solution, and initial condition (225) (d) is not fulfilled.
- (2) The Δz effect--If the velocity of the convection currents across the capillary mouth is too large, there will be a length, Δz , at the open end of the capillary in which the concentration of labelled molecules is zero. Then boundary condition (225) (c) is not fulfilled.

Cursory experiments with open-end capillaries indicated that the second source of error was very large.

Modified Capillary Cell

To minimize the immersion and Δz effects and to facilitate the radioactive analysis of the cell contents after a diffusion run, a modified capillary cell, shown

in Figure 5, was devised. The cell consisted of a capillary tube, covered at one end with a thin porous glass frit. Diffusion occurred through the pores of the frit but convective transport, and hence, the immersion and Δz effects, were eliminated by the small size of the pores. The other end of the capillary was sealed with a metal foil disk, held in place with a funnel-shaped screw cap. After a diffusion run, the cell contents were analyzed with a standard liquid scintillation technique (55). This method requires the cell contents to be dissolved in a liquid scintillation medium. Therefore, the metal foil seal was punctured with a medical syringe needle and the cell contents flushed, with scintillation liquid, into a counting vial. The funnel-shaped design of the screw cap permitted a liquid seal to be maintained around the syringe needle during the flushing process, thereby preventing loss of capillary contents.

The screw caps were made of Type 304 Stainless Steel, chrome plated for corrosion resistance. A teflon washer was inserted into each cap to insure complete closure of the capillary end.

Disks of 0.001 inch thick metal foil were used to form the seal at the closed end of the capillary. The disks were thin enough to be easily punctured with a medical syringe needle.

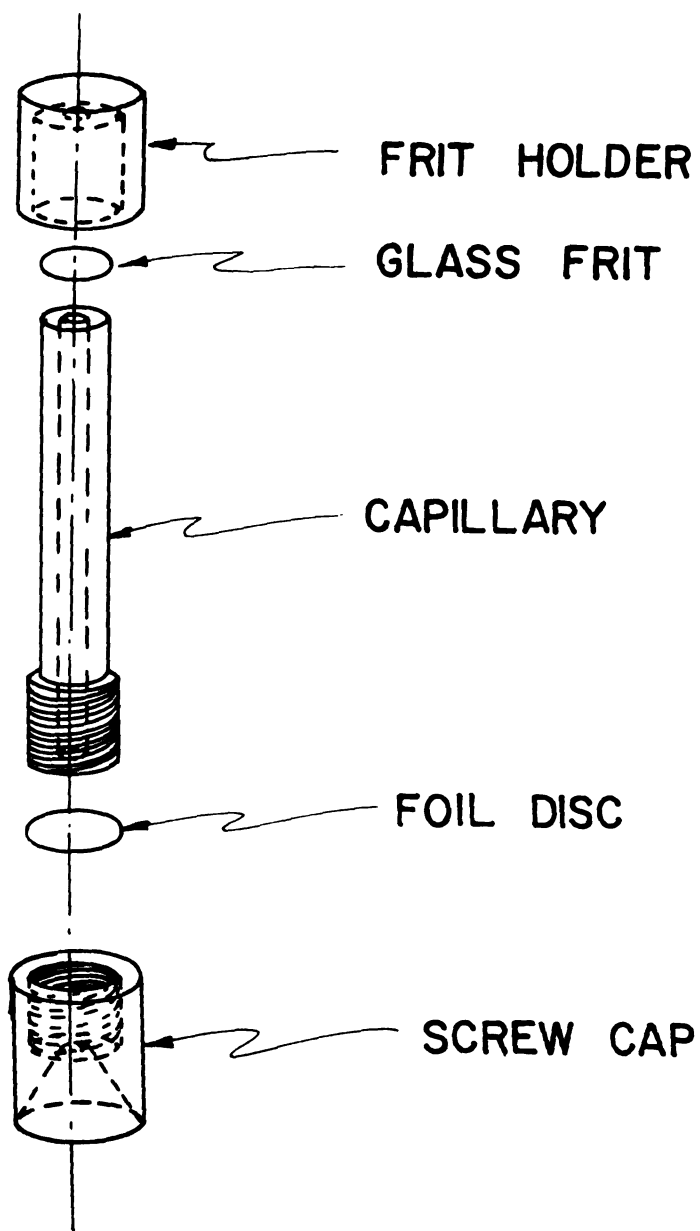


Figure 5. Schematic Diagram of the Modified Capillary Cell.

The capillary tubes were constructed of teflon. The six tubes were machined to 6.78 cm. in length, each having the same length to within 0.1 mm. The bore of each capillary was 0.2 cm. Threads were machined on the capillaries so that they could be screwed into the caps. Each tube was individually numbered.

The glass frits were manufactured by the Kontes Glass Company and were of their "M" porosity. The frits were hand-lapped to a thickness of 0.047 ± 0.004 cm. and numbered to correspond to a capillary tube. In all experiments, cells were assembled using frits and capillaries having corresponding numbers.

The frit holders were made of teflon; machined to fit tightly when pushed over the capillary end. The tapered lip held the frit in place while obstructing the capillary end as little as possible. Six cells of this design were used in this project.

Procedure

Mixtures were made up gravimetrically from the pure components. Bulk solutions were prepared by weighing on a large analytical balance to the nearest 50 milligrams. Approximately 800 cc. of mixture were required to fill the bulk solution containers. Labelled capillary solutions were prepared in 20 cc. screw cap glass vials with metal foil lined lids. The amount of

each component was determined to the nearest tenth of a milligram. An additional foil cap was added to the vials to prevent evaporation during weighing. Solutions were transferred with glass medical syringes by inserting the syringe needle through a pin hole in the foil cap.

Three capillary cells were run simultaneously in the same bulk solution. The tracer diffusion coefficients determined from each cell were averaged and one number reported for the run. A detailed procedure for a run is presented in Appendix II.

The mutual diffusion coefficients were determined with a Mach-Zehnder diffusimeter. The diffusimeter measures the refractive index of the solution in a glass-windowed diffusion cell with an optical interferometer. The instrument was patterned after a similar diffusimeter described by Caldwell, Hall and Babb (8, 9) and was constructed by Bidlack (7). Bidlack presents very complete operation instructions and data analysis procedures, so they will not be discussed here.

A Cannon-Fenske capillary tube viscosimeter was used to determine the viscosity of solutions. It was calibrated with spectro-quality carbon tetrachloride and benzene, following the procedure outlined by Daniels and Alberty (15).

Calculation of Diffusion Coefficients

The large Δz effect noted for the open-end capillaries showed that there were relatively strong convection currents in the bulk solution. Therefore, it is assumed that these currents maintain zero concentration of labelled molecules at the exterior surface of the frit. If the frit is very thin, a quasi steady state concentration distribution is rapidly attained in the frit after diffusion starts. Then the frit can be considered a resistance to diffusion and the following equation describes the process.

$$\frac{\partial C_i^*}{\partial \theta} = D_i^* \frac{\partial^2 C_i^*}{\partial z^2} \quad (a)$$

$$\frac{\partial C_i^*}{\partial z} = 0 \text{ at } z = 0, \theta > 0 \quad (b)$$

(226)

$$-D_i^* \frac{\partial C_i^*}{\partial z} = \frac{1}{R} C_i^* \text{ at } z = L, \theta > 0 \quad (c)$$

$$C_i^* = C_{i0}^* \text{ at } \theta = 0, L > z > 0 \quad (d)$$

where R is the resistance of the frit. The length variable, z , is defined in Figure 6.

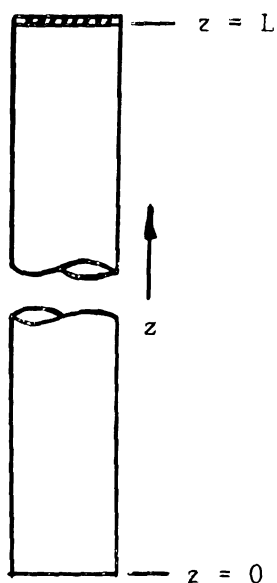


Figure 6. Diffusion Cell Coordinates

The solution of equation (226) follows by separation of variables as shown in Appendix III. The result is:

$$\frac{C_{iavg}^*}{C_{io}^*} = 2 \sum_{n=1}^{\infty} \left[\frac{\sin^2 \beta_n}{\beta_n (\beta_n + \sin \beta_n \cot \beta_n)} \exp \left(- \beta_n^2 \frac{D_{i0}^* \theta}{L^2} \right) \right] \quad (a)$$

where β_n is defined by: (227)

$$\cot \beta_n = \beta_n \frac{RD_1^*}{L} . \quad (b)$$

The term C_{iavg}^* is the average concentration of labelled molecules in the capillary after a time θ .

At first inspection, it seems very difficult to obtain a value of D_i^* from experimentally determined θ , L and C_{iavg}^*/C_{io}^* . However, the problem can be greatly simplified by examination of diffusion in the frit. Transport of material across the frit occurs by ordinary molecular diffusion through the liquid-filled pores. Hence, the resistance of the frit, R , is inversely proportional to the diffusivity, D_i^* . The proportionality constant will be a function of the frit porosity and thickness. As a result, the group RD_i^*/L is independent of D_i^* and is a function of cell geometry only. Now, only the exponential portion of equation (227) (a) contains D_i^* .

A computer program, shown in Appendix IV, was written to calculate C_{iavg}^*/C_{io}^* for various values of $D_i^*\theta/L^2$ and RD_i^*/L . Then, C_{iavg}^*/C_{io}^* was plotted versus $D_i^*\theta/L^2$ for particular RD_i^*/L as shown in Figure 7. Using a value of RD_i^*/L , determined by calibration of the cells, and experimentally determined values of C_{iavg}^*/C_{io}^* , θ and L , D_i^* was obtained from this plot.

Calibration of the Cells

Rathbun and Babb (57) analyzed the results of several investigations and concluded that the tracer diffusion coefficient of pure carbon tetrachloride was 1.32×10^{-5} (cm.²/sec.). The six cells employed in this study were calibrated using this as a standard.

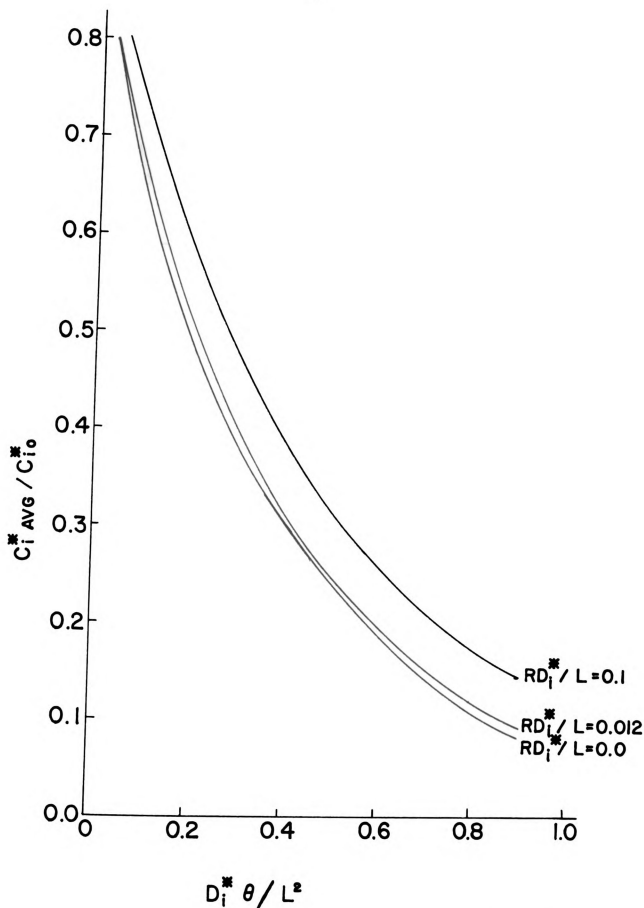


Figure 7. $C_{i \text{ avg}}^* / C_{i0}^*$ as a Function of D_i^* / L^2 and RD_i^* / L .

The cells were calibrated as follows. Values of C_{iavg}^*/C_{io}^* and $D_i^*\theta/L^2$ were calculated for three experimental observations of each cell. Then three values of the cell constant, RD_i^*/L were determined from Figure 7 and averaged for each cell. Table I is a listing of these average cell constants for the six cells.

Table I. Capillary Cell Calibration Results

Cell	$RD_i^*/L^{(a)}$
1	0.012
2	0.014
3	0.011
4	0.014
5	0.013
6	0.010
	0.012 average

(a) average of three determinations

It is apparent from Figure 7 that C_{iavg}^*/C_{io}^* is nearly independent of RD_i^*/L when RD_i^*/L is as small as 0.012. In fact, the $\pm 9\%$ deviation of the cell constants listed in Table I corresponds to only a $\pm 0.7\%$ deviation in D_i^* when $C_{iavg}^*/C_{io}^* = 0.5$. Since this deviation in the diffusion coefficient is not significant, the cell constants of the six cells were averaged and one value, 0.012,

used for all cells. Later, to determine diffusion coefficients, three cells were run simultaneously and the three resulting values of D_1^* were averaged. This process greatly reduces any error caused by using one cell constant for all cells.

Analysis of Radioactive Samples

At the end of a diffusion run, the contents of each capillary were analyzed by a Packard Tri-Carb liquid scintillation spectro-photometer. The scintillation solution consisted of 4 grams of PPO (disphenyl oxazole) and 50 milligrams of POPOP (1, 4 of di 2, 5 phenyl-oxazole benzene) dissolved in 1 liter of toluene as suggested by Price (55).

It is generally assumed that the count rate measured by a counter is proportional to the amount of labelled material present in the sample. However, this assumption is not always a good one. Changes in the chemical composition of the sample can cause varied degrees of absorption (quenching) of the light pulses emitted by the scintillation liquid. Also, some of the older counters give results which are dependent upon the count rate.

To study the effects of quenching, experiments were made on mixtures containing various mole fractions. The count rate from a given quantity of solution (0.15 cc.)

was determined in each case. The results are shown in Figures 8 and 9 for two systems: methyl ethyl ketone - carbon tetrachloride and chloroform - carbon tetrachloride. Carbon tetrachloride was the labelled component in each case. The linear graphs indicate that there is no change in quenching with composition of the capillary solution.

The experiments were then repeated for solutions with $1/2$ the activity in the first experiments. At each mole fraction, the ratio of counts obtained from samples with two different activities remained constant. This demonstrated that the counts from mixtures having different amounts of radioactivity but the same composition were quenched in the same proportion. Hence, the observed count rates were proportional to the concentration of labelled molecules and could be substituted directly into equation (227) to obtain the diffusing coefficients. Based on the results for the above two systems, this conclusion is assumed valid for all the systems of interest.

Except for samples very dilute in tracer, a total of one million counts was recorded for each sample. This reduced the statistical error involved in the count rates to a negligible amount.

Materials

Spectroquality chemicals were used when calibrating the diffusion cells and the viscometer. Analytical reagent grade chemicals were used elsewhere. The

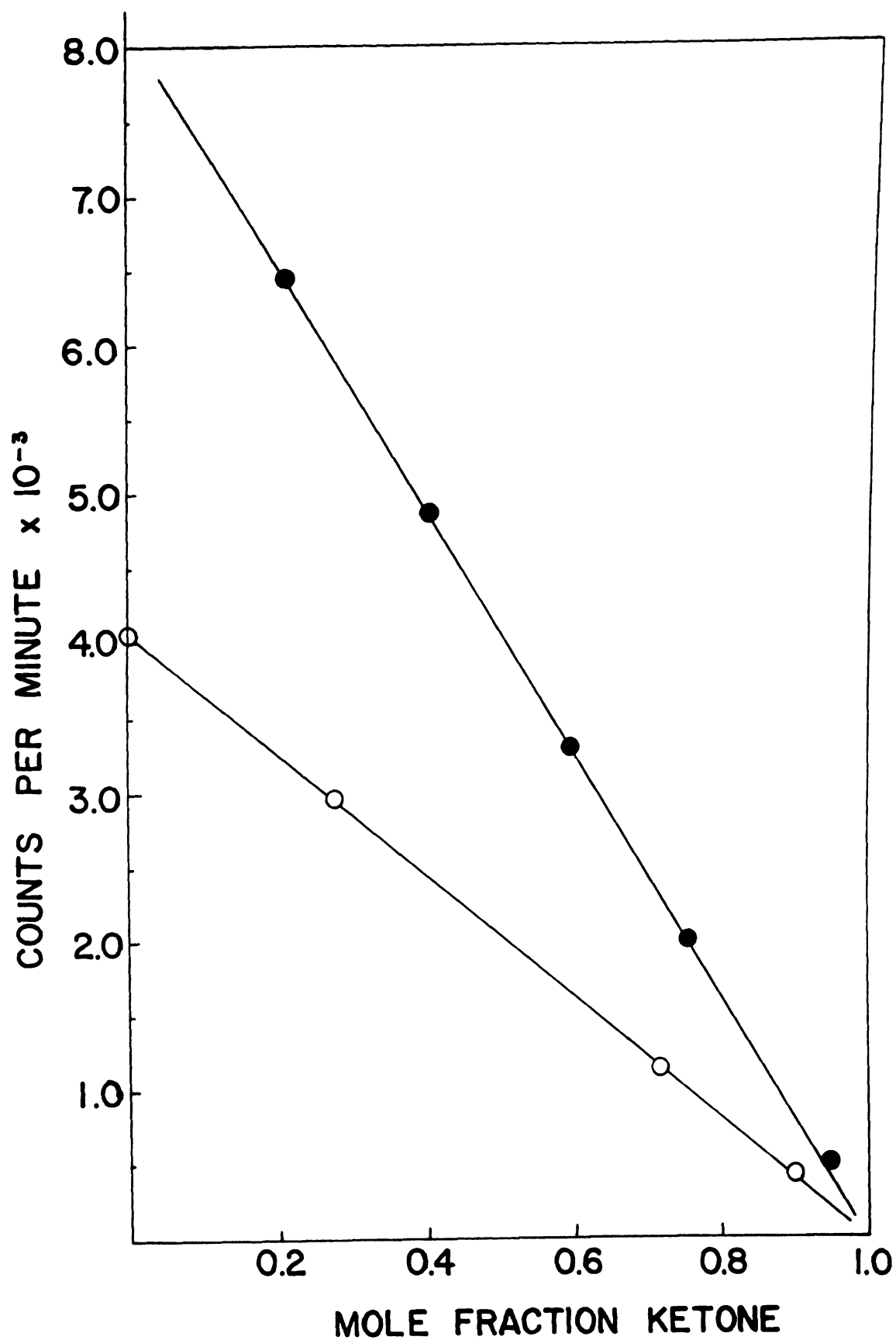


Figure 8. Count Rate as a Function of Mole Fraction for the Methyl Ethyl Ketone - Carbon Tetrachloride System.

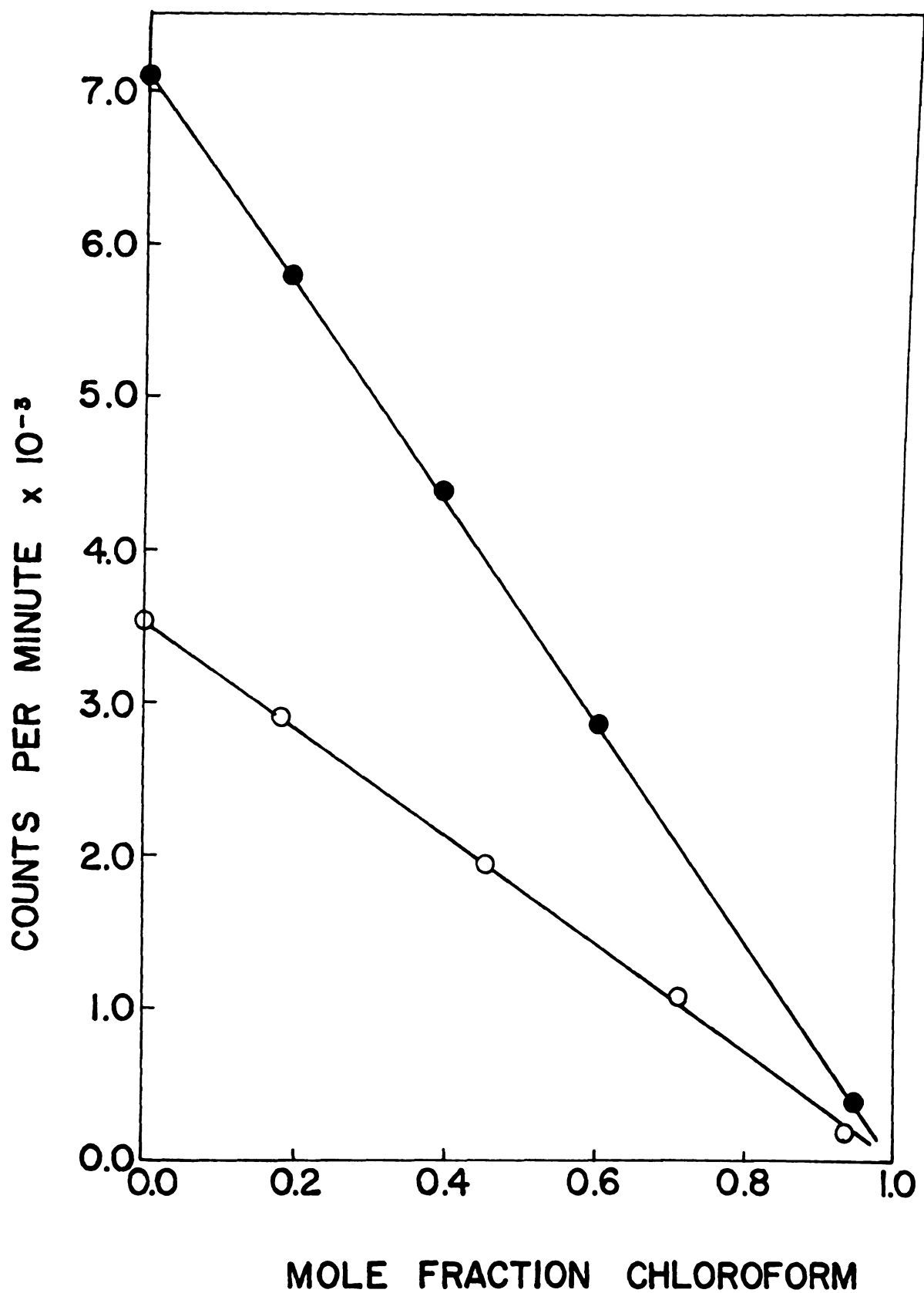


Figure 9. Count Rate as a Function of Mole Fraction for the Chloroform - Carbon Tetrachloride System.

refractive indexes of the materials were measured and compared to literature values (65) as a purity check.

Carbon - 14 labelled materials were obtained from the Nuclear Equipment Chemical Corporation and the Nuclear-Chicago Corporation. The manufacturers' statement of purity was accepted with no further purity check.

Discussion of Error

The accuracy of a given run of three cells is governed by the calibration of the cells and the experimental precision of the method. The cell calibration is based on the tracer diffusivity of pure carbon tetrachloride suggested by Rathbun and Babb (57). Since they obtained this value from consideration of several investigations, it is probably accurate and the resulting cell calibration is, therefore, reliable. However, further evidence of the accuracy of the cell calibration can be obtained from the tracer diffusion data collected in this work. In dilute binary solutions, theory predicts that tracer and mutual diffusivities are equal. For five binary mixtures studied here, intercepts of the mutual and tracer diffusivity curves were determined by graphically extrapolating to zero concentration. The intercepts agree to within 0.5% for the five systems. Based on these results, errors in the tracer diffusion coefficients resulting from uncertainties in calibration are estimated to be 0.5%.

The accuracy of one given run of three cells is, therefore, affected more by the precision of the method. A measure of the precision was obtained by making several duplicate runs for six different solutions. The reproducibility of these runs ranged from $\pm 0.7\%$ for pure carbon tetrachloride to $\pm 2\%$ for pure benzene with an average precision of $\pm 1.25\%$. Therefore, the accuracy of the method was assumed to be within $\pm 2.0\%$.

RESULTS AND DISCUSSION

Theoretical

From the application of the intrinsic diffusion concept, the medium fixed reference plane and the chemical model of solution nonideality, equations were derived which express the tracer and mutual diffusion coefficients in terms of concentration dependent quantities and friction coefficients--one for each species in solution. These equations (see Table II) can be empirically fit to experimental diffusion data by adjusting the values of the friction coefficients to give the best prediction. However, one can justly argue that, given enough arbitrary constants, any curve can be closely approximated. Therefore, the fact that these equations can be made to fit the data does not necessarily constitute support of the concepts from which they were derived. If, on the other hand, the friction coefficients were determined from independent measurements and the equations still predicted the diffusion coefficients accurately, the bases of the equations are probably valid. It is shown in Appendix V that, for the systems studied in this work, the frictional coefficients can be determined strictly

Table II. Summary of Diffusion Equations
Type of

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Components	Type of Association	Diffusion Equations
A and B	No Association	$D_A^* = \frac{kT}{\eta f_A} \quad (88)$
		$D_B^* = \frac{kT}{\eta f_B} \quad (89)$
		$D_{AB} = [X_A D_B^* + X_B D_A^*] \frac{\partial \ln A}{\partial \ln X_A} \quad (90)$
A and B	A...A, B inert	$D_A^* = \frac{kT}{\eta} \left[\left(\frac{1}{f_1} - \frac{1}{\tilde{f}_{11}} \right) \frac{x_1^0}{X_A} + \frac{1}{\tilde{f}_{11}} \right] \quad (164)$
		$D_B^* = \frac{kT}{\eta f_B} \quad (166)$
		$D_{AB} = \left[X_A D_B^* + X_B D_A^* + 2 \frac{kT}{\eta} \frac{\tilde{x}_{11}^0}{\tilde{f}_{11}} \frac{X_B}{X_A} \right] \frac{\partial \ln A}{\partial \ln X_A} \quad (167)$
A and B	A...B	$D_A^* = \frac{kT}{\eta} \left[\left(\frac{1}{f_1} - \frac{1}{\tilde{f}_{12}} \right) \frac{x_1^0}{X_A} + \frac{1}{\tilde{f}_{12}} \right] \quad (191)$
		$D_B^* = \frac{kT}{\eta} \left[\left(\frac{1}{f_2} - \frac{1}{\tilde{f}_{12}} \right) \frac{x_2^0}{X_B} + \frac{1}{\tilde{f}_{12}} \right] \quad (192)$

Table II., Continued

Components	Type of Association	Diffusion Equations	
		$D_{AB} = \left[X_A D_B^* + X_B D_A^* - 2 \frac{kT}{\eta} \tilde{x}_{12}^O \frac{\partial \ln A^C}{\partial \ln X_A} \right] \frac{1}{\tilde{f}_{12}}$	(193)
A, B and C	A...B, C inert	$D_A^* = \frac{kT}{\eta} \left[\left(\frac{1}{\tilde{f}_1} - \frac{1}{\tilde{f}_{12}} \right) \frac{x_1^O}{X_A} + \frac{1}{\tilde{f}_{12}} \right]$	(218)
		$D_B^* = \frac{kT}{\eta} \left[\left(\frac{1}{\tilde{f}_1} - \frac{1}{\tilde{f}_{12}} \right) \frac{x_2^O}{X_B} + \frac{1}{\tilde{f}_{12}} \right]$	(219)
		$D_C^* = \frac{kT}{\eta f_3}$	(220)

from tracer diffusion intercepts alone; a source independent of mutual diffusion measurements. Thus, it follows that the relations which are most significant are those between mutual and tracer diffusivities, equations (90), (167), and (193). The tracer diffusion relations [equations (87), (164), (166), (191), (192), (218), (219) and (220)] are significant in that the degree to which they predict the concentration dependence of the tracer diffusivities across the concentration range reflects on the concentration dependence of the friction coefficients and the accuracy of the chemical model in predicting the association of the systems.

It was pointed out earlier that the activity term in equation (90) over corrects when it is applied to an associated system. Similar equations derived here for associated systems predict this over correction.

$$D_{AB} = \left[X_A D_B^* + X_B D_A^* \right] \frac{\partial \ln A_A^C}{\partial \ln X_A} \quad (90)$$

$$D_{AB} = \left[X_A D_B^* + X_B D_A^* + 2 \frac{kT}{\eta} \frac{\tilde{x}_{11}^O}{\tilde{f}_{11}} \frac{X_B}{X_A} \right] \frac{\partial \ln A_A^C}{\partial \ln X_A} \quad (167)$$

$$D_{AB} = \left[X_A D_B^* + X_B D_A^* - 2 \frac{kT}{\eta} \frac{\tilde{x}_{12}^O}{\tilde{f}_{12}} \right] \frac{\partial \ln A_A^C}{\partial \ln X_A} \quad (193)$$

Equation (167) describes diffusion in a binary mixture where component A associates with itself to form a dimer cluster. In such solutions, the thermodynamic factor is less than unity and equation (90) would predict a diffusion coefficient which is too small. Equation (167),

on the other hand, has the additional term, $2 \frac{kT}{\eta} \frac{\tilde{x}_{11}^0}{\tilde{f}_{11}} \frac{X_B}{X_A}$,

which increases the value predicted by equation (90) and the over correction is reduced.

A similar circumstance arises when equation (193) is applied to binary systems where the components associate with each other. The activity term is greater than unity for such mixtures and equation (90) would predict a mutual diffusivity which would be too large. The term,

$-2 \frac{kT}{\eta} \frac{\tilde{x}_{12}^0}{\tilde{f}_{12}}$, lowers this value in equation (193) and better

agreement with experiment is expected.

Both equation (167) and (193) reduce to the form of equation (90) when there is no association, since the psuedo mole fraction of the dimer cluster is zero in each case. Also, both of these equations have the correct limiting behavior as either X_A or X_B approaches zero. That is, the limit of D_{AB} equals D_A^* as X_B or X_A , respectively, approaches zero.

Experimental

Density and viscosity data for the benzene-carbon tetrachloride and chloroform - carbon tetrachloride systems are shown on Figures 10 and 11. Diffusion coefficient data for these systems are shown on Figures 12 and 13. Friction coefficients were determined from the tracer diffusivities and viscosities of the pure component as described in Appendix V. The tracer diffusion coefficients of each component were then calculated from equations (88) and (89) assuming the friction coefficients to be independent of concentration and plotted on Figures 12 and 13.

$$D_A^* = \frac{kT}{\eta f_A} \quad (88)$$

$$D_B^* = \frac{kT}{\eta f_B} \quad (89)$$

It can be seen that the agreement between theoretical and experimental values is very good across the entire concentration range for both systems. Tracer diffusivities of benzene in carbon tetrachloride mixtures by Johnson and Babb (40) are also plotted on Figure 12. While less precise than the data collected in this study, they are in general agreement with the curve calculated from equation (88). From these results, one can conclude that equations

DENSITY (g/cm³)

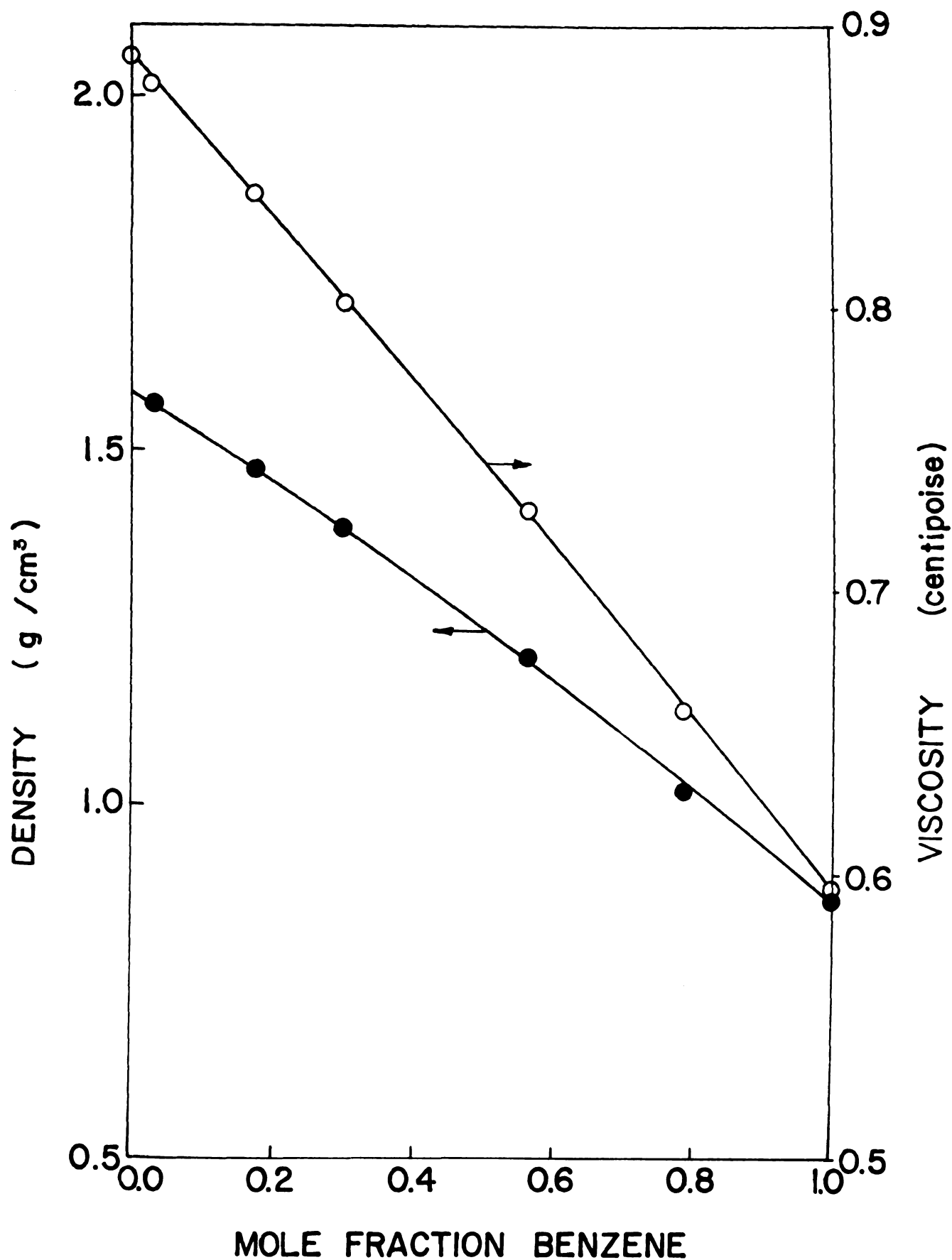


Figure 10. Density and Viscosity of the Benzene - Carbon Tetrachloride System at 25°C. ● Density Data; ○ Viscosity Data.

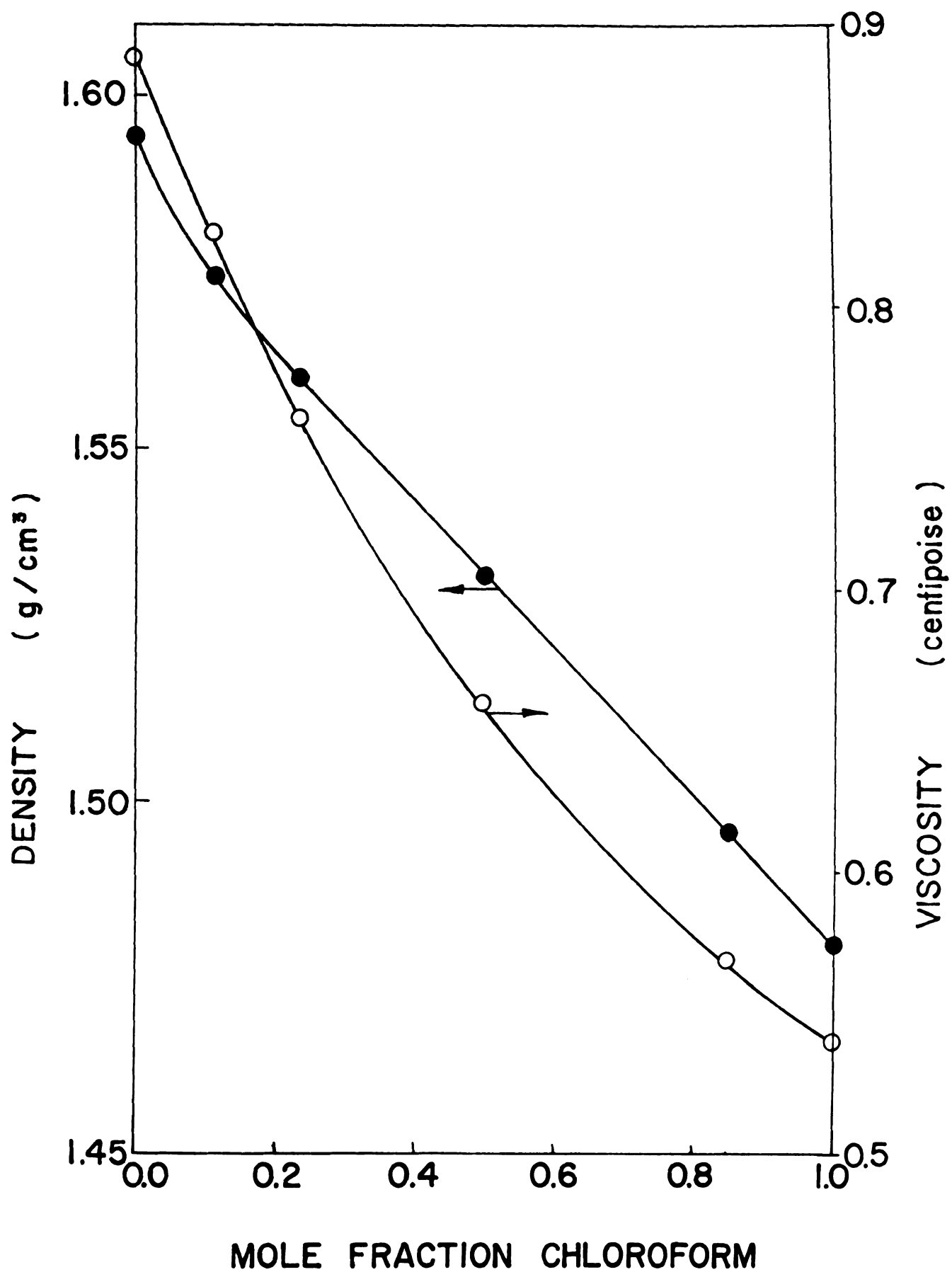


Figure 11. Density and Viscosity of the Chloroform - Carbon Tetrachloride System at 25°C. ● Density Data; ○ Viscosity Data.

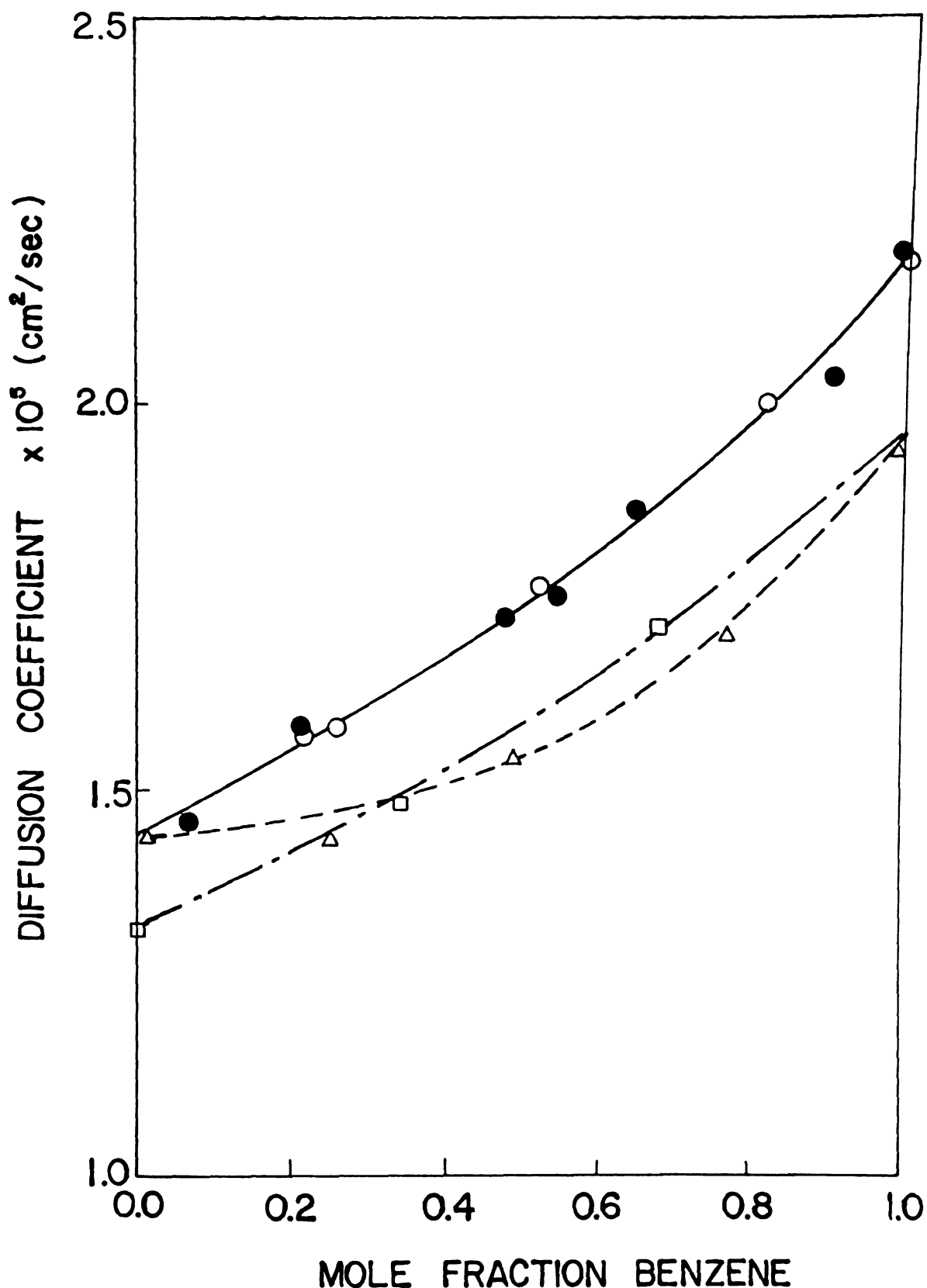


Figure 12. Tracer and Mutual Diffusion Coefficients for the Benzene - Carbon Tetrachloride System at 25°C . $\circ$ Tracer Diffusion Data for Benzene; $\bullet$ Tracer Diffusion Data for Benzene, Reference (40); $\square$ Tracer Diffusion Data for Carbon Tetrachloride; Δ Mutual Diffusion Data; — Equation (88); — — — Equation (89); - - - - Equation (90).

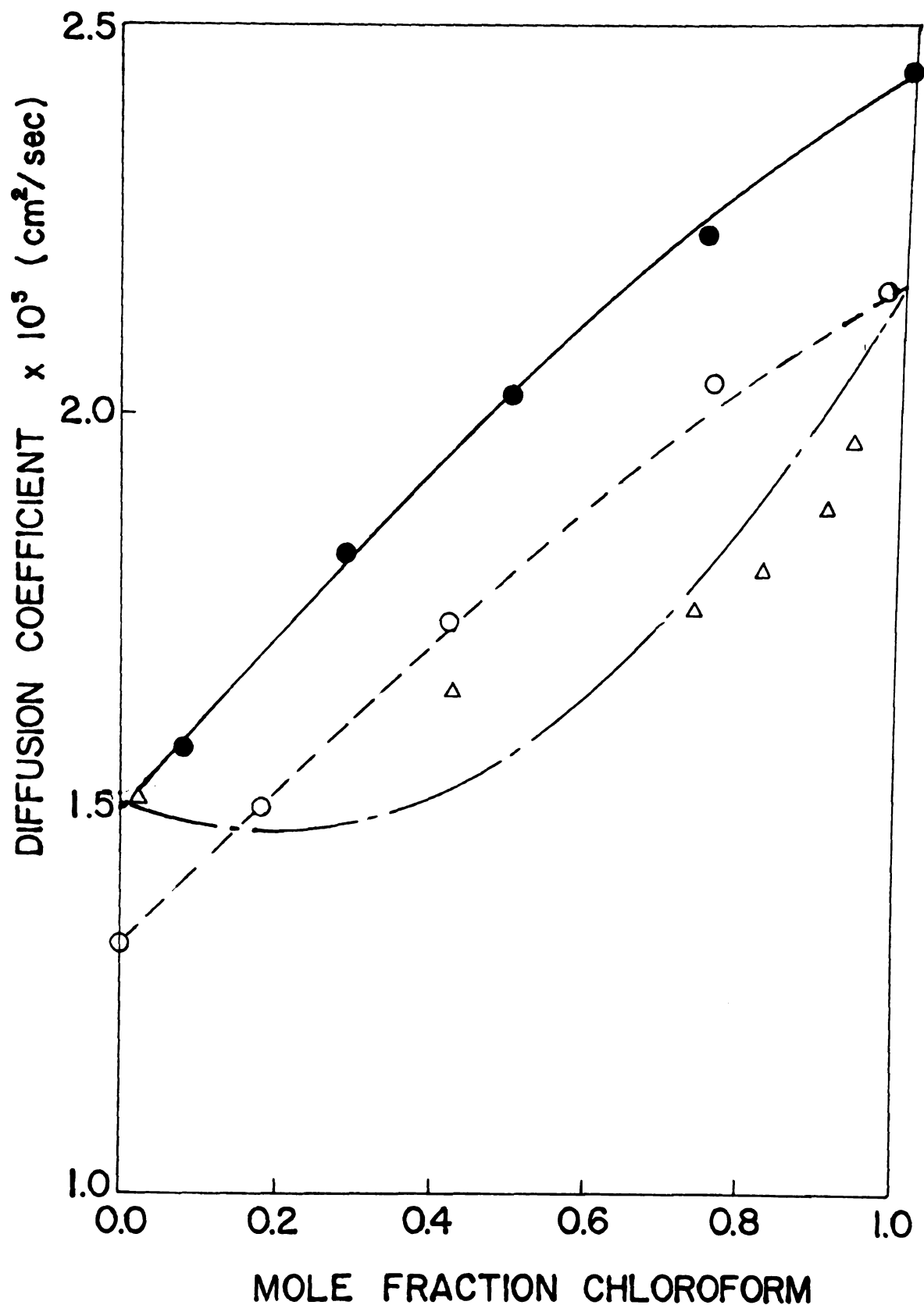


Figure 13. Tracer and Mutual Diffusion Coefficients for the Chloroform - Carbon Tetrachloride System at 25°C. ● Tracer Diffusion Data for Chloroform; ○ Tracer Diffusion Data for Carbon Tetrachloride; Δ Mutual Diffusion Data; — Equation (88); ---- Equation (89); - - - Equation (90).

(88) and (89) describe the tracer diffusivities of the benzene - carbon tetrachloride and chloroform-carbon tetrachloride systems very well with constant friction coefficients.

The behavior of the mutual diffusion coefficients are predicted by equation (90) is also shown on Figures 12 and 13.

$$D_{AB} = \left[X_A D_B^* + X_B D_A^* \right] \frac{\partial \ln A_A^C}{\partial \ln X_A} \quad (90)$$

The activity terms were calculated from equations (221) and (222). Equation (90) predicts the mutual diffusivities of the benzene - carbon tetrachloride system very well. As can be seen from Figure 13, this is not the case for chloroform-carbon tetrachloride mixtures where mutual diffusivities calculated by equation (90) differ by as much as 10% from the experimental data. This discrepancy can be attributed to an error in the measurement of the mutual diffusivities for this system. Although the data form a smooth curve with intercepts which are consistent with the tracer diffusion intercepts, attempts to duplicate these data were not successful. Cordes and Steinmeien (14) also measured mutual diffusivities in this system. Their data differ from the data collected here and are not consistent with the tracer diffusivities

at infinite dilution. Therefore, it is not reasonable to attribute the poor agreement to fault of equation (90).

Experimental results for the methyl ethyl keton - carbon tetrachloride system are shown on Figure 14. Anderson's (3) viscosity and mutual diffusion data were used for this system.

Equation (166) was applied to the tracer diffusion data of carbon tetrachloride. As can be seen from Figure 14, there is excellent agreement between predicted and experimental results.

$$D_B^* = \frac{kT}{\eta f_2} \quad (166)$$

$$D_A^* = \frac{kT}{\eta} \left[\left(\frac{1}{f_1} - \frac{1}{\tilde{f}_{11}} \right) \frac{\tilde{x}_1^0}{X_A} + \frac{1}{\tilde{f}_{11}} \right] \quad (164)$$

$$D_{AB} = \left[X_A D_B^* + X_B D_A^* + 2 \frac{kT}{\eta} \frac{\tilde{x}_{11}^0}{\tilde{f}_{11}} \frac{X_B}{X_A} \right] \frac{\partial \ln A_A^C}{\partial \ln X_A} \quad (167)$$

Labelled methyl ethyl ketone was not available from commercial suppliers so the tracer diffusivities of this component could not be measured. However, it is possible to predict these data from the tracer diffusivities for carbon tetrachloride and the mutual diffusivities. The friction coefficient of the carbon tetrachloride molecules, f_2 , was determined from the tracer diffusivities of carbon

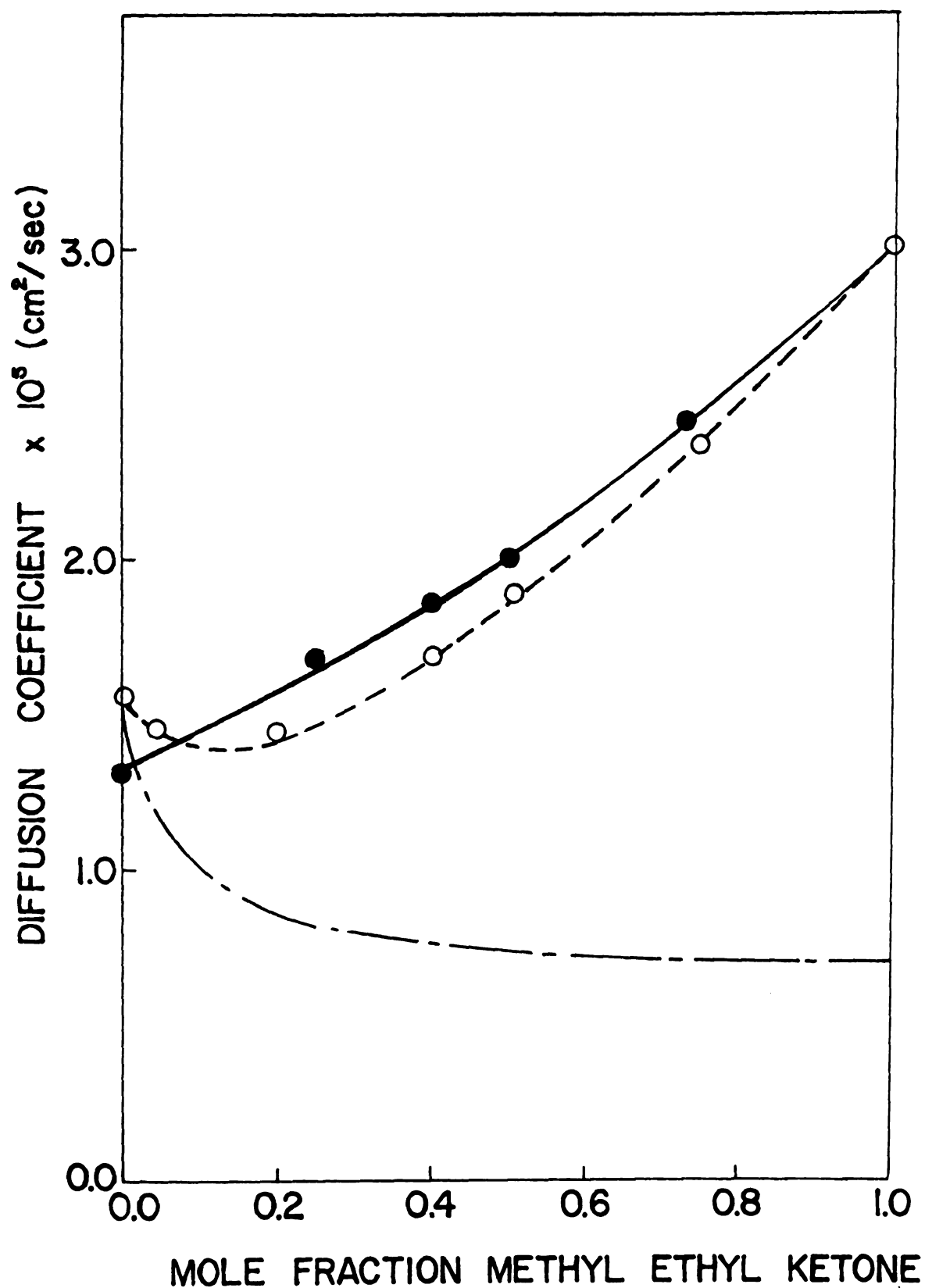


Figure 14. Tracer and Mutual Diffusion Coefficients for the Methyl Ethyl Ketone - Carbon Tetrachloride System at 25°C . ● Tracer Diffusion Data for Carbon Tetrachloride; ○ Mutual Diffusion Data, Reference (3); — Equation (166); ---- Equation (167); — — — Equation (164).

tetrachloride. Then, equations (164) and (167), together, were fit to the mutual diffusion data to get the best values of f_1 and $\tilde{f}_{11}$. The activity term was calculated from equation (141). The curve for the tracer diffusion of the ketone, in Figure 14, was then calculated from equation (164).

Although this curve has not been quantitatively verified, it is qualitatively correct. At low ketone concentrations, the diffusion coefficient is relatively high because the ketone is diffusing as individual molecules. As the ketone concentration increases, the diffusion coefficient decreases as the ketone molecules form the larger and more slowly diffusing dimer clusters. At the same time, the viscosity of the solution decreases, causing the diffusion coefficient to increase. In this case, both effects cancel and the diffusion coefficient is relatively constant after an initial decrease.

Diffusion data for the acetic acid-carbon tetrachloride system are shown on Figure 14. The viscosity and mutual diffusion data are by Anderson and Babb (3).

A reliable value of the equilibrium constant is not available in the literature. So, it was necessary to find f_1 , f_2 , $\tilde{f}_{11}$ and K from the diffusion data. To find f_1 , $\tilde{f}_{11}$ and K , equation (164) and (167) were empirically fit to the mutual diffusivities and the tracer diffusivities of acetic acid. f_2 was calculated from the

tracer diffusion coefficient of pure carbon tetrachloride and equation (166). The curves shown on Figure 15 were calculated from equations (164) and (167) using $K = 4000$ (mole fraction)⁻¹, a value within the range of the literature values.

It can be seen that, while the equations predict the qualitative behavior of the data, quantitatively there is disagreement. Also, the disagreement is generally greatest at higher acid concentrations.

The disagreement can be attributed to two effects. First the acid molecules may associate to form higher order clusters. Since the concentration of these higher clusters increases with acid concentration, it follows that the disagreement between the dimer model and experiment should also be greatest at the higher concentrations. Second, the chemical model may not accurately describe the activity of the system. The thermodynamic term, as calculated by equation (141), is 0.45 at $X_A = 0.00642$. While this seems abnormally small, the activity data available in the literature cannot be used as a check because they were not taken at low concentrations (73).

Thus, it would appear that little can be concluded as to the validity of equations (164) and (167) from the results of this system. However, three points should be restated. First, the equilibrium constant determined from the data is within the range of literature values. Second,

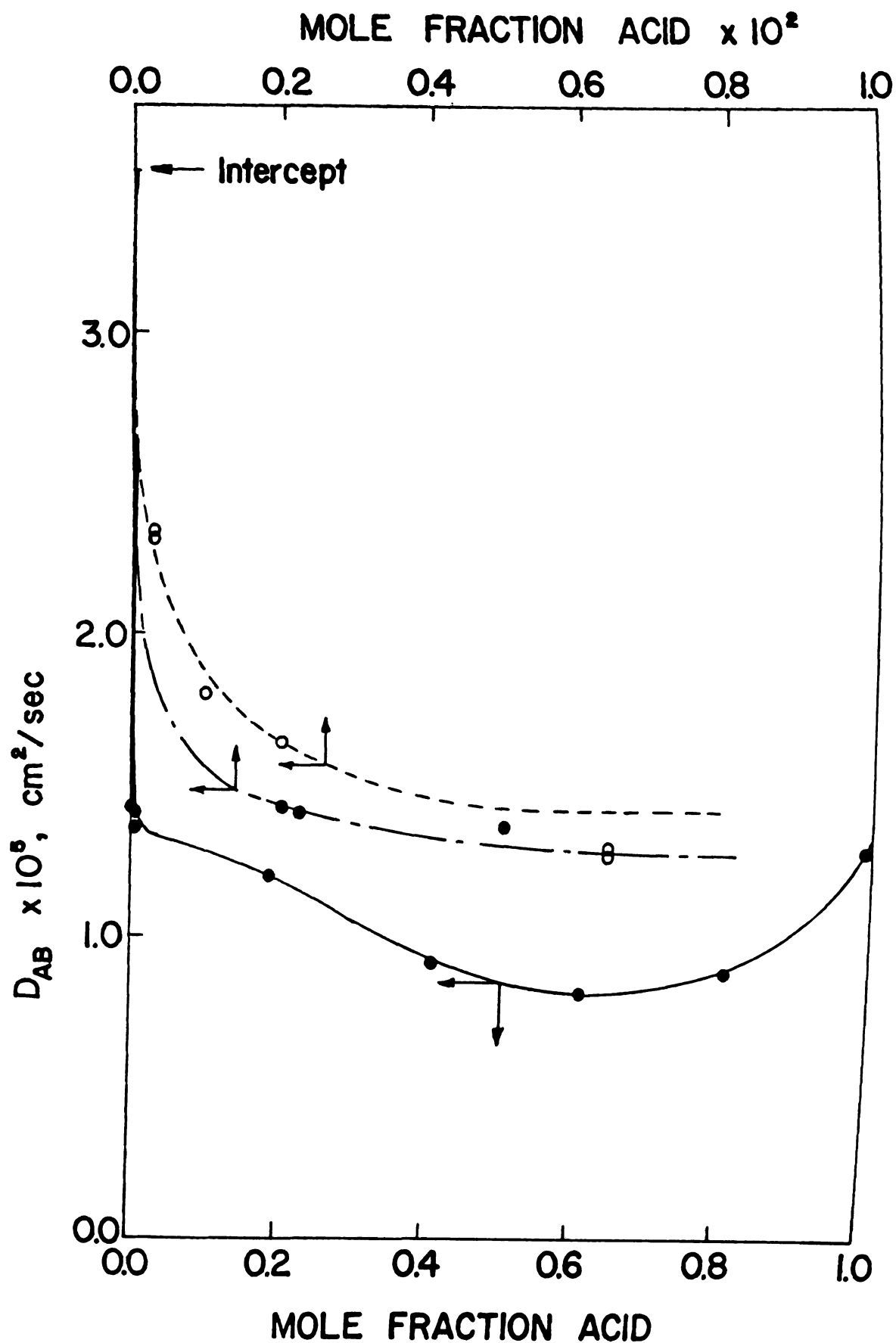


Figure 15. Tracer and Mutual Diffusion Coefficients for the Acetic Acid Carbon Tetrachloride System at 25°C. o Tracer Diffusion Data for Acetic Acid; ●, ——— Mutual Diffusion Data, Reference (3); - - - - - Equation (164); — · — Equation (167).

the diffusion equations can be fit to the qualitative behavior of the data. And third, this system is a rigid test of any model because the diffusion coefficient more than doubles in a concentration span of less than 1%. Thus, it is felt that this system does indicate the validity of the diffusion equations even though they do not predict the data well.

Diffusion data for the ether-chloroform system are shown on Figure 16. Again, the mutual diffusion and viscosity data are those of Anderson and Babb (2). f_1 and $\tilde{f}_{12}$ were determined from the intercepts of the ether tracer diffusion data and f_2 and $\tilde{f}_{12}$ were determined from the intercepts of the chloroform tracer diffusion data as described in Appendix V. The two values of $\tilde{f}_{12}$, determined in this manner, were different by approximately 3%. Therefore, an average $\tilde{f}_{12}$ was used with f_1 and f_2 in equations (191), (192) and (193) to predict the mutual and tracer diffusivities over the whole concentration range.

$$D_A^* = \frac{kT}{\eta} \left[\left(\frac{1}{\tilde{f}_1} - \frac{1}{\tilde{f}_{12}} \right) \frac{x_1^0}{X_A} - \frac{1}{\tilde{f}_{12}} \right] \quad (191)$$

$$D_B^* = \frac{kT}{\eta} \left[\left(\frac{1}{\tilde{f}_2} - \frac{1}{\tilde{f}_{12}} \right) \frac{x_2^0}{X_B} - \frac{1}{\tilde{f}_{12}} \right] \quad (192)$$

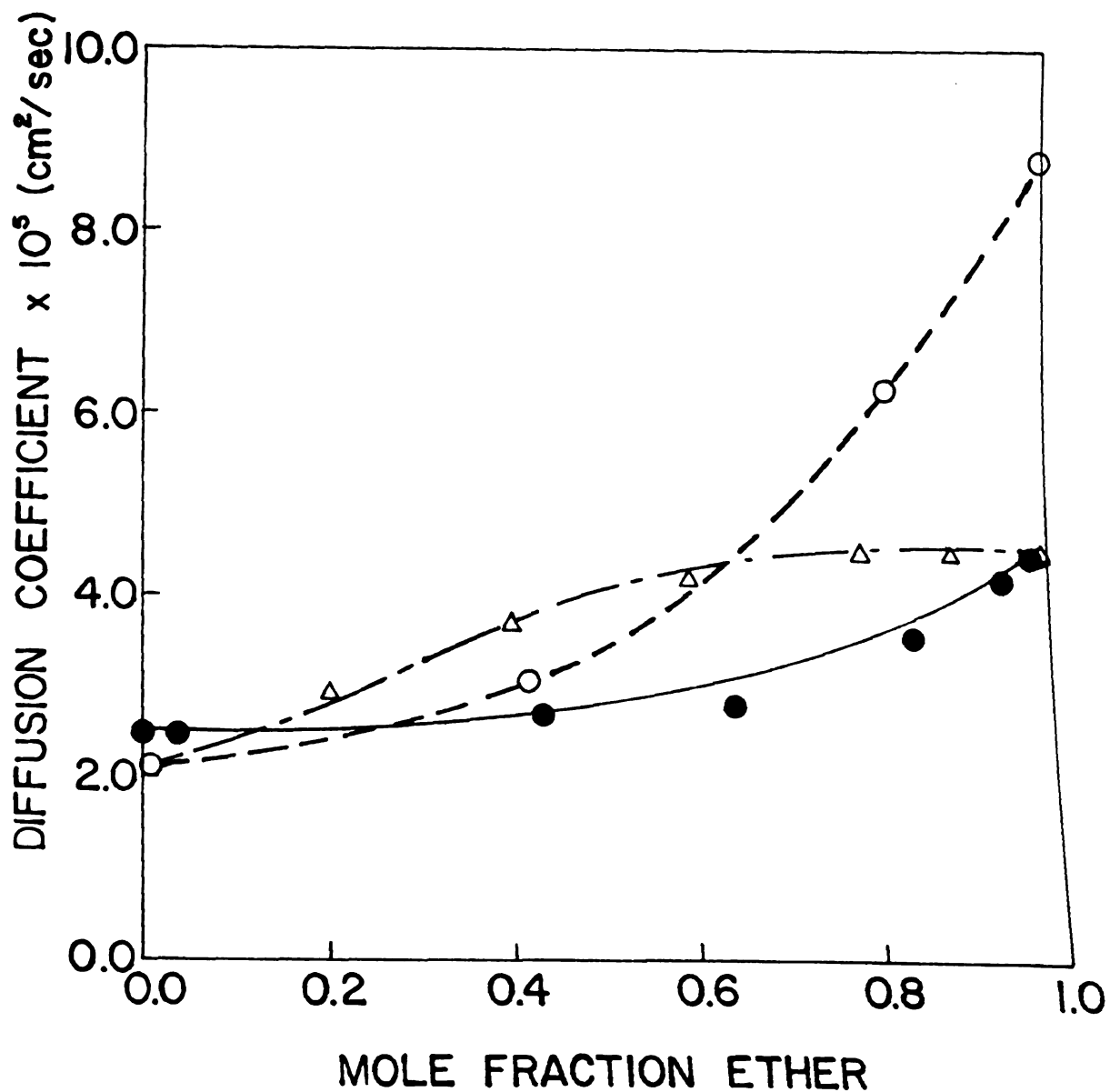


Figure 16. Tracer and Mutual Diffusion Coefficients for the Ether - Chloroform System at 25°C. O Tracer Diffusion Data for Ether; ● Tracer Diffusion Data for Chloroform; Δ Mutual Diffusion Data, Reference (2); ----- Equation (191); _____ Equation (192); - - - - - Equation (193).

$$D_{AB} = \left[X_A D_B^* + X_B D_A^* - 2 \frac{kT}{\eta} \frac{\tilde{x}_{12}^0}{\tilde{f}_{12}} \right] \frac{\partial \ln A_A^C}{\partial \ln X_A} \quad (193)$$

The plots of these equations are shown in Figure 16. The activity term in equation (193) was calculated from equation (184). The agreement between data and the predicted values is very good for the mutual diffusivities and the tracer diffusivities of ether. However, a small but consistent error is noted for the tracer diffusion of chloroform. There are two factors which could cause this error. First, the chemical model may not adequately describe association in the system. This is not likely for it can be used to predict the tracer diffusivities of ether very well. The second explanation for this error is suggested by comparing the effective molecular sizes as indicated by the molar volumes of the pure components. The molar volumes of ether and chloroform are 104 and 81 cc/mole, respectively. Thus, chloroform is a relatively small molecule surrounded by larger molecules of ether and ether-chloroform clusters. As discussed earlier, the friction coefficients should be constant when the medium surrounding a diffusing molecule can be considered a continuum. Since the chloroform molecules are smaller than the molecules in the surrounding medium, the medium cannot be considered a continuum and, therefore, the friction

coefficient of chloroform is a function of concentration. This system provides very strong support for equations (191), (192) and (193).

Viscosity and density data for the ether-chloroform-carbon tetrachloride system are presented in Figure 17 and the tracer diffusivity data in Figure 18. For simplicity, the mole fraction of the carbon tetrachloride was 0.5 for all measurements. Since this is a ternary system, the procedure discussed in Appendix V cannot be used to evaluate the friction coefficients from the data taken for this system. Therefore, the friction coefficients found for the binary ether-chloroform system were used. Tracer diffusivities for ether and chloroform were calculated from equation (218) and (219), using these friction coefficients, and plotted in Figure 18.

$$D_A^* = \frac{kT}{\eta} \left[\left(\frac{1}{\tilde{f}_1} - \frac{1}{\tilde{f}_{12}} \right) \frac{x_1^0}{X_A} + \frac{1}{\tilde{f}_{12}} \right] \quad (218)$$

$$D_B^* = \frac{kT}{\eta} \left[\left(\frac{1}{\tilde{f}_2} - \frac{1}{\tilde{f}_{12}} \right) \frac{x_2^0}{X_B} + \frac{1}{\tilde{f}_{12}} \right] \quad (219)$$

It can be seen from this figure that the agreement between theory and experiment is excellent for ether but, as in the ether-chloroform system, it is not as good for chloroform. Again, a comparison of molar volumes (104, 97 and 81 (cc/mole), respectively, for ether, carbon

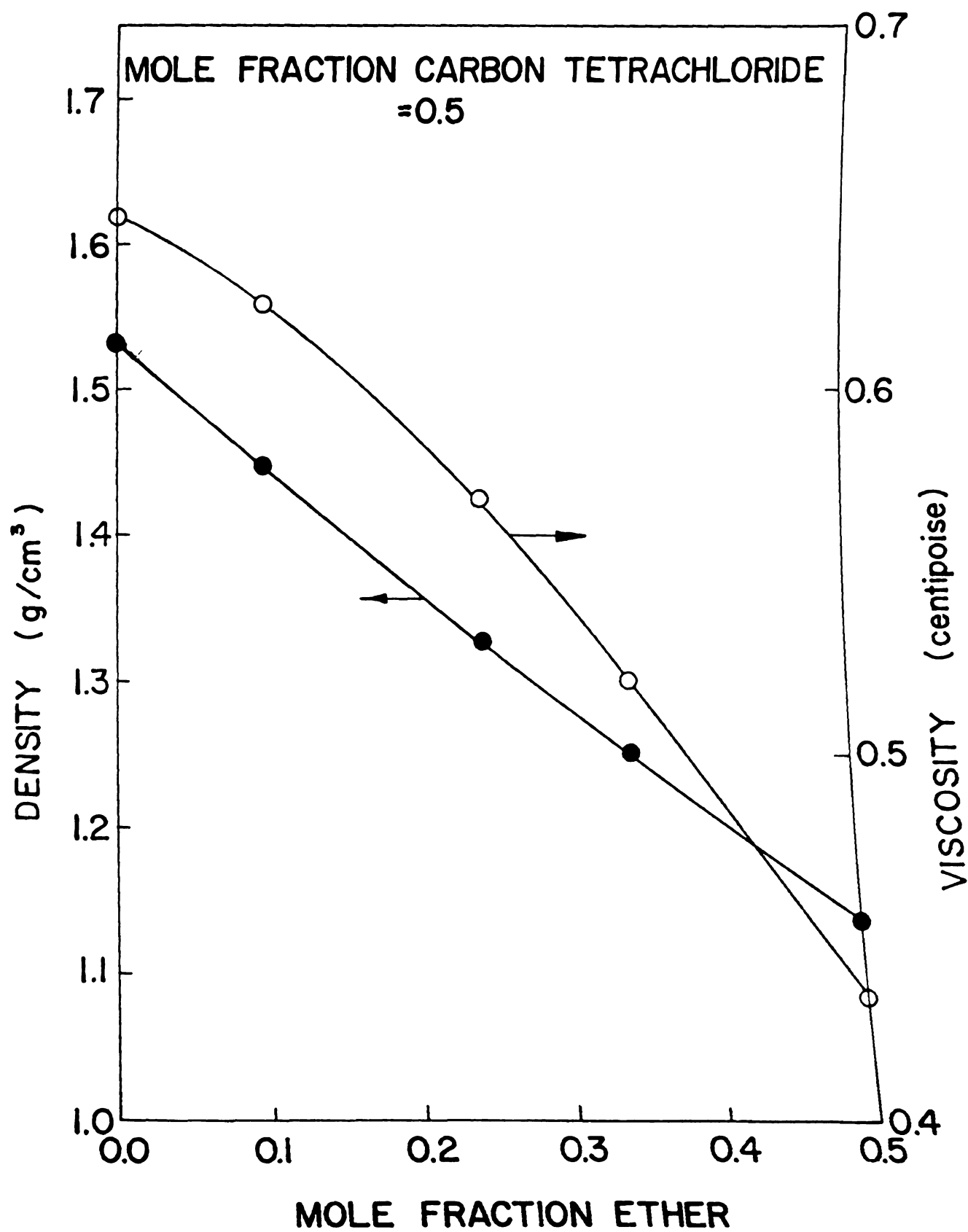


Figure 17. Density and Viscosity of the Ether - Chloroform - Carbon Tetrachloride System at 25°C.
 ● Density Data; O Viscosity Data.

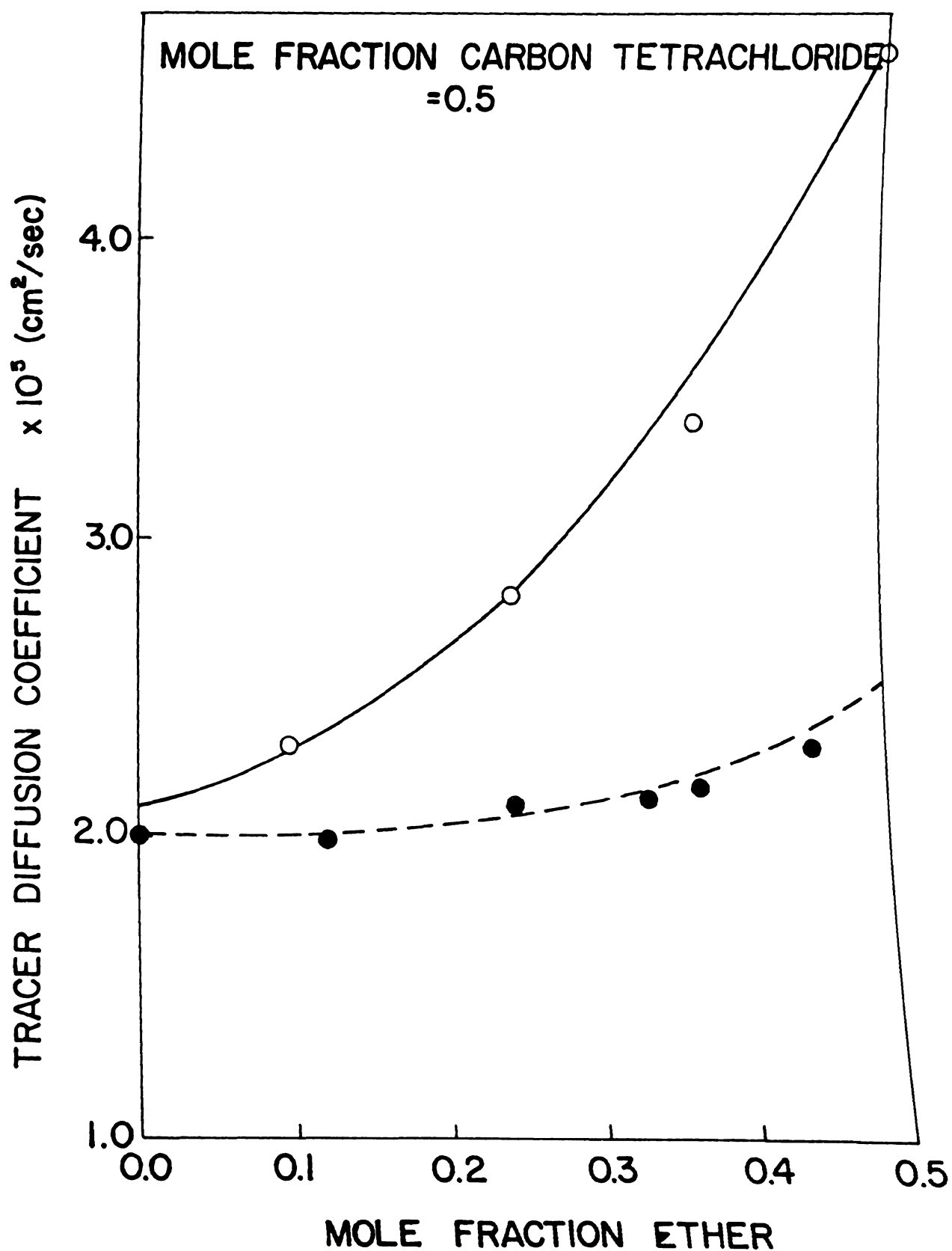


Figure 18. Tracer Diffusion Coefficients for the Ether-Chloroform - Carbon Tetrachloride System at 25°C. O Tracer Diffusion Data for Ether; ● Tracer Diffusion Data for Chloroform; — Equation (218); ---- Equation (219).

tetrachloride and chloroform) indicates that chloroform is a smaller molecule diffusing through relatively large molecules. The resulting concentration dependence of the chloroform friction coefficient accounts for the disagreement between theory and experiment. The tracer diffusivities of ether and chloroform in this ternary system can be predicted from the tracer diffusivities of the same two components in binary mixtures.

The experimental tracer diffusion, mutual diffusion, density and viscosity data collected in this study are tabulated in Appendixes VI, VII, and VIII, respectively, for detailed reference.

CONCLUSIONS

It can be concluded from this study that the intrinsic mechanism of liquid diffusion and the concept of the medium fixed reference can be combined with the chemical model of solution nonideality to derive equations which accurately predict tracer and mutual diffusion coefficients in systems whose components associate in simple, specific ways. To make these predictions, it is necessary to specify friction coefficients--one for each diffusing species. This study shows that in a binary mixture the friction coefficients can be determined directly from the intercepts of tracer diffusion coefficients alone. Further, it is concluded that the friction coefficient of a component, whose molecules are smaller than those of the other components, is a function of composition.

This study provides evidence which substantiates the model that in binary mixtures, ether and chloroform cross associate to form bimolecular clusters. Tracer diffusion data indicate that the same cross association of ether and chloroform occurs when nonassociating carbon tetrachloride is added to binary ether-chloroform mixtures.

The friction factors for ether and chloroform are concluded to be the same in the binary ether-chloroform system and the ternary ether-chloroform-carbon tetrachloride system. It is also shown that the friction factor of chloroform is concentration dependent for both the binary and ternary systems.

The Hartley-Crank equation (equation (71)) and the Darken equation (equation (90)) are shown to be valid for nonassociated binary systems.

It is the opinion of this author that the intrinsic model of diffusion is very likely the true mechanism by which diffusion occurs. This opinion is based on the fact that the intrinsic model leads to equations from which mutual diffusivities can be predicted from measurements of tracer diffusivities and viscosity and, in the case of associated systems, from an equilibrium constant which can be determined from thermodynamic data. It would seem more than fortuitous that this would be the case if the intrinsic model were not correct.

FUTURE WORK

Theory

More work should be done in the development of the chemical model to remove one of its primary faults; the assumption that the species form an ideal solution. The assumption was made to derive an expression for the component activities in terms of measurable quantities.

One method of attack can be seen by recalling that the activity of a component is equal to the activity of its monomeric species. Since the component activities can be calculated from vapor pressure data, for example, and since the mole fractions of the species can be determined from spectroscopic techniques, the activity coefficients of the monomeric species can be determined as a function of composition.

Most likely, the species form a nearly ideal solution, so any simple, thermodynamically consistent set of equations (multi-component van Laar, Porter, etc.) can be fit to the activity coefficient data. The resulting expressions could then be used to modify equation (120) to give a more accurate thermodynamic description of the system of interest.

The most logical extension of the intrinsic model of diffusion is to multicomponent systems. Kett and Anderson (76) have made a study of the intrinsic model as applied to ordinary diffusion in ternary systems. It would also be of interest to investigate relationships between tracer and ordinary diffusion for these systems.

Experimental

The accuracy of the capillary technique could be increased if the average concentration (in equation (227)) could be measured several times during the run. A technique of this type was used by Mills (51) for materials labelled with an isotope whose nuclear emission is capable of penetrating the walls of the capillary. Counters were placed outside the capillary. When carbon - 14 or tritium labelled materials are used, absorption of the relatively soft beta particles in even the thinnest capillary walls precludes the use of Mills' method.

Instead, the capillary itself could be constructed of a scintillation crystal that is inert to the solvent action of the system of interest. Calcium fluoride is one material that is resistant to many mixtures of this type studied here. The crystal could be viewed from the side by a photomultiplier detection system and the count rate determined at prescribed time intervals.

Anticipated problems are in the areas of contamination of the crystal with radioactive materials and poor conversion of radioactive disintegrations to detectable light pulses.

Another area for future experiment work is in the area of activity determination. To check the validity of the diffusion equations, the thermodynamic term, $\frac{\partial \ln a_A^C}{\partial \ln x_A}$, must be known quite accurately. Much of the activity data in the literature is very bad. Therefore, it would be desirable to have good activity data on carefully selected systems.

APPENDIXES

APPENDIX I

Fortran Computer Program for the Determination of Equilibrium Constants

C THIS PROGRAM FITS TOTAL PRESSURE DATA TO THE TYPE (B)
C ASSOCIATION MODEL. NOMENCLATURE: W = WEIGHT FRACTION,
C X=MOLE FRACTION, A=VAP. PRES. OF A, B=VAP. PRES. OF B,
C PI=TOTAL PRES., AK=EQUIL. CONSTANT

```
      DO 2 I = 1, 3
      SZ2XX = 0.
      SXX = 0.
      SZ2 = 0.
      SXX2 = 0.
      READ 100, T
      READ 102, A, B
      DO 1 J=1, 9
      READ 102, WA, PI
      WB = 1.-WA
      XA = WA
      SB = 1.-XA
      XX=XA*XB
      A = ((XA-XB)*(A-B)-PI)/(PI-A-B)
      Z2 = Z*Z
      SZ2XX = SZ2XX + Z2*XX
      SXX = SXX + XX
      SZ2 = SZ2 + Z2
      SXX2 = SXX2 + XX*XX
1 PRINT 103, XA,XX,Z2
      SLOPE = (9.*SZ2XX-SXX*SZ2)/(9.*SXX2-SXX*SXX)
      AK = -SLOPE/(SLOPE+4)
      PRINT 100, T
2 PRINT 102, SLOPE, AK
100 FORMAT (F7.4)
102 FORMAT (2F7.4)
103 FORMAT (3F7.4)
      END
```

APPENDIX II

Experimental Procedure

- (1) Bulk solution of the desired concentration was prepared and placed in a bulk solution container. The container was in turn placed in a constant temperature bath for at least one hour before the run was started.
- (2) Capillary solution of the same chemical concentration as the bulk solution was weighed out. A small portion of one component consisted of labelled material, added with the component.
- (3) The capillary solution was degassed by allowing the solution to equilibrate at approximately 30°C.
- (4) The capillaries and frits were washed three times with acetone and dried. Three cells were assembled.
- (5) The bulk solution was removed from the water bath. Each cell was filled in turn and placed into the bulk solution. The container was then returned to the water bath and diffusion allowed to proceed for three to six days.
- (6) After the run, 5 cc. of scintillation liquid were measured into each of three counting vials.

- (7) Each capillary was then emptied by the following procedure.
 - (a) The frit holder was removed.
 - (b) The cell was inverted into the counting vial.
 - (c) The funnel-shaped portion of the screw cap was filled with scintillation liquid.
 - (d) The metal foil disk was punctured and the capillary flushed with 10 cc. of scintillation liquid.
 - (e) The porous frit was removed from the counting vial.
- (8) The cells were cleaned, reassembled, filled with capillary solution and emptied as per the above procedure.
- (9) The vials were placed in the scintillation counter and the activities were determined. If the count rate of any one of the three samples deviated more than 5% from the mean activity of the three, the run was discarded.

APPENDIX III

Solution of Equation (226)

$$\frac{\partial C_i^*}{\partial \theta} = D_i^* \frac{\partial^2 C_i^*}{\partial z^2} \quad (a)$$

$$\frac{\partial C_i^*}{\partial z} = 0 \text{ at } z = 0, \theta > 0 \quad (b)$$

(226)

$$-D_i^* \frac{\partial C_i^*}{\partial z} = \frac{1}{R} C_i^* \text{ at } z = L, \theta > 0 \quad (c)$$

$$C_i^* = C_{i0}^* \text{ at } \theta = 0, L > z > 0 \quad (d)$$

Following the general procedure of separation of variables, a product solution is assumed of the form $C_i^* = \Gamma(z) \cdot \Psi(\theta)$. Then, the differential equation becomes:

$$\frac{1}{\Gamma} \frac{d^2 \Gamma}{dz^2} = \frac{1}{D_i^* \Psi} \frac{d\Psi}{d\theta} = -\lambda^2, \quad (III-1)$$

a constant. Or,

$$\frac{d^2 \Gamma}{dz^2} + \lambda^2 \Gamma = 0 \quad (III-2)$$

and

$$\frac{d\psi}{d\theta} + D_1^* \lambda^2 \psi = 0. \quad (\text{III-3})$$

The product of the solutions of these two equations is:

$$C_1^* = (k_1 \cos(\lambda z) + k_2 \sin(\lambda z) \exp(-\lambda^2 D_1^* \theta)). \quad (\text{III-4})$$

Also,

$$\frac{\partial C_1^*}{\partial z} = (k_2 \lambda \cos(\lambda z) - k_1 \lambda \sin(\lambda z) \exp(-\lambda^2 D_1^* \theta)). \quad (\text{III-5})$$

To satisfy boundary condition (226) (b), k_2 from equation (III-5) must be zero. Then with $k_2 = 0$, combine equation (III-4) and (III-5) with boundary condition (226) (c) with the following result:

$$-\exp(-\lambda^2 D_1^* \theta) k_1 \lambda \sin(\lambda L) = -\frac{1}{RD_1^*} \exp(-\lambda^2 D_1^* \theta) k_1 \cos(\lambda L) \quad (\text{III-6})$$

Or, after simplifying,

$$\cot(\lambda_n L) = RD_1^* \lambda_n \quad (\text{III-7})$$

where the subscript n on λ indicates the infinite number of roots.

Since the differential equation is linear, this infinite number of solutions may be added. Then, from

equations (III-4),

$$C_i^* = \sum_{n=1}^{\infty} k_n \exp(-\lambda_n D_i^* \theta) \cos(\lambda_n z) \quad (\text{III-8})$$

Now, substitute this expression into boundary condition (226) (b), multiply both sides of the resulting equation by $\cos \lambda_m z dz$ and integrate between $z = 0$ and L .

Then,

$$C_{i0}^* \int_0^L \cos(\lambda_m z) dz = \int_0^L \sum_{n=1}^{\infty} k_n \cos(\lambda_n z) \cos(\lambda_m z) dz \quad (\text{III-9})$$

When $m \neq n$, the integral on the right side is zero and when $m = n$, it is:

$$k_n \left(\frac{L}{2} + \frac{1}{2\lambda_n} \sin(\lambda_n L) \cos(\lambda_n L) \right) \quad (\text{III-10})$$

The integral on the left is:

$$\frac{1}{\lambda_n} \sin(\lambda_n L). \quad (\text{III-11})$$

So,

$$k_n = \frac{2C_{i0}^* \sin(\lambda_n L)}{\lambda_n L + \sin(\lambda_n L) \cos(\lambda_n L)}. \quad (\text{III-12})$$

The final solution is then:

$$\frac{C_i^*}{C_{i0}^*} = 2 \sum_{n=1}^{\infty} \left[\left(\frac{\sin \lambda_n L}{\lambda_n L + \sin(\lambda_n L) \cos(\lambda_n L)} \right) \exp \right. \\ \left. (-\lambda_n^2 D_i^* \theta) \cos(\lambda_n z) \right]. \quad (\text{III-13})$$

The solution in this form is not useful, for the concentration ratio is not conveniently measured as a function of position and time. It is more convenient to measure the ratio of average concentration to initial concentration as a function of time. An expression for the average concentration can be obtained by combining (III-13) and (III-14).

$$C_{iavg}^* = \frac{\int_0^L C_i^* dz}{\int_0^L dz} \quad (\text{III-14})$$

The result is:

$$\frac{C_{iavg}^*}{C_{i0}^*} = 2 \sum_{n=1}^{\infty} \left[\frac{\sin^2 \beta_n}{\beta_n (\beta_n + \sin \beta_n \cos \beta_n)} \exp \right. \\ \left. -\beta_n^2 \frac{D_i^* \theta}{L^2} \right] \quad (227) (a)$$

where

$$\beta_n = \lambda_n L. \quad (\text{III-16})$$

Equation (III-7) can now be rewritten as:

$$\cot \beta_n = \beta_n \frac{RD_1^*}{L} \quad (227) (b)$$

By defining the new variable, β_n , the concentration ratio can be written as a convenient function of two dimension-

less groups, $\frac{RD_1^*}{L}$ and $\frac{D_1^* \theta}{L^2}$.

APPENDIX IV

Fortran Computer Program for Diffusion Coefficient Calculations

```

C R=NUMBER OF TERMS IN THE SUM
C W = RD*/L
C AN=BETA N

      PRINT 100
      DO 8 J=1, 100
        R = J
        R = R/50
        DT = R
        W = 50.0
        R = 1.0
        CAVG = 0.0
        DO 11 = 1,10
          7 AN = (2. *R-1.)*3.1416/2.
          3 G=AN-(AN/W-COTF (AN))/(1./W+1./SINF(AN))**2)
            IF (ABSF(AN/W-COTF(AN))- .00001) 2,2,4
          4 AN = G
            GO TO 3
          2 AN = G
            SUM = (SINF(AN))**2/(AN*(AN+(SINF(AN))*(COSF(AN))))*
1          1EXP(-AN*AN*DT)
            CAVG=CAVG+SUM
            IF(SUM/CAVG-.00001) 5,5,6
          6 R=R+1.0
            GO TO 7
          5 CAVG = 2.*CAVG
            PRINT 101,CAVG,W,DT,R
            R=1.
            CAVG=0.0
          1 W=W+5.0
          8 CONTINUE
100  FORMAT(*0*10X*CAVG*10X*W*12X*DTL2*10X*R*)
101  FORMAT (*0*,4(7X,F7,4))
      END

```

APPENDIX V

Determination of Friction Coefficients From Tracer Diffusivities

If the diffusion relations derived in this work are to be used for quantitative predictions, the friction coefficients, f_i , must be specified. For components of a nonassociated system or for a nonassociated component of an otherwise associated system, the tracer diffusivities are given by equation (79)

$$D_i^* = \frac{kT}{\eta f_i} \quad (79)$$

Given viscosity and tracer diffusion data, one can calculate f_i at any concentration.

The situation is more complex for an associated component of a mixture. When component A associates itself to form dimer clusters,

$$D_A^* = \frac{kT}{\eta} \left[\left(\frac{1}{f_1} - \frac{1}{\tilde{f}_{11}} \right) \frac{x_1^0}{X_A} + \frac{1}{\tilde{f}_{11}} \right]. \quad (164)$$

Here it is not possible to calculate a value for both f_1 and $\tilde{f}_{11}$ from viscosity and tracer diffusion data at any one concentration. However, the frictional coefficients

can be calculated directly from the experimental tracer diffusion intercepts. Using equation (135) and l' Hospital's rule, it can be shown that

$$\lim_{X_A \rightarrow 0} \left(\frac{x_1^0}{X_A} \right) = 1. \quad (V-1)$$

It follows directly from equations (V-1) and (164) that

$$\lim_{X_A \rightarrow 0} D_A^* = \frac{kT}{\bar{f}_1 r}. \quad (V-2)$$

Therefore, $\bar{f}_1$ can easily be calculated from the intercept of D_A^* at $X_A = 0$. Also from equation (135),

$$\lim_{X_A \rightarrow 1} \left(\frac{x_1^0}{X_A} \right) = \frac{1 + (1+4K)^{1/2}}{1 + (1+4K)^{1/2} + 4K} \quad (V-3)$$

and hence,

$$\lim_{X_Z \rightarrow 1} D_A^* = \frac{kT}{\eta} \left[\left(\frac{1}{\bar{f}_1} - \frac{1}{\tilde{f}_{11}} \right) \left(\frac{1 + (1+4K)^{1/2}}{1 + (1+4K)^{1/2} + 4K} + \frac{1}{\tilde{f}_{11}} \right) \right] \quad (V-4)$$

The friction coefficient, $\tilde{f}_{11}$, can now be calculated from this equation after $\bar{f}_1$ has been determined from equation (V-2).

The following limiting expressions are applicable when the two components associate with each other to form a dimer cluster:

$$\lim_{X_A \rightarrow 1} D_A^* = \frac{kT}{\eta f_1} , \quad (V-5)$$

$$\lim_{X_B \rightarrow 1} D_B^* = \frac{kT}{\eta f_2} , \quad (V-6)$$

$$\lim_{X_A \rightarrow 0} D_A^* = \frac{kT}{\eta} \frac{1}{K+1} \left(\frac{1}{f_1} + \frac{K}{\tilde{f}_{12}} \right) \quad (V-7)$$

and

$$\lim_{X_B \rightarrow 0} D_B^* = \frac{kT}{\eta} \frac{1}{K+1} \left(\frac{1}{f_2} + \frac{K}{\tilde{f}_{12}} \right) . \quad (V-8)$$

After f_1 and f_2 have been calculated from equations (V-5) and (V-6), $\tilde{f}_{12}$ can be calculated from either equation (V-7) or equation (V-8). If different values are obtained, an average $\tilde{f}_{12}$ can be used.

APPENDIX VI

Experimental Tracer Diffusion Data at 25°C.

Table III. Tracer Diffusion Data for the
Benzene (A) - Carbon Tetrachloride (B) System

x_A	$D_A^* \times 10^5 \text{ (cm}^2\text{/sec)}$	$D_B^* \times 10^5 \text{ (cm}^2\text{/sec)}$
0.0	--	1.32
0.216	1.57	--
0.26	1.58	--
0.34	--	1.48
0.523	1.76	--
0.677	--	1.71
0.82	2.00	--
1.00	2.14	--

Table IV. Tracer Diffusion Data for the
Chloroform (A) - Carbon Tetrachloride (B) System

x_A	$D_A^* \times 10^5 \text{ (dm}^2\text{/sec)}$	$D_B^* \times 10^5 \text{ (cm}^2\text{/sec)}$
0.0	--	1.32
0.08	1.57	--
0.18	--	1.49
0.29	1.82	--
0.42	--	1.73
0.50	2.02	--
0.75	2.23	--
0.76	--	2.04
0.98	--	2.16
1.00	2.44	--

Table V. Tracer Diffusion Data for the Methyl Ethyl Ketone (A) - Carbon Tetrachloride (B) System

X_A	$D_B^* \times 10^5 \text{ (cm}^2/\text{sec)}$
0.0	1.32
0.25	1.55
0.40	1.88
0.50	2.00
0.73	2.35

Table VI. Tracer Diffusion Data for the Acetic Acid (A) - Carbon Tetrachloride (B) System

X_A	$D_A^* \times 10^5 \text{ (cm}^2/\text{sec)}$	$D_B^* \times 10^5 \text{ (cm}^2/\text{sec)}$
0.0	--	1.32
0.027	2.31	
0.027	2.33	
0.101	1.80	
0.201	1.65	
0.642	1.27	
0.642	1.28	

Table VII. Tracer Diffusion Data for the Ether (A) - Chloroform (B) System

X_A	$D_A^* \times 10^5 \text{ (cm}^2/\text{sec)}$	$D_B^* \times 10^5 \text{ (cm}^2/\text{sec)}$
0.0	--	2.44
0.04	2.15	2.44
0.42	3.05	--
0.44	--	2.65
0.65	--	2.80
0.82	6.23	--
0.85	--	3.55
0.95	--	4.13
1.00	8.75	--

Table VIII. Tracer Diffusion Data for the Ether
(A) - Chloroform (B) - Carbon Tetrachloride (C) System

$$[X_C = 0.5]$$

X_A	$D_A^* \times 10^5 \text{ (cm}^2\text{/sec)}$	$D_B^* \times 10^5 \text{ (cm}^2\text{/sec)}$
0.0	--	2.03
0.1	2.32	--
0.1253	--	1.99
0.2505	2.81	--
0.2510	--	2.11
0.3411	--	2.13
0.3751	--	2.17
0.3742	3.38	--
0.4511	--	2.30
0.5014	4.62	--

APPENDIX VII

Experimental Mutual Diffusion Data at 25°C.

(X_A is the average concentration of the solutions above and below the boundary in the diffusion cell.)

Table IX. Mutual Diffusion Data for the
Benzene (A) - Carbon Tetrachloride (B) System

X_A	$D_{AB} \times 10^5 \text{ (cm}^2\text{/sec)}$
0.0150	1.450
0.2548	1.439
0.4936	1.451
0.7656	1.755
0.9964	1.945

Table X. Mutual Diffusion Data for the
Chloroform (A) - Carbon Tetrachloride (B) System

X_A	$D_{AB} \times 10^5 \text{ (cm}^2\text{/sec)}$
0.0265	1.505
0.4311	1.644
0.7389	1.752
0.8255	1.796
0.0966	1.881
0.9418	1.972

APPENDIX VIII

Experimental Density and Viscosity Data at 25°C.

Table XI. Density and Viscosity Data for the Benzene (A) - Carbon Tetrachloride (B) System

X_A	η (Centipoise)	ρ (g/cc)
0.0	0.8888	1.5945
0.0301	0.8794	1.5639
0.1711	0.8393	1.4745
0.2953	0.7992	1.3902
0.5606	0.7205	1.2036
0.7864	0.6563	1.0386
1.0	0.5970	0.8736

Table XII. Density and Viscosity Data for the Chloroform (A) - Carbon Tetrachloride (B) System

X_A	η (Centipoise)	ρ (g/cc)
0.0	0.8888	1.5945
0.1118	0.8263	1.5744
0.2318	0.7611	1.5600
0.4915	0.6608	1.5322
0.8450	0.5680	1.4955
1.0	0.5401	1.4798

Table XIII. Density and Viscosity Data for the Ether (A) - Chloroform (B) - Carbon Tetrachloride (B) System

X_A	η (Centipoise)	ρ (g/cc)
0.0	0.6475	1.5307
0.1031	0.6298	1.4428
0.2501	0.5702	1.3288
0.3495	0.5189	1.2509
0.5010	0.4343	1.1370

NOMENCLATURE

A_{kj}	algebraic complement of the element, v_{kj} , in the G determinant
A_i	activity
B	constant in equations (100) and (101)
c_i	concentration of a species, (moles/cc)
c	number of components
C_i	concentration of a component (moles/cc)
D_{AB}	mutual diffusion coefficient (cm^2/sec)
D_i^*	tracer diffusion coefficient (cm^2/sec)
D_{im}	intrinsic diffusion coefficient (cm^2/sec)
D_{iv}	a diffusion coefficient defined relative to the volume fixed plant (cm^2/sec)
f_i	friction coefficient (cm)
G	determinant of stoichiometric coefficients
ΔH_m	heat of mixing (calories/mole)
ΔH_R	heat of reaction (calories/mole)
J_{im}	molar flux relative to the medium fixed reference plant
J_{iM}	molar flux relative to the mass fixed reference plane
J_{iN}	molar flux relative to the number fixed reference plane
J_{io}	molar flux relative to the component fixed reference plane

k	Boltzmann's constant
K	equilibrium constant
L	capillary length (cm)
M_i	molecular weight of the i -th component
ΔM_i	change in the number of moles of a component
Δm_i	change in the number of moles of a species
n	number of species
N	Avogadro's number
p^C	vapor pressure of a component
p	partial pressure
Q_{jk}	the j -th species taking part in the k -th association reaction
r_i	Stokes' radius of a molecule (equation (5))
r	number of association reactions
R	resistance of a glass frit to diffusion
R	universal gas constant
T	absolute temperature
U	function defined by equation (213)
$\bar{V}_i$	partial molar volume (cc/mole)
v_{iC}	velocity of the i -th species relative to the coordinate fixed plane
v_{im}	velocity of the i -th species relative to the medium fixed plane
v_{iM}	velocity of the i -th species relative to the mass fixed plane
v_{iN}	velocity of the i -th species relative to the number fixed plane

v_{iO}	velocity of the i-th species relative to the component fixed plane
v_{iV}	velocity of the i-th species relative to the volume fixed plane
v_{mC}	medium average velocity
v_{MC}	mass average velocity
v_{NC}	number average velocity
v_{OC}	component average velocity
v_{VC}	volume average velocity
X_i	mole fraction of a component
x_i	mole fraction of a species
Y	function defined by equation (140)
z	distance variable defined by Figure 6
Z	function defined by equation (183)
α_{jk}	function defined by equation (112)
β_n	parameter defined by equation (III-16)
Γ	a function of distance only
γ	activity coefficient
δ_k	the extent of reaction
η	viscosity
θ	time
λ_n	n-th root of equation (III-7)
μ	chemical potential
v_{jk}	stoichiometric coefficient of the j-th species in the k-th reaction
π	total vapor pressure

ρ	density
Ψ	a function of time only

Subscripts

A,B,C,	refer to components
i,j,k	running indexes
AVG	refers to the average value of a parameter
o	refers to a reference condition like standard state, zero time, etc.

Superscripts

*	refers to an isotopically labelled molecule
~	refers to a basic species (cluster)
o	refers to a psuedo quantity
c	refers to a component
n	refers to a species
u	refers to an unlabelled molecule of the labelled component in tracer diffusion

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