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KINETICS OF DIFFUSIONAL DROPLET GROWTH IN A LIQUID/LIQUID TWO-PHASE SYSTEM

BY

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Preface

This report contains experimental results for the interdiffusion coefficient of the system, succinonitrile + water, at a number of compositions and temperatures in the single phase region of the phase diagram. The concentration and temperature dependence of the measured diffusion coefficient has been analyzed in terms of Landau - Ginzburg theory, which assumes that the Gibbs free energy is an analytic function of its variables, and can be expanded in a Taylor series about any point in the phase diagram. At most points in the single phase region this is adequate. Near the consolute point (critical point of solution), however, the free energy is non-analytic, and the Landau - Ginzburg theory fails. The solution to this problem dictates that the Landau - Ginzburg form of the free energy be replaced by Widom scaling functions with irrational values for the scaling exponents. As our measurements of the diffusion coefficient near the critical point reflect this non-analytic character, we are preparing for publication in a refereed journal a separate analysis of some of the data contained herein as well as some additional measurements we have just completed. When published, reprints of this article will be furnished to NASA.

ABSTRACT

Interdiffusion coefficients may be determined using a variety of experimental techniques. In this study, the interdiffusion coefficients of succinonitrile and water were determined using the diaphragm cell method. Since succinonitrile and water form a non-ideal solution, their diffusion coefficients depend on concentration. This functional form was determined by varying the concentration of succinonitrile at a constant temperature of 60.0°C. The diffusion coefficient at the consolute point was also studied. Experiments based on the theory of the diaphragm cell were used to accurately determine the diffusion coefficient at the critical composition and at 60.0°C. When the temperature was lowered to the critical temperature, a decrease in the diffusion coefficient was observed.

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INTRODUCTION

There are four commonly measured transport properties of solutions: viscosity, conductivity, diffusion, and transference number. In diffusion, there is a transport, or flow, of mass across a concentration gradient. Several experimental techniques are available to determine the interdiffusion coefficient given by Fick's First Law.

$$J_i = -D_i \frac{\partial c_i}{\partial x} \qquad (1.1)$$

where J_i is the flux (moles/cm^2•s), D_i is the diffusion coefficient (cm^2/s) and $\partial c_i/\partial x$ is the concentration gradient (moles/cm^4) of the i^{th} component.

One of these methods is the diaphragm cell, which allows for diffusion by molecular motion but prevents bulk flow. For example, if a cylinder is half filled with a solution of copper sulfate and the rest is carefully filled with pure water so that no mixing occurs and there is a sharp boundary between the two layers, over time, the copper sulfate will diffuse into the water layer and water will likewise diffuse into the copper sulfate solution. Eventually, the solution in the cylinder will be of a uniform concentration. The mixing of the two solutions, however, may not be limited to diffusion, but may also be affected by the bulk flow of the solutions. Bulk flow will obviously occur if the solutions are physically mixed by stirring or vibration, but bulk flow can also occur more subtly by

convection due to temperature or density gradients. If bulk flow occurs, the rate at which mass transport occurs due to diffusion cannot be accurately calculated.

The diaphragm cell was originally proposed by Northrop and Anson[1] in 1928. Their design focused on separating the two diffusing solutions by a sintered glass frit. The frit, or diaphragm, would permit the diffusion of the components, but the small pore size would prevent convective flows. Later, McBain[2] and others modified this original design. McBain's cell was based on two sealed compartments separated by a frit. One difficulty with both of these designs, however, was that one could not be certain that the solutions above and below the frit were uniform in composition and that the concentration gradient was confined to the frit. It had to be assumed that the solutions above and below the frit would mix efficiently as a result of density changes alone. Moquin and Cathcart[3] demonstrated that this assumption was incorrect. They proved this by comparing the diffusion results of a cell which was mechanically stirred with one which was not stirred. They found large discrepancies between the two and concluded that without mechanical stirring, the top and bottom solutions would not be uniform. Their design, however, was unnecessarily complicated. Stokes[4] proposed a much simpler method of stirring the cells and his basic design is still widely used today.[5] Figure 1 represents the cell used by Stokes, as well as the cells used in this study. The top and bottom compartments are kept at a uniform concentration by stir bars sweeping along the surface of the diaphragm.

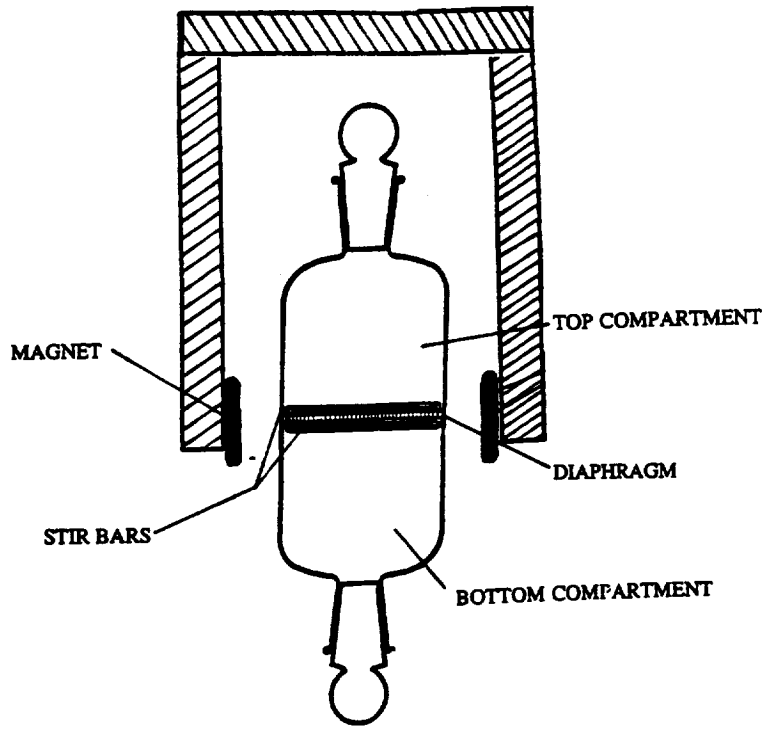

Figure 1. The Diaphragm Cell

In this study, the theory of the diaphragm cell was examined and the diaphragm cell method was applied to the determination of interdiffusion coefficients of succinonitrile and water solutions. The purpose of these experiments was to determine the interdiffusion coefficients, their concentration dependence, and their temperature dependence.

The theory of the diaphragm cell predicts that the measured interdiffusion coefficient will also depend on other variables, including, to a certain extent, the concentration difference between the two diffusing solutions. These variables were also examined.

The system of succinonitrile and water is an aqueous non-electrolyte system that demonstrates consolute (critical) point behavior as a function of composition and temperature. Therefore,

in addition to studying the diffusion of solutions above the coexistence curve, the diffusion coefficient was examined as the solution composition and temperature approached the consolute point. In this case, previous experiments and theory predict that as the consolute point is approached, the interdiffusion coefficient should approach zero.

Chapter II

DIAPHRAGM CELL THEORY

A. Introduction

As previously stated, interdiffusion is described by Fick's first law:

$$J_i = - D_i \frac{\partial c_i}{\partial x} \qquad (2.1)$$

We should point out that the diffusion coefficient in the equation above is called the interdiffusion coefficient. For the remainder of this paper, when the term diffusion coefficient is used, it is assumed to be the interdiffusion coefficient unless otherwise stated. There are, however, other diffusion coefficients with different definitions. Among the more common terms are trace diffusion, intradiffusion, tracer diffusion, and self diffusion coefficients. [6,7]

Trace diffusion is a special case of interdiffusion. The trace diffusion coefficient is the interdiffusion coefficient of a two component system where one component is at infinite dilution. Figure 2 illustrates the relationship between theses two terms where D_{AB} represents the interdiffusion coefficient, $D_A{}^oB$ and $D_{AB}{}^o$ are the trace diffusion coefficients when component A and component B, respectively, are infinitely dilute. The mole fraction of component, A, in the figure is χ_A.

The term intradiffusion coefficient was first introduced by Albright and Mills[6]. Previously, the term tracer (as opposed to trace) diffusion coefficient had been used to describe the diffusion

of a small amount of isotopically labeled (frequently, a radioisotope)

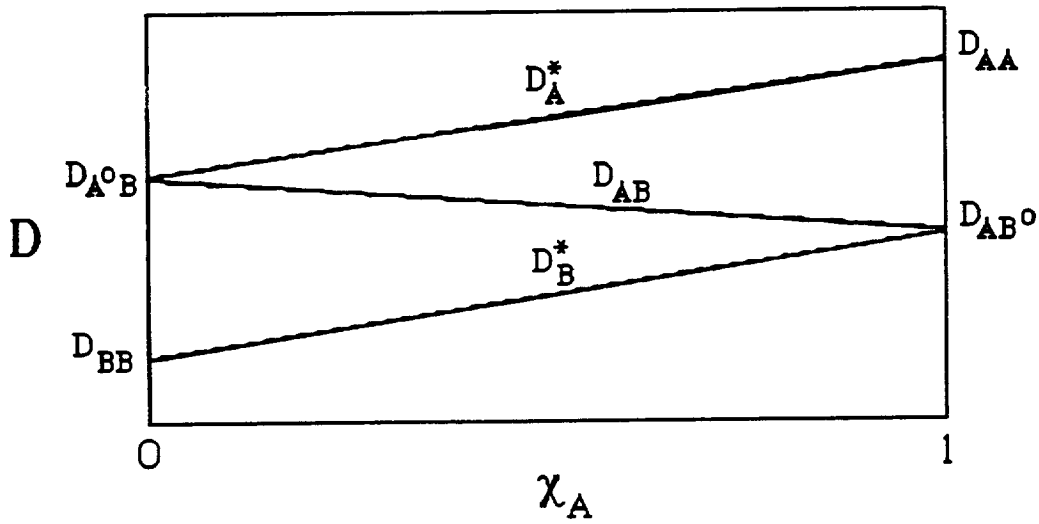

Figure 2. Schematic Representation of Various Diffusion Coefficients

species in a system. The term, "tracer diffusion coefficient", led to confusion, however, because the labeled species could be added to a single or multicomponent system and the unlabeled species did not necessarily have to be present in the system. To specify clearly the process occurring during their experiments, Albright and Mills defined intradiffusion coefficients. These coefficients only apply when a small amount of an isotopically labeled species is substituted for some of the unlabeled species in an otherwise homogeneous multicomponent system, creating a concentration gradient between the labeled and unlabeled species. Albright and Mills also noted that the tracer and intradiffusion coefficients would be numerically equal, but the new term would clarify the process by which the diffusion occurred. The tracer diffusion coefficient is represented as D^*_A and D^*_B in Figure 2.

Another term that describes a special case of diffusion is the self diffusion coefficient. Self diffusion applies to the diffusion of an isotopically labeled species which is added to a pure unlabeled sample of the species. In Figure 2, the self diffusion coefficients are D_{AA} and D_{BB}.

As already mentioned, diffusion that occurs in the water and succinonitrile system or any other two component system is described by an interdiffusion coefficient (some authors refer to it as a mutual diffusion coefficient). This diffusion coefficient is the same for both components in a fixed volume system such as the diaphragm cell, where there is no significant change in volume upon mixing. Mills and Woolf[8] provide a simple proof of this, which is outlined below.

In a two component system, the flux for each component, i, is given by Fick's first law, as in equation 2.1. When the molar flux, J_i, is converted to a volume flux by multiplying by the partial molar volume of each component, V_i, the sum of the two volume fluxes must be zero if the volume of the system is to remain constant. Therefore, we may write

$$J_1V_1=J_2V_2 \tag{2.2}$$

or,

$$-D_1V_1\frac{\partial c_1}{\partial x} = -D_2V_2\frac{\partial c_2}{\partial x} \tag{2.3}$$

Since the volume of the system may be written as

$$V = n_1V_1 + n_2V_2 \tag{2.4}$$

The terms, n_1 and n_2, are the number of moles of components 1 and 2 respectively. Dividing by volume puts the right hand side of equation 2.4 in terms of concentration:

$$1 = c_1V_1 + c_2V_2 \qquad (2.5)$$

Taking the derivative of this equation with respect to the spatial coordinate, x, yields

$$0 = V_1\frac{\partial c_1}{\partial x} + V_2\frac{\partial c_2}{\partial x} + c_1\frac{\partial V_1}{\partial x} + c_2\frac{\partial V_2}{\partial x} \qquad (2.6)$$

Using the Gibbs-Duhem equation, the last two terms can be shown to be zero. This leaves the first two terms which are now related by equation 2.7.

$$-V_1\frac{\partial c_1}{\partial x} = V_2\frac{\partial c_2}{\partial x} \qquad (2.7)$$

Comparing this result to equation 2.3, we see that, indeed, $D_1 = D_2$.

B. Simple Theory

Fick's first law is not particularity useful in the experimental determination of the diffusion coefficient in the diaphragm cell. Therefore, a theory of the cell should produce an equation that utilizes the measurable parameters in the experiment. The simplest treatment of the diaphragm cell theory is a stepping stone for a more rigorous treatment.

First, the frame of reference by which the flux will be measured must be established. One way to measure the flux in a diaphragm cell is along a spatial coordinate parallel to the axis of the cell. This would be a cell-fixed frame of reference. Since fluid in the diaphragm cell is confined by gravity to occupy a fixed volume, the flux measured from the cell's spatial frame of reference, i.e. the diaphragm, is the same as the flux measured with respect to a volume fixed frame of reference, if there is no volume change on mixing. This is not true, however, of a mass frame of reference,

since the center of mass must move in the diaphragm cell during diffusion. Therefore, the flux referred to henceforth is based on the cell or the volume fixed frame of reference.

Two more assumptions are necessary before the simple theory of the diaphragm cell can be reviewed. The first of these is that there is a steady concentration gradient throughout the diaphragm which forms the interface between the two compartments of the cell. Secondly, the diffusion coefficient is assumed to be constant and therefore independent of concentration. The latter assumption is not essential and is obviated in a more advanced theory which we shall derive subsequently.

Examination of Fick's first law from the perspective of these two assumptions, however, demonstrates that since the diffusion coefficient is constant, the concentration gradient is the same at every point within the frit. Additionally, since the concentration gradient is steady, the flux, J, at any point within the frit is also a constant.

The assumption that the concentration gradient, once established, will follow the relaxation of the concentration difference across the frit is also known as a "steady-state" approximation[5]. For this reason, the diaphragm cell is classified as a steady state method as opposed to other methods which measure interdiffusion with a variable concentration gradient. For example, the free interface method measures the concentration changes along a diffusion cell where two solutions of different concentration are brought in contact with one another. As diffusion occurs between the two solutions, the sharp concentration boundary between them

widens. The time development of this boundary layer is followed by optical interference methods which depend upon the concentration dependence of the refractive index of the solution. Specifically, in the interference method, coherent light rays passing through adjacent layers of solution have different optical path lengths and when joined produce an interference pattern.

The first step in deriving the simple theory of diffusion in a diaphragm cell is to write equations for the changes in concentration of the top and bottom compartments. Once the two compartments of the cell are filled with solution, and the concentration gradient is established, the change in the concentration of the top compartment, C_T, can be represented mathematically as the number of moles of solute entering the top compartment per unit time, JA, divided by the volume of the top compartment, V_T

$$\frac{dC_T}{dt} = \frac{JA}{V_T} \tag{2.8}$$

where A represents the cross sectional area of the frit, V_T, the volume of the top compartment and J as the flux in units of $(moles/cm^2 \cdot s)$.

Likewise, the change in concentration of the bottom compartment is related to the flux of solute molecules out of the bottom by

$$\frac{dC_B}{dt} = \frac{-JA}{V_B} \tag{2.9}$$

where C_B and V_B are, respectively, the concentration and volume of the bottom compartment.Using Fick's first law and looking at the

concentration gradient across the entire frit with an effective thickness, ℓ, the flux can be expressed as

$$J = - D\frac{\partial c}{\partial x} = - D\frac{(C_B - C_T)}{\ell} \tag{2.10}$$

Subtracting the rate of concentration change in the top from the rate of concentration change in the bottom we have

$$\frac{d(C_B - C_T)}{dt} = -JA\left(\frac{1}{V_B} + \frac{1}{V_T}\right) \tag{2.11}$$

and solving for J

$$J = \frac{-d(C_B - C_T)}{dt}\frac{1}{A\left(\frac{1}{V_B} + \frac{1}{V_T}\right)} \tag{2.12}$$

Setting the two flux terms equal

$$\frac{-d(C_B - C_T)}{dt}\frac{1}{A\left(\frac{1}{V_B} + \frac{1}{V_T}\right)} = -D\frac{(C_B - C_T)}{\ell} \tag{2.13}$$

then separating variables and integrating from t = 0 to some time, t

$$\ln\frac{(C_{B(0)} - C_{T(0)})}{(C_{B(t)} - C_{T(t)})} = \frac{DA}{\ell}\left(\frac{1}{V_B} + \frac{1}{V_T}\right)t \tag{2.14}$$

This equation requires that the term, ℓ, the effective length of the frit, be known. Since the frit consists of a porous glass material, the path length or effective length is not simply the outside thickness of the frit. Therefore an indirect method of determining this length is to set all of the cell's parameters equal to one constant, which can be empirically determined for the cell:

$$\beta = \frac{A}{\ell}\left(\frac{1}{V_B} + \frac{1}{V_T}\right) \tag{2.15}$$

This reduces the equation for diffusion for the diaphragm cell to

$$\ln\left[\frac{(C_{B(0)} - C_{T(0)})}{(C_{B(t)} - C_{T(t)})}\right] = \beta D t \qquad (2.16)$$

The cell constant, β, is determined by calibration with a solution that has a well established diffusion coefficient. Stokes[4,9] performed much of this work on calibrating cells in 1950 and these techniques are still used today[5]. The cell constant is determined by allowing a 0.5M potassium chloride solution to diffuse into pure water over a period of time. The cell constant is then calculated by substituting the initial and final concentration differences, the time in seconds of the diffusion experiment, and the diffusion coefficient for the 0.5 M KCl solution into equation 2.16.

This treatment of the diffusion equation is based on some assumptions that are rarely correct. In particular, the diffusion coefficient is not independent of concentration in a non-ideal solution.

Ideal solutions are said to follow Raoult's law and will have uniform intermolecular forces. In other words, the intermolecular forces of the components making up an ideal solution cannot be differentiated and solutions made up of similar molecules such as benzene and toluene do exhibit ideal behavior.

Most solutions, however, are not ideal and the assumption that their diffusion coefficients are independent of concentration is not valid. For this reason, a theory to treat concentration dependent diffusion coefficients was developed by Gordon[10] and by Stokes[9].

C. The Theories of Gordon and Stokes

Gordon[10] realized that for a non-ideal solution, the diffusion coefficient in equation 2.16 was not the actual diffusion coefficient, D(c), for a particular concentration, c, but was instead, an average over time of all diffusion coefficients present within the diaphragm. Therefore, Gordon proposed a relationship between D(c) and D = D', the integral (average) diffusion coefficient measured in equation 2.16. This relationship is given in equation 2.17.

$$D' = \frac{1}{(\bar{C}_B - \bar{C}_T)} \int_{\bar{C}_T}^{\bar{C}_B} D(c)\, dc \qquad (2.17)$$

The symbols $\bar{C}_B$ and $\bar{C}_T$ represent the bottom and top compartments' arithmetic mean concentration over the length of the diffusion experiment. In this equation, D' represents an approximation to the average of the actual diffusion coefficients present in the diaphragm over time and is not exact. The concentrations, $\bar{C}_B$ and $\bar{C}_T$, do not represent the time average concentrations present over the length of the run because the concentrations change rapidly at first and then less rapidly as the concentrations approach one another. The actual average over time of concentrations present in either compartment probably lies closer to the final concentration than the arithmetic mean concentration does.

Although it is not exact, Gordon and Stokes claimed that this approximation could be used to produce results accurate to within .02%. A summary of the technique used by Stokes is presented below.

First, the general form of the actual diffusion coefficient is represented graphically as in Figure 3. This figure is not meant to represent the exact form of the diffusion coefficient. In fact, the exact nature of D(c) is not known at this time in the development of this method. If we set up a diffusion experiment such that the initial concentrations for the top and bottom are $C_{T(0)}$ and $C_{B(0)}$ respectively, and the final concentrations are $C_{T(t)}$ and $C_{B(t)}$, then, when the compartments are of equal volume, the mean concentrations of the top and bottom compartments are $\bar{C}_T$ and $\bar{C}_B$, as shown in Figure 3.

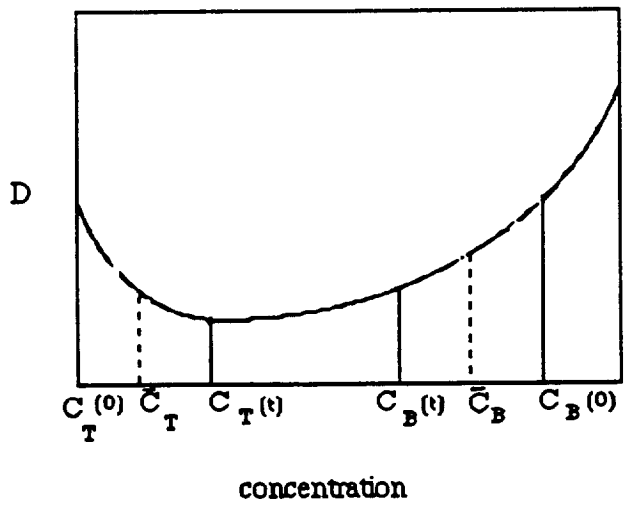

Figure 3. Diffusion Coefficient versus Concentration

By equation 2.17, the integral diffusion coefficient, D', is just the mathematical average of D(c) between $\bar{C}_T$ and $\bar{C}_B$. Notice, however, that the final and mean concentrations depend on how long the diffusion experiment runs.

Next a hypothetical diffusion experiment is used such that the top compartment is filled with pure solvent, i.e. $C_{T(0)}=0$, and the

bottom compartment is filled with some concentration, c. This hypothetical experiment is allowed to run for an infinitely short period of time, thus the hypothetical nature of the experiment. The average concentrations of the top and bottom would be be the same as the initial concentrations, 0 and c respectively. Using equation 2.17, the integral diffusion coefficient for this hypothetical run would be given by

$$D'^{\circ} = \frac{1}{c} \int_0^c D(c)\ dc \tag{2.18}$$

where the superscript represents the infinitely short nature of this run.

Writing equations for two such experiments where the bottom concentrations are $\bar{C}_B$ and $\bar{C}_T$ from Figure 1, we get

$$D'^{\circ}(\bar{C}_T) = \frac{1}{\bar{C}_T} \int_0^{\bar{C}_T} D(c)\ dc \tag{2.19}$$

$$D'^{\circ}(\bar{C}_B) = \frac{1}{\bar{C}_B} \int_0^{\bar{C}_B} D(c)\ dc \tag{2.20}$$

Equation 2.20 may also be written as

$$D'^{\circ}(\bar{C}_B) = \frac{1}{\bar{C}_B} \left[\int_0^{\bar{C}_T} D(c)\ dc + \int_{\bar{C}_T}^{\bar{C}_B} D(c)\ dc \right] \tag{2.21}$$

The two integrals in this equation may be substituted with other terms. Equation 2.19 is substituted for the first integral in equation 2.21 and equation 2.17 is substituted for the second integral. The result of these substitutions is equation 2.22.

$$D'^{\circ}(\bar{C}_B) = \frac{1}{\bar{C}_B} [\bar{C}_T\ D'^{\circ}(\bar{C}_T) + (\bar{C}_B - \bar{C}_T)D'] \tag{2.22}$$

Simplifying this further, the following equation represents one of Stokes's central results used in approximating values for D(c):

$$D'^{\circ}(\bar{C}_B) = D' - \frac{\bar{C}_T}{\bar{C}_B}\left[D' - D'^{\circ}(\bar{C}_T)\right] \qquad (2.23)$$

Next, D' versus concentration is plotted and extrapolated to infinite dilution. The values of $\bar{C}_B$, $\bar{C}_T$, and D' in equation 2.23 are taken from actual runs. Then, using the curve of D' versus concentration, a value for $D'^{\circ}(\bar{C}_T)$ is obtained by assuming it is approximately equal to $D'(\bar{C}_T)$. Substituting these four values into equation 2.23, produces a value for $D'^{\circ}(\bar{C}_B)$. After repeating this procedure for each of diffusion experiment, at each concentration, $\bar{C}_B$, it is possible to graph $D'^{\circ}(\bar{C}_B)$ versus $\bar{C}_B$. Stokes's $D'^{\circ}(\bar{C}_B)$ results were within 1 % of the values for D' that he had previously plotted.

When the derivative of equation 2.18 is taken, the result is equation 2.24.

$$D(c) = D'^{\circ} + c\frac{dD'^{\circ}}{dc} \qquad (2.24)$$

Equation 2.24 is used to find the actual diffusion coefficient. Since the derivative of this equation is the slope of the D'° at some concentration, all of the terms in equation 2.24 can be taken from the graph of D'°.

Stokes tested his results for D(c) by running experiments in which the top compartment was filled with a solution of known concentration, not pure solvent. Then he compared the value of D' he measured, with the value of D' he expected to get by integrating his curve of D(c) between the two mean concentrations as in equation 2.17. He found excellent agreement between the two values of D'.

D. Baird's Theory

A more rigorous theory of the diaphragm cell was developed by Baird[11,12]. In this theory, the diffusion equation has been evaluated in terms of a new variable, average concentration of the cell. The derivation of the general case, when the top and bottom compartments are not necessarily equal in volume, is presented below.

The volume average concentration within the diaphragm cell is a constant[10] throughout the length of the diffusion experiment and may be represented as

$$\overline{c} = \frac{(V_B C_{B(t)} + V_T C_{T(t)})}{(V_B + V_T)} \tag{2.25}$$

Also, the time rate of change of concentration in the top and bottom compartments is rewritten from equation 2.8 and 2.9

$$\frac{dC_T}{dt} = \frac{JA}{V_T} \tag{2.26}$$

$$\frac{dC_B}{dt} = \frac{-JA}{V_B} \tag{2.27}$$

Fick's law is also rewritten, but now, represents the concentration dependent nature of the diffusion coefficient

$$J = -D(c)\frac{\partial c}{\partial x} \tag{2.28}$$

After seperating variables and preparing for integration, the equation becomes

$$\int_0^{\ell} J dx = -\int_{C_{T(t)}}^{C_{B(t)}} D(c) dc \tag{2.29}$$

Because J is independent of x, the left hand side of equation 2.29 may be integrated, but without knowing the form of D(c), the right hand side cannot be integrated at this time. Continuing on as in the simple theory, equations 2.26 and 2.27 are subtracted to yield

$$\frac{d[C_{B(t)}-C_{T(t)}]}{dt} = -JA\left(\frac{1}{V_B}+\frac{1}{V_T}\right) \qquad (2.30)$$

Using equation 2.29 to substitute for J, and equation 2.15 to substitute for the cell constant, equation 2.30 becomes

$$\frac{d[C_{B(t)}-C_{T(t)}]}{dt} = -\beta \int_{C_{T(t)}}^{C_{B(t)}} D(c)dc \qquad (2.31)$$

At this point the integral in equation 2.31 is prepared for a Taylor series expansion about $\bar{c}$, by substituting for $C_B(t)$, $C_T(t)$, and dc. Defining the concentration as $c=y+\bar{c}$, we get dy=dc because $\bar{c}$ is constant. The upper integral limit becomes $C_B=y+\bar{c}$, and solving in terms of y, $y=C_B-\bar{c}$. Substituting for c as given in equation 2.25, the upper and lower limits become

$$y = \frac{V_T(C_B-C_T)}{V_T+V_B} \qquad (2.32)$$

$$y = -\frac{V_B(C_B-C_T)}{V_T+V_B} \qquad (2.33)$$

To simplify expansion and integration, a new variable, x, is defined such that $x=(C_B-C_T)/(V_B+V_T)$, or $x=\Delta c/(V_B+V_T)$. Equation 2.31 is now

$$\frac{d\Delta c}{dt} = (V_B+V_T)\frac{d(x)}{dt} = -\beta \int_{-V_Bx}^{V_Tx} D(y+\bar{c})dy \qquad (2.34)$$

Expanding $D(y+\bar{c})$ in a Taylor series about $\bar{c}$ yields

$$D(y+\bar{c}) = D(\bar{c}) + D^{(1)}(\bar{c})y + \frac{D^{(2)}(\bar{c})\,y^2}{2!} + \sum_{n=3}^{\infty} \frac{D^{(n)}(\bar{c})\,y^n}{n!} \tag{2.35}$$

Substituting equation 2.35 into the integral of equation 2.34 and then integrating, the result is

$$\int_{-V_B x}^{V_T x} D(y+\bar{c})\,dy = D(\bar{c})\,[V_B+V_T]\,x + \frac{D^{(1)}(\bar{c})}{2}\left[V_T^2 - V_B^2\right]x^2 + \sum_{n=2}^{\infty} \frac{D^{(n)}(\bar{c})}{(n+1)!}\left[(V_T)^{n+1} - (-V_B)^{n+1}\right] x^{n+1} \tag{2.36}$$

When the expression for x is substituted back into equation 2.36, the result is

$$\frac{d\Delta c}{dt} = -\beta D(\bar{c})\Delta c\left[1 + \sum_{n=1}^{\infty} \frac{D^{(n)}(\bar{c})}{D(\bar{c})(n+1)!} \frac{(V_T^{n+1} - (-V_B)^{n+1})}{(V_T+V_B)^{n+1}} \Delta c^n\right] \tag{2.37}$$

Since $(dt/d\Delta c)=1/(d\Delta c/dt)$, taking the reciprocal of equation 2.37 yields

$$\frac{dt}{d\Delta c} = \left(\frac{1}{-\beta D(\bar{c})\Delta c}\right) \frac{1}{\left[1 + \sum_{n=1}^{\infty} \frac{D^n(\bar{c})}{(n+1)!D(\bar{c})} \frac{(V_T^{n+1} - (-V_B)^{n+1})}{(V_T+V_B)^{n+1}} \Delta c^n\right]} \tag{2.38}$$

Expanding the second term on the right in a geometric series such that $\frac{1}{(1+Z)} = 1 - Z + Z^2 - Z^3 + \ldots$, then equation 2.38 may be rewritten

in terms of this series. After grouping like ordered terms, the diaphragm cell diffusion equation is:

$$\frac{dt}{d\Delta c} = \frac{1}{-\beta D(\bar{c})\Delta c}\left[1 - \left(\frac{D^{(1)}(\bar{c})(V_T^2-V_B^2)}{2D(\bar{c})(V_T+V_B)^2}\right)\Delta c + \right.$$

$$\left.\left(\frac{-D^{(2)}(\bar{c})(V_T^3+V_B^3)}{3!D(\bar{c})(V_T+V_B)^3} + \left[\frac{D^{(1)}(\bar{c})V_T^2-V_B^2}{2D(\bar{c})(V_T+V_B)^2}\right]^2\right)\Delta c^2 + \cdots \right. \tag{2.39}$$

When the left side is integrated from 0 to t and the right from $\Delta C_{(o)}$ to $\Delta C_{(t)}$, the equation becomes

$$t = \frac{1}{\beta D(\bar{c})}\ln\frac{\Delta C_0}{\Delta C_t} - \left[\frac{D^{(1)}(\bar{c})}{2!\beta(D(\bar{c}))^2}\frac{(V_T^2-V_B^2)}{(V_T+V_B)^2}\right](\Delta C_{(0)} - \Delta C_{(t)})$$

$$+ \left[\frac{-D^{(2)}(\bar{c})}{2\cdot 3!\beta D(\bar{c})^2}\frac{(V_T^3-V_B^3)}{(V_T+V_B)^3} + \frac{1}{2\beta D(\bar{c})}\left(\frac{D^{(1)}(\bar{c})}{2!(D(\bar{c}))}\frac{(V_T^2-V_B^2)}{(V_T+V_B)^2}\right)^2\right]((\Delta C_{(0)})^2 - (\Delta C_{(t)})^2)$$

$$+ \cdots \tag{2.40}$$

This is the general diaphragm cell equation. It can be evaluated further for the special case when $V_T = V_B$. When this is true, the coefficients of all odd ordered powers of ΔC are zero, and the diffusion equation becomes

$$t = \frac{1}{\beta D(\bar{c})}\ln\frac{\Delta C_0}{\Delta C_t} - \frac{D^{(2)}(\bar{c})}{48\beta D(\bar{c})^2}((\Delta C_{(0)})^2 - (\Delta C_{(t)})^2) + \cdots \tag{2.41}$$

The most significant result of this equation is found by comparing it to the equation 2.16 for the simple diaphragm cell theory equation, which assumed no dependence of D on concentration. If this is the

case, equation 2.41 may be rewritten with D(c) = D', and becomes simply

$$t = \frac{1}{\beta D'} \ln \frac{\Delta C_{(o)}}{\Delta C_{(t)}} \qquad (2.42)$$

since all concentration derivatives are zero. Thus in the case that the diffusion coefficient does not depend upon concentration, the rigorous equation reduces to equation 2.42.

When D is a function of concentration, however, all of the higher order terms become correction terms that depend on the nature of $D(\bar{c})$. These correction terms are an infinite series and for the case where $V_T = V_B$ are limited to the even powers of Δc. Baird has pointed out that the number of correction terms that should be included is left to the experimenter to determine but in any case, should never exceed the number of data points.[11,12] Hall and Knight[13] state that in an infinite series such as the equation 2.41, if $\Delta C_{(0)}$ is small enough, then we may choose the last term kept and be assured that the sum of all terms that follow is some small fraction of the last term.

E. The Second Ordered Term

Without a priori knowledge of the nature of D(c), the experimenter does not know how many data points must be taken or how many correction terms to include. Therefore, an examination of the second ordered term was made to see what effect this term might have on the measured diffusion coefficient. The hope was that by evaluating the second ordered term, experimental conditions could be determined so that the effect of

this term, or any higher ordered term, would be negligible. We started with equation 2.41 and, dropping the terms that contribute to any correction greater that the second order, we have

$$t = \frac{1}{\beta D(\bar{c})} \ln\frac{\Delta C_{(0)}}{\Delta C_{(t)}} - \frac{D^{(2)}(\bar{c})}{48\beta D(\bar{c})^2}((\Delta C_{(0)})^2 - (\Delta C_{(t)})^2) \qquad (2.43)$$

Also, from the simple theory of the diaphragm cell we have

$$t = \frac{1}{\beta D'} \ln\frac{\Delta C_{(0)}}{\Delta C_{(t)}} \qquad (2.44)$$

where D' represents the measured diffusion coefficient. Then setting the two equations equal we have

$$\frac{1}{\beta D'} \ln\frac{\Delta C_{(0)}}{\Delta C_{(t)}} = \frac{1}{\beta D(\bar{c})} \ln\frac{\Delta C_{(0)}}{\Delta C_{(t)}} - \frac{D^{(2)}(\bar{c})}{48\beta D(\bar{c})^2}((\Delta C_{(0)})^2 - (\Delta C_{(t)})^2) \qquad (2.45)$$

Factoring out $(1/\beta)\ln(\Delta C_{(0)}/\Delta C_{(t)})$ we have

$$\frac{1}{D'} = \frac{1}{D(\bar{c})} - \frac{D^{(2)}(\bar{c})}{48(D(\bar{c}))^2} \frac{(\Delta C_{(0)}^2 - \Delta C_{(t)}^2)}{\ln(\Delta C_{(0)}/\Delta C_{(t)})} \qquad (2.46)$$

Replacing the coefficient of the second order term, $D^{(2)}_{(\bar{c})}/48D_{(\bar{c})}^2$, with A and factoring out $(\Delta C_{(0)})^2$, the equation may be represented as

$$\frac{1}{D'} = \frac{1}{D(\bar{c})} - A\,(\Delta C_{(0)})^2 \frac{[((\Delta C_{(t)})^2/(\Delta C_{(0)})^2) - 1]}{\ln(\Delta C_{(0)}/\Delta C_{(t)})} \qquad (2.47)$$

Replacing the term $\frac{[((\Delta C_{(t)})^2/(\Delta C_{(0)})^2) - 1]}{\ln(\Delta C_{(0)}/\Delta C_{(t)})}$ with f(x) where $x=\Delta C_{(0)}/\Delta C_{(t)}$ and $f(x) = (x^{-2} - 1)/\ln(x)$.

$$\frac{1}{D'} = \frac{1}{D(\bar{c})} - A\,(\Delta C_{(0)})^2 f(x) \qquad (2.48)$$

Noting that the coefficient term, A, depends only on D(c) evaluated at $\bar{c}$ and that $\Delta C_{(0)}$ is determined by the experimental conditions, we can evaluate the second order correction term by examining the nature of f(x). A plot of this function is shown in Figure 4. The values of x can vary from 1 (when t=0), to infinity (when $\Delta C_{(t)}$ approaches zero at equilibrium). When x=1, the function f(x), is an indeterminate form, but by L'Hopitals Rule, its value is calculated as -2. As x increases, f(x) approaches 0.

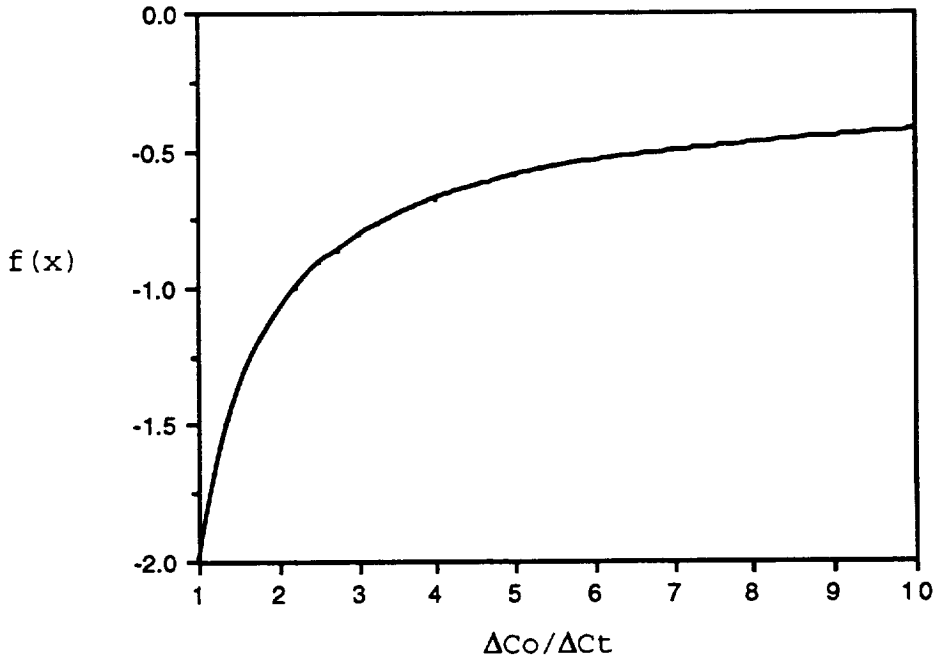

Figure 4. The Diminishing Second Order Term

From Figure 4, it is apparent that any second order effects are diminished as the diffusion experiment proceeds, i.e., $\Delta C_{(0)}/\Delta C_{(t)}$ increases. If the experiment is allowed to run for a period of time such that x is very large, then f(x) would be small. In order to determine the total effect of allowing the experiment to run a very

long period of time, we compared two examples where the value of A is some unknown constant.

In the first example, $\Delta C_{(0)}$ equals 0.5M and the diffusion experiment runs until $\Delta C_{(t)}$ is approximately 0.167M so that x = 3 and f(x) = -0.4. Substituting these two values into the second ordered term, we see it becomes -0.2A. In the second case, we set $\Delta C_{(0)}$ = 5.0M. In order to see the same second order effect as in the first case, f(x) must equal -0.008 which translates to a value of 5×10^{-50}M for $\Delta C_{(t)}$. This is clearly beyond the sensitivity of any analytical method. We, therefore, conclude that the easiest way to control the second order effect without some prior knowledge of A, i.e. $D(\bar{c})$, is to minimize $\Delta C_{(0)}$ within the limits of the analytical methods available to measure concentrations. Additionally, unless $\frac{D^{(2)}(\bar{c})}{48D(\bar{c})^2}$ is small, we may still find a second order effect that we cannot diminish without extremely accurate quantitative techniques.

F. n^{th} Ordered Term

When we examine the diffusion equation in the form stated earlier, we note it is an infinite series:

$$\frac{dt}{d\Delta c} = \frac{1}{-\beta D(\bar{c})\Delta c}[1 - Z + Z^2 - Z^3 + \ldots] \qquad (2.49)$$

We also note that Z is a representation of an infinite series such that

$$Z = \sum_{n=1}^{\infty} \frac{D^n(\bar{c})}{(n+1)!D(\bar{c})} \frac{(V_T^{n+1} - (-V_B)^{n+1})}{(V_T + V_B)^{n+1}} \Delta C^n = \sum_{n=1}^{\infty} a_n x^n \qquad (2.50)$$

By using the multinomial theorem[14], we are able to arrive at a means of determining the coefficient of any n^{th} ordered term

without manually expanding both of these series to such a point that all possible n^{th} ordered terms are included.

First, if we consider the multinomial theorem which states that the coefficient, A_n, of the n^{th} order term in the multinomial expansion of $(a_1x^1+a_2x^2+a_3x^3+...)^p$, where p is a positive integer, is given by the formula

$$A_n = \sum \frac{p!}{m_1!\, m_2!\, \ldots m_j!} \left[a_1^{m_1}\, a_2^{m_2} \ldots\, a_j^{m_j} \right] \qquad (2.51)$$

The sum is taken over m_1 to m_j such that the following conditions on m_j are met:

$$1)\ p = \sum m_j \qquad \text{for } j=1 \text{ to } n-p+1$$

$$2)\ n = \sum j m_j \qquad \text{for } j=1 \text{ to } n-p+1$$

The symbol m_j refers to the number of times the jth ordered term of the polynomial is used to generate the nth ordered term of the expansion. For example, in squaring the polynomial above (p = 2)there are two ways to generate the 4^{th} ordered term. In the first case, one must use the term a_2x^2 two times ($m_2 = 2$), and in the second case, one must use a_1x^1 once along with a_3x^3 once ($m_1=1, m_3=1$). The whole nth ordered term can thus be represented as

$$A_n\, x^{\,m_1 + 2m_2 + \ldots jm_j} = A_n x^n \qquad (2.52)$$

This holds true for an infinite series where the power, p, to which the polynomial is raised is fixed. In the case of the diaphragm cell equation, however, we have an infinite series of these polynomials, represented by Z. Within this series, the polynomials are raised to all possible powers. We must not only sum the possible coefficients for a particular term when the multinomial is raised to a power, p, but

also include all possible powers to which the mulitnomial may be raised.

$$A_n = \sum_{p=1}^{n} \sum \frac{p!}{m_1!\, m_2!\, \ldots m_j!} \left[a_1^{m_1}\, a_2^{m_2} \ldots\, a_j^{m_j} \right] \qquad (2.53)$$

The first sum is taken from p=1 to an upper limit of p=n. This limit has been set to exclude any coefficient terms which could not possibly contribute to the n^{th} order coefficient. For example, in a search for all contributing components of the 7th order coefficient (n=7), we can exclude any term of the 8th order expansion or higher. The second sum is taken with the same conditions as we applied to equation 2.51.

Our formula for calculating the nth ordered coefficient is useful if there were some easy way of calculating all values of m_j such that the conditions of $[m_j]^p$ are met. Fortunately, the groups of m_j, known as partitions and represented by π, meeting the conditions of $[m_j]^p$ are tabulated by Abramowitz and Stegun.[14] Abramowitz and Stegun have also gone to some length to provide n^{th} order coefficient solutions to more complex multinomials but do not include a general formula for a multinomal resembling ours. With the partitions tabulated by Abramowitz and Stegun, it is possible to determine the factor $p!/m_1!m_2!\ldots m_j!$. These factors are shown in Table 1 for all partitions up to an 8th order expansion of our multinomial. The term M, represents $p!/m_1!m_2!\ldots m_j!$. Additionally, using the table of partitions, the correct coefficients of the terms in the polynomial, a_1, a_2, etc. may be selected. In the case of the diffusion equation, these coefficients refer to the terms in the expression for Z as given in equation 2.50.

Table 1. Partitions and Coefficients

n	p	π	M
1	1	1	1
2	1	2	1
	2	1^2	1
3	1	3	1
	2	1,2	2
	3	1^3	1
4	1	4	1
	2	1,3	2
		2^2	1
	3	1^2,2	3
	4	1^4	1
5	1	5	1
	2	1,4	2
		2,3	2
	3	1^2,3	3
		1,2^2	3
	4	1^3,2	4
	5	1^5	1
6	1	6	1
	2	1,5	2
		2,4	2
		3^2	1
	3	1^2,4	3
		1,2,3	6
		2^3	1
	4	1^3,3	4
		1^2,2^2	6
	5	1^4,2	5
	6	1^6	1
7	1	7	1
	2	1,6	2
		2,5	2
		3,4	2
	3	1^2,5	3
		1,2,4	6
		1,3^2	3
		2^2,3	3
	4	1^3,4	4
		1^2,2,3	12
		1,2^3	4
7	5	1^4,3	5
		1^3,2^2	10
	6	1^5,2	6
	7	1^7	1
8	1	8	1
	2	1,7	2
		2,6	2
		3,5	2
		4^2	1
	3	1^2,6	3
		1,2,5	6
		1,3,4	6
		2^2,4	3
		2,3^2	3
	4	1^3,5	4
		1^2,2,4	12
		1^2,3^2	6
		1,2^2,3	12
		2^4	1
	5	1^4,4	5
		1^3,2,3	20
		1^2,2^3	10
	6	1^5,3	6
		1^4,2^2	15
	7	1^6,2	7
	8	1^8	1

Also note that this is a general solution to the general diaphragm cell equation. If we look at the special case were V_1 equals V_2, we may use the same solution but drop the odd ordered terms of Z. For example, if we want to determine the fourth ordered term using Table 1, we select all partitions for n = 4. There are 5 different possibilities but three of these can be dropped because they include odd partitions. The odd partitions for the case where $V_1 = V_2$ result
in the volumes in the numerator cancelling each other out. Therefore, the fourth ordered coefficient becomes

$$[\sum\sum M(a_1x^1a_2x^2\ldots a_j^{mj})]\Delta c^4 =$$

$$\left[\left[\frac{-D^{(4)}(\bar{c})}{4\cdot 5!\beta D(\bar{c})^2}\frac{1}{2^4}\right]+\frac{1}{2\beta D(\bar{c})}\left[\frac{D^{(2)}(\bar{c})}{3!(D(\bar{c}))^2}\frac{1}{2^2}\right]^2\right]((\Delta C_{(0)})^4 - (\Delta C_{(t)})^4) \tag{2.54}$$

G. Concluding Remarks on The Diaphragm Cell Theories

The theories of Gordon[10], Stokes[9], and Baird[11,12] point out several factors that influence the value of D' as measured experimentally using the simple theory diaphragm cell equation. The theories have been derived differently yet result in many of the same conclusions about the value of D' with respect to different experimental factors.

First, Gordon and Stokes imply that D' is affected by the length of the experiment since the length of the diffusion run affects how much of the D(c) curve is being averaged. Two experiments, initially identical, would be expected to yield different D' values if they ran for different lengths of time because they would have different

mean, as well as final, concentrations. Baird's theory states this explicitly, as we can see from the term $\Delta C_{(t)}$ appearing after integration of equation 2.39.

Secondly, $\Delta C_{(0)}$ is also important in both theories. If we look at Gordon's assumption that D' is an average of the actual diffusion coefficients present in the diaphragm over time, then as $\Delta C_{(0)}$ approaches zero, $\Delta C_{(t)}$ approaches zero, and the diffusion coefficient, D', approaches the actual diffusion coefficient D(c) at this concentration. This is illustrated graphically in Figure 5. This effect of $\Delta C_{(0)}$ is also explicitly stated in Baird's theory, since all correction terms involve $\Delta C_{(0)}$. As $\Delta C_{(0)}$ approaches zero, the correction terms also approach zero and D', the measured diffusion coefficient, approaches $D(\bar{c})$.

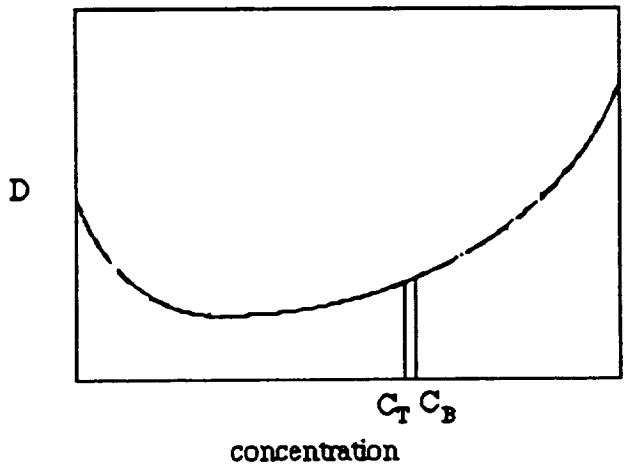

Figure 5. The Effect on D' as ΔC Diminishes

If we examine the effect of $\Delta C_{(0)}$ more closely, we see a difference between the two theories. If we begin with Gordon and Stokes, we can compare two hypothetical experiments with ΔC's, as

illustrated in Figure 6. In experiment 1, the curve of D(c) is rather flat in the region of $\Delta C_{(t)}$. Therefore, regardless of the magnitude of $\Delta C_{(t)}$, the average (measured) diffusion coefficient D' will closely resemble the value of D(c). Next, if we look at experiment 2, we see that with the same $\Delta C_{(t)}$ given, there is less agreement between the average diffusion coefficient, D', and the value of D(c) because the slope is so great. In other words, the first derivative of D(c) between the average top and bottom concentrations also plays a role in how well D' represents D(c).

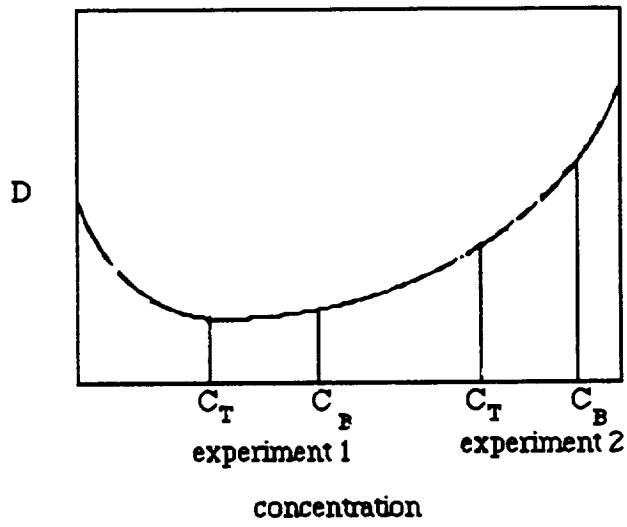

Figure 6. The Effect of Slope on D'

In Baird's theory, there are no odd order derivative terms when $V_1 = V_2$. Instead, it is the second and higher even order derivatives that influence whether or not D' resembles $D(\bar{c})$. The source of this discrepancy is not immediately clear. Nor is it apparent how significant this difference actually is. Despite this one

difference, both theories point out factors effecting D' that were not apparent in the simple theory.

H. Thermodynamic Theories of Diffusion

The theories discussed so far are based on a kinetic approach to diffusion. This is the basis of Fick's Law. This approach, while allowing us to determine experimentally the diffusion coefficients as a function of concentration, does not explain or predict the behavior of the diffusion coefficient as a function of concentration. Additionally, when the diffusion of liquids with critical point behavior is studied, the diffusion coefficient is found to drop to zero as the critical temperature, T^c, is approached. This phenomena is not addressed in Fick's law.

A more general approach to diffusion is based on thermodynamics. One of the first theories founded upon the thermodynamic properties of solutions was developed by Onsager[15]. In fact, Onsager predicted diffusion coefficients would approach zero as the critical temperature and composition are approached, before it was observed experimentally.

Turner[16,17] developed a simple approach that will be reviewed here. In Turner's theory, molecules move around as a result of forces acting upon them. For isothermal interdiffusion, the force is the chemical potential gradient, and the velocity of molecules is proportional to this force. More specifically, when u_i is the mobility of component i, and $\frac{\partial \mu_i}{\partial x}$ is the chemical potential gradient, then the velocity of component i is given by

$$v_i = u_i \frac{\partial \mu_i}{\partial x} \tag{2.55}$$

Also, the flux of component i is $J_i = c_i v_i$ so the flux, written in terms of chemical potential is

$$J_i = c_i\, u_i \frac{\partial \mu_i}{\partial x} \tag{2.56}$$

Converting chemical potential to activity, the term for flux becomes

$$J_i = u_i\, c_i\, RT \frac{d\ln a_i}{dx} \tag{2.57}$$

This equation may also be written as

$$J_i = u_i\, c_i\, RT \frac{d\ln a_i}{d\ln \chi_i} \frac{d\ln \chi_i}{d\ln c_i} \frac{d\ln c_i}{dx} \tag{2.58}$$

Where χ_i represents mole fraction. This equation reduces to

$$J_i = u_i\, RT \frac{d\ln a_i}{d\ln \chi_i} \frac{d\ln \chi_i}{d\ln c_i} \frac{dc_i}{dx} \tag{2.59}$$

When this equation is compared to Fick's law, the expression for D_i becomes

$$D_i = u_i\, RT \frac{d\ln a_i}{d\ln \chi_i} \frac{d\ln \chi_i}{d\ln c_i} \tag{2.60}$$

This expression predicts that the diffusion coefficient equals zero at the consolute point since $\frac{d\ln a_i}{d\ln c_i}$ equals zero at this point. The systems of n-hexane - nitrobenzene and triethlyamine - water have both been extensively studied[18] and demonstrate this dependence.

At a temperature other than the critical temperature, the diffusion coefficient depends on the form of $\frac{d\ln a_i}{d\ln \chi_i}$. The relationship between $\frac{d\ln a_i}{d\ln \chi_i}$ and temperature can be demonstrated by taking the derivative of the chemical potential with respect to the natural logarithm of mole fraction, $\ln \chi_1$, for the case of a regular solution

$$\mu_i = \mu_i^o + RT \ln \chi_1 + \omega \chi_2^2 \qquad (2.61)$$

Therefore, the derivative becomes

$$\frac{\partial \ln \mu_1}{\partial \ln \chi_1} = RT\frac{\partial \ln a_1}{\partial \ln \chi_1} = RT - 2\omega\chi_1(1-\chi_1) \qquad (2.62)$$

Using $\omega = 2RT^c$ the term $\frac{\partial \ln a_1}{\partial \ln \chi 1}$ reduces to

$$\frac{\partial \ln a_1}{\partial \ln \chi_1} = 1-4\frac{T^c}{T}\chi_1 \chi_2 \qquad (2.63)$$

Additionally, for a regular solution at the consolute composition, $\chi_1=\chi_2=0.5$, so that the equation becomes

$$\frac{\partial \ln a_1}{\partial \ln \chi_1} = \left[\frac{T-T^c}{T}\right] \qquad (2.64)$$

Cussler[19], however, criticizes this relationship because equation 2.64 does not accurately predict the manner in which the diffusion coefficient varies with temperature. The diffusion coefficient has been shown, experimentally, to vary in an other than linear manner. Turner's theory however, predicts a linear relationship.

Another thermodynamic approach uses a Taylor expansion of the Gibbs free energy. Lupis[20] uses this technique to evaluate the behavior of the coexistence curve and spinodal line but the theory can be extended to develop an equation for the diffusion coefficient.

First, we may rewrite equation 2.60 in terms of mole fraction,

$$D_1 = u_1 \chi_1 \chi_2 \frac{\partial \mu_1}{\partial \chi_1} \qquad (2.65)$$

The symbol χ_i, is the mole fraction of component, i. Using the Gibbs-Duhem equation, $n_1 d\mu_1 + n_2 d\mu_2 = 0$, the diffusion coefficient can be

put in terms of a single composition variable. When the Gibbs-Duhem equation is divided by the total number of moles, n_1+n_2, the result is

$$\frac{n_1}{n_1+n_2} d\mu_1 + \frac{n_2}{n_1+n_2} d\mu_2 = 0 \qquad (2.66)$$

Using the definition of mole fraction, $\chi_1 = \frac{n_1}{n_1+n_2}$, and the relationship, $\chi_1 = 1 - \chi_2$, we can show

$$D_1 = u_1 \chi_2^2 \frac{d\mu_2}{d\chi_2} \qquad (2.67)$$

Next, the Gibbs free energy, G, is defined in terms of the Gibbs free energy per mole of solution, g, by

$$G = (n_1 + n_2)g \qquad (2.68)$$

Using equation 2.68, the chemical potential defined in terms of the Gibbs free energy per mole of solution is

$$\mu 2 = \frac{\partial G}{\partial n_2} = \frac{\partial[(n_1 + n_2)g]}{\partial n_2} \qquad (2.69)$$

The right hand side of equation 2.69 can also be written as $g + (n_1+n_2)\frac{\partial g}{\partial \chi_2}\frac{d\chi_2}{dn_2}$, and $\frac{d\chi 2}{dn_2}$ written as $\frac{d\chi_2}{dn_2} = \frac{\chi_1}{n_1+n_2}$. Using these two equations, the chemical potential becomes

$$\mu_2 = g + \frac{dg}{d\chi_2}(1-\chi_2) \qquad (2.70)$$

Taking the derivative of μ_2 with respect to the composition of component 2, the result is

$$\frac{\partial \mu_2}{\partial \chi_2} = \chi_1 \frac{\partial^2 g}{\partial \chi_2^2} \qquad (2.71)$$

When this equation is substituted into equation 2.69, the form for the diffusion coefficient becomes

$$D_1 = u_1 \chi_2^2 \chi_1 \frac{\partial^2 g}{\partial \chi_2^2} \tag{2.72}$$

Next, we take the Taylor series expansion of $g(\chi_2,T)$ about (χ_2^c,T^c) to yield

$$\begin{aligned} g(\chi_2,T) = {} & g(\chi_2^c,T^c) + g_\chi(\chi_2^c,T^c)(\chi_2-\chi_2^c) + g_T(\chi_2^c,T^c)(T-T^c) + \\ & \frac{1}{2!}[g_{\chi\chi}(\chi_2^c,T^c)(\chi_2-\chi_2^c)^2 + 2g_{\chi T}(\chi_2^c,T^c)(\chi_2-\chi_2^c)(T-T^c) + \\ & \quad g_{TT}(\chi_2^c,T^c)(T-T^c)^2] + \\ & \frac{1}{3!}[g_{\chi\chi\chi}(\chi_2^c,T^c)(\chi_2-\chi_2^c)^3 + 3g_{\chi\chi T}(\chi_2^c,T^c)(\chi_2-\chi_2^c)^2(T-T^c) + \\ & \quad 3g_{\chi TT}(\chi_2^c,T^c)(\chi_2-\chi_2^c)(T-T^c)^2 + g_{TTT}(\chi_2^c,T^c)(T-T^c)^3] + \\ & \frac{1}{4!}[g_{\chi\chi\chi\chi}(\chi_2^c,T^c)(\chi_2-\chi_2^c)^4 + 4g_{\chi\chi\chi T}(\chi_2-\chi_2^c)^3(T-T^c) + \\ & \quad 6g_{\chi\chi TT}(\chi_2^c,T^c)(\chi_2-\chi_2^c)^2(T-T^c)^2 + 4g_{\chi TTT}(\chi_2^c,T^c)(\chi_2-\chi_2^c)(T-T^c)^3 \\ + & \quad g_{TTTT}(\chi_2^c,T^c)(T-T^c)^4] + \ldots \end{aligned} \tag{2.73}$$

The subscripts, χ and T, on g refer to the degree of differentiation of g with respect to χ and T, respectively. Since we are expanding about the critical composition, the second and third derivatives of the molar Gibbs free energy with respect to composition are zero[20]. When the second derivative of the molar Gibbs energy, as expanded above, is taken with respect to χ_2, many terms become zero. The final result is

$$\begin{aligned} \frac{\partial^2 g(\chi_2^c,T^c)}{\partial \chi_2^2} = {} & g_{\chi\chi T}(\chi_2^c,T^c)(T-T^c) + \frac{1}{2} g_{\chi\chi TT}(\chi_2^c,T^c)(T-T^c)^2 + \\ & g_{\chi\chi\chi T}(\chi_2^c,T^c)(\chi_2-\chi_2^c)(T-T^c) + \frac{1}{2} g_{\chi\chi\chi\chi}(\chi_2^c,T^c)(\chi_2-\chi_2^c)^2 + \cdots \end{aligned} \tag{2.74}$$

When this result is substituted back into equation 2.72, the diffusion coefficient becomes

$$D_1 = u_1 \chi_2^2 \chi_1 [\, g_{\chi\chi T}(\chi_2^c, T^c)(T-T^c) + \frac{1}{2} g_{\chi\chi TT}(\chi_2^c, T^c)(T-T^c)^2 + g_{\chi\chi\chi T}(\chi_2^c, T^c)(\chi_2-\chi_2^c)(T-T^c) + \frac{1}{2} g_{\chi\chi\chi\chi}(\chi_2^c, T^c)(\chi_2-\chi_2^c)^2 + \cdots] \quad (2.75)$$

With this result, it is possible to examine the effect of approaching the critical temperature if $\chi_2$is set at the critical composition. In this case, only the first two terms would remain but the equation can easily be extended to include higher ordered terms. These two terms represent both a first and second order relationship between diffusion coefficients and temperature, that is, if we assume that the series converges, and we can ignore the higher ordered terms that have been left out. With this theory, we are not limited to a simple first order relationship between temperature and diffusion as we were with Turner's theory.

Chapter III

EXPERIMENTAL

A. The Diaphragm Cell

The diaphragm cells used in this study are of the same design used by Stokes[4]. The cells were constructed so that the top and bottom compartments were nearly equal in volume, varying in volume by less than 1%. The top and bottom compartment volumes were approximately 60 ml each. Since the volumes are assumed to be equal, we were able to restrict our data analysis to theories where $V_T=V_B$.

The two compartments of our cells were separated by glass frits obtained from Chemglass. The frits were made of glass beads about 10 to 15 microns in diameter. The top and bottom compartments were closed off by ground glass stoppers.

There appears to be some disagreement as to whether or not stop-cock grease applied to ground glass stoppers affects the diffusion coefficients. Hartely and Runnicles[21] found that stop-cock grease could cause erratic results in the diaphragm cell determination of diffusion coefficients. Gordon[10] found that careful cleaning of the diaphragm to remove any trace of stop-cock grease was sufficient to ensure precise results, and Stokes[4] chose to use rubber stoppers to avoid using stop-cock grease.

When stop-cock grease was not used with our cells, the ground glass stoppers would occasionally stick in the neck of the opening. Therefore, during some runs, stop-cock grease was used. The

amount of grease used was minimal and care was taken to avoid contact between the solutions filling the compartments and the grease placed on the stoppers.

Stir bars were placed in the compartments and rotated by two permanent magnets fixed to a U-frame which was turned by a Talboy Model 134-1 motor. The speed of rotation of the U-frame was controlled by adjusting the voltage supplied to the motor. The stir bar in the bottom compartment floats while the bar in the top compartment sinks. In both compartments, the bar rests gently against the diaphragm. Figure 2.1 represents the general diaphragm cell set up used for these experiments.

Moquin and Cathcart[3] demonstrated that stirring the solutions in each compartment has an obvious effect on the measured diffusion coefficient. Stokes[4] later demonstrated that the speed of rotation had an effect on the measured diffusion coefficient up to a speed of 25 RPM. Between 25 and 80 RPM, the measured diffusion coefficient had leveled off and did not change. Stokes concluded this to be a result of complete compartment mixing at speeds of 25 RPM and greater. In each of our experiments, the stir bars were rotated at speeds that varied slightly between 40 and 50 rpm.

B. Temperature Control

The diaphragm cells were kept at a constant temperature throughout the diffusion period. Temperature control was achieved by the use of water baths designed by Clunie[22]. These baths consisted of an insulated fish tank filled with a water/ethylene glycol mixture. Ethylene glycol was added to reduce evaporation at

the operating temperatures, which were as high as 60°C. The bath water was circulated by a propeller mounted to a Talboy Model 105 stirring motor. Philadelphia Roto-Stat Company Differential Range Thermoregulators were placed in each bath and set at the desired temperature. The thermostats were relayed through a DynaSense Model 2149, or Model 2149-20, which controlled the heating element. The temperatures were held to within 0.05°C of the thermostat's setting. The thermoregulators were actually able to control temperatures to within 0.005°C. The limiting factor, however, was the accuracy of the thermometers.

C. Solution Preparation

Succinonitrile, $NCCH_2CH_2CN$, was obtained from Aldrich Chemical Company. Although the succinonitrile was marked as 99% pure, it arrived slightly discolored and with a distinctly pungent odor indicating impurities. Succinonitrile is essentially odorless and clear in it's pure form. GC/MS analysis showed the principle impurity to be $NC(CH_2)_3CN$. Therefore, the as received material was purified by redistillation. Distilled water with a conductivity of approximately 1.5 mho/cm was deaerated before the succinonitrile and water solutions were prepared. The water was either deaerated by a water vacuum pump or by boiling. Boiling proved to be the fastest and easiest way to deaerate the distilled water. Careful deareation immediately prior to solution preparation was necessary to avoid air bubbles from forming in the diaphragm cell after reaching thermal equilibrium in the heated water baths. In some cases, despite careful deaeration, a bubble formed in the diaphragm

cell after the diffusion experiment was started. Extremely large bubbles (approximately 0.1 ml in volume) in the bottom compartment were removed by stopping the experiment and replacing the bubble with solution.

The solutions were prepared by weight to the appropriate initial concentrations. The density data for succinonitrile and water solutions collected by Frazier and Facemire[23] were used to convert weight percent water to concentration and visa versa. Since the solutions were to be used at approximately 60°C, we used the density of succinonitrile and water solutions at 60.8°C. This temperature was the closest to our actual operating temperatures. We assumed any effects on the actual density, as a result of using the slightly higher temperature data, would be negligible.

The solutions and the diaphragm cells were pre-warmed to a temperature of 60°C. This procedure was necessary to minimize phase separations that could occur at temperatures below the consolute temperature of 56.17°C. In general, the bottom compartment and frit were filled first with the higher concentration solution. Then the top compartment was filled with its solution. Once the cells were filled with solution, they were placed in the heated baths. The diffusion period was assumed to begin at this point, although technically, the concentration gradient within the frit takes some time to become established. The time required for a concentration gradient to achieve a steady state is on the order of several hours so it could be safely assumed that this time would be negligible compared to the length of the run, which took from several days to a week. Additionally, after the first run with a

particular cell, there was already an established concentration gradient so that when the compartments were filled for the next run, there was no requirement for a pre-diffusion period to relax the gradient to the new conditions. Before filling, for a second run, the compartments were carefully cleaned, however, to remove any excess solution or moisture that may have been present from a previous run. There was no attempt at washing out the solution remaining in the frit. The pre-warmed solutions were then poured into their appropriate compartments with the higher concentration solution always filling the bottom compartment. Nearly all diffusion experiments were run back to back in this manner. Moreover, there was no obvious difference in the "first run" diffusion coefficients and the subsequent run diffusion coefficients.

D. Cell Constants

The cell constant for each diaphragm cell was calculated using the method described by Stokes[4]. New cells were washed with boiling concentrated hydrochloric acid to remove any impurities and then repeatedly flushed with distilled water until conductivity measurements confirmed that no more acid was present. Next, the bottom compartment was filled with 0.500M KCl solution and the top was filled with water. The compartments were stirred for at least two hours to allow a concentration gradient to form in the frit. Since these runs lasted a comparatively short period of time, it was important to allow the concentration gradient to form prior to starting the diffusion period. Once the concentration gradient had formed, the top and bottom compartments were emptied and

refilled with the KCl solution and water. The cell and cell holder were placed in a water bath kept at 25°C. The diffusion period lasted one to two days. When the diffusion run was terminated, the top and bottom solutions were collected and analyzed by conductimetric methods. The experiment was repeated to verify the cell constant.

Before using the cells for succinonitrile and water diffusion experiments, the cells were, once again, washed repeatedly with distilled water.

E. Analytical Methods

One of the greatest difficulties that had to be overcome was to develop a quantitative analytical method to determine the amount of water or succinonitrile in the top and bottom compartments after diffusion. Previous work by Clunie[22] on a Kjeldahl method to determine the amount of succinonitrile proved to be tedious and frequently inaccurate. Attempts to quantify the amount of succinonitrile by UV-Visible spectroscopy also proved inaccurate due to succinonitrile's extremely small extinction coefficient in the ultraviolet region. Quantitative analysis by gas chromatography-mass spectroscopy also failed to give reproducible results[22].

An azeotropic distillation method developed by Bidwell and Sterling[24], however, provided fairly consistent results, accurate to within 1%. As this method requires between 5 and 12 grams of solution, the diffusion experiment was terminated in order to sample the top and bottom concentrations. Extraction of small samples throughout a diffusion experiment, by contrast, would provide much more information and greater flexibiltiy.

The amount of water present in a pre-weighed sample of the solution was determined by distilling with toluene. Water is denser than toluene and was collected in a graduated Dean and Stark flask. The calibration curve in Figure 7 was calculated from known weight percent water samples of succinonitrile and water. This curve was used to determine the weight percent water of the unknown top and bottom solutions. From that information, the concentration of the solution at 60°C was calculated.

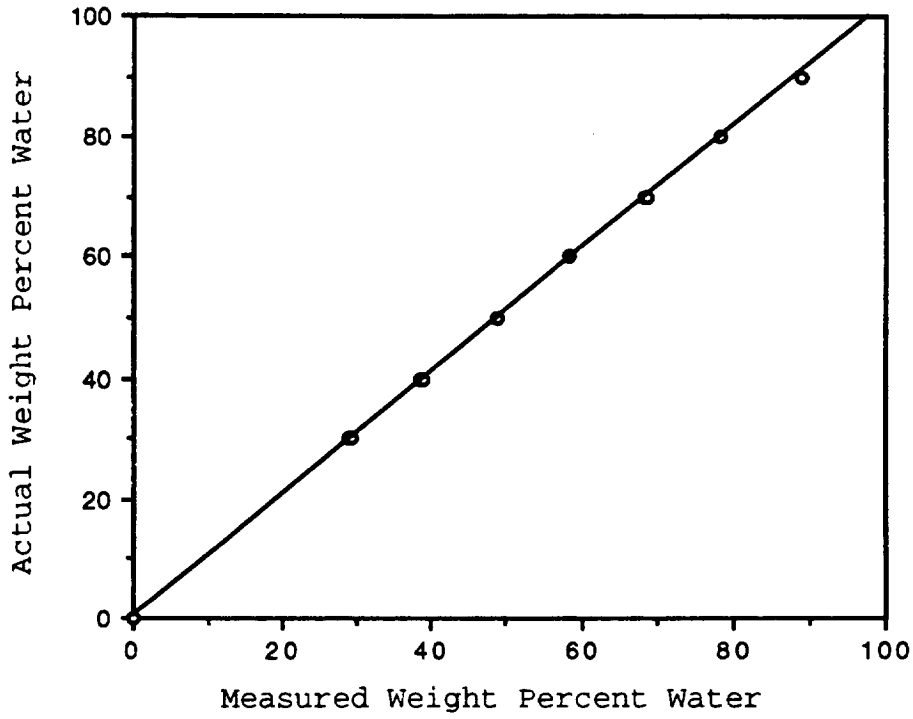

Figure 7. Calibration Curve for Quantitative Distillation

F. Succinonitrile Recovery

Succinonitrile was recovered from the toluene and succinonitrile mixtures left over from the distillation method as well as unused succinonitrile and water solutions. Most of the toluene and water could be distilled from the solutions using conventional

methods. The material from the conventional distillations was further vacuum distilled to recover pure succinonitrile.

Chapter IV

RESULTS AND DISCUSSION

A. Introduction

We began our experiment with the goal of examining the observed diffusion coefficient near the consolute point. As a result of our preliminary experiments at the critical composition, we realized that there were several variables affecting the observed diffusion coefficient and expanded the scope of the experiment to examine the effects of these variables. Our results will be presented in three parts. The first part is based on Baird's theory of the diaphragm cell and the second order effect discussed previously. We studied the effect of $\Delta C_{(0)}$ on the observed diffusion coefficient, D'. The second part of our study was to determine the nature of D' as concentration varied, and to draw some conclusions about D(c). The final part dealt with diffusion coefficients as the consolute point was approached by lowering the temperature.

B. $\Delta C_{(0)}$

The effect of $\Delta C_{(0)}$ was examined at two different concentrations. First, we studied $\Delta C_{(0)}$ at the critical concentration (51.81 weight percent water, or 5.904 M succinonitrile). The temperature for each diffusion run was 60.0°C which is about 4 degrees above the consolute point. The results of our experiment are shown below in Table 2.

Table 2: Diffusion Coefficients at $\bar{c}$=5.9M as $\Delta C_{(o)}$ Varies

$\Delta Co(M)$	$\Delta Ct(M)$	$\bar{c}(M)$	$D'(10^{-6}\ cm^2\ s^{-1})$
1.996	1.806	5.903	2.01
1.996	1.635	5.903	2.39
1.996	1.671	5.903	1.97
4.442	3.502	5.902	2.27
5.659	4.430	5.898	2.52
6.885	4.991	5.899	3.49
8.106	5.765	5.895	4.93
9.339	6.617	5.898	4.59
11.818	5.172	5.909	5.76
11.818	5.542	5.909	7.35

We assumed that the variation in the diffusion coefficient is a result of the second order effect and that any higher order effect was negligible in comparison to the second order effect. In order to test this conclusion, we plotted the data according to the second order effect equation

$$\frac{1}{D'} = \frac{1}{D(\bar{c})} - \frac{D^{(2)}(\bar{c})}{48(D(\bar{c}))^2} (\Delta C_{(0)})^2 \frac{[(\Delta C_{(t)}^2/\Delta C_{(0)}^2) - 1]}{\ln(\Delta C_{(0)}/\Delta C_{(t)})} \qquad (4.1)$$

The values of D', $\Delta C_{(o)}$, and $\Delta C_{(t)}$ were taken from the experimental data. If our assumption of a second order effect were correct, we would expect to find a straight line when this equation is plotted. The graph would have a slope of $[D^{(2)}(\bar{c})/48(D(\bar{c}))^2]$ and a y-intercept of $1/D(\bar{c})$. Such a graph is shown in Figure 8.

Figure 8 shows that there is apparently, a significant second order effect at the critical composition. Some scatter about the straight line was observed and this is assumed to be because of

experimental error in calculations of $\Delta C_{(t)}$, although it is possible that the next order (fourth) effect may have had some influence on the results. This approach has also been used on other systems, with satisfactory results.[25]

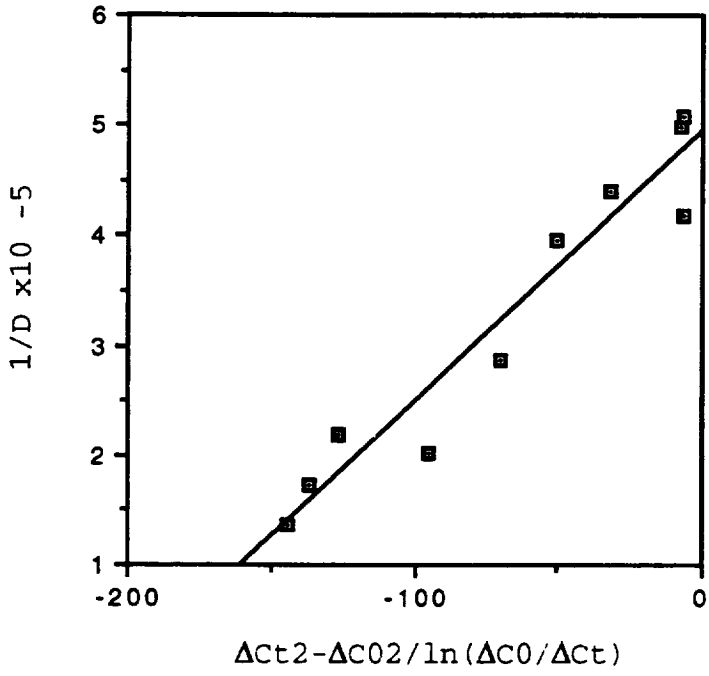

Figure 8. Second Order Effect at $\bar{C}$ = 5.9M

The second order effect was also examined at a point away from the critical region. For these experiments, an average concentration of 3.5 M was chosen. The results from these diffusion runs are presented in Table 3.

The data in Table 3 lack sufficient precision to form a straight line when plotted in Figure 8. The average diffusion coefficient for the five different runs was 6.48×10^{-6} cm^2 sec^{-1}. Also, the diffusion coefficients range from only 5.41×10^{-6} to 7.16×10^{-6} cm^2 sec^{-1}.

Therefore, we conclude that at an average concentration of 3.5M, there is a negligible second order effect.

Table 3: Diffusion Coefficients at $\bar{c}$=3.5 M as $\Delta C_{(0)}$ Varies

ΔCo(M)	ΔCt(M)	D' (10^{-6} cm^2 s^{-1})
3.000	1.524	7.16
4.000	2.154	5.41
5.000	2.555	6.88
6.000	3.419	5.85
7.000	3.532	7.12

Since there was no significant effect on D', however, we concluded that the actual second derivative of D($\bar{c}$) at C=3.5M is quite small and minimized any second order effect regardless of $\Delta C_{(0)}$.

C. D(c)

The study of D(c) began by determining D' at various concentrations. These diffusion runs were conducted at 60.0°C, with $\Delta C_{(0)}$=4M. Each run lasted approximately 4 days. Figure 9, illustrates the relationship between the integral diffusion coefficient, D', and mean concentration. The general shape of this curve agrees with previous studies on non-electrolyte systems[5]. We also note that a minima occurs near the critical composition, which has also been observed in other systems were the components exhibit critical point behavior.[5]

The third order best fit equation for these points was determined to be

$$D'x10^6 = 40.4 - 15.8\ \bar{c} + 2.0\ \bar{c}^2 - 7.8x10^{-2}\ \bar{c}^3 \qquad (4.2)$$

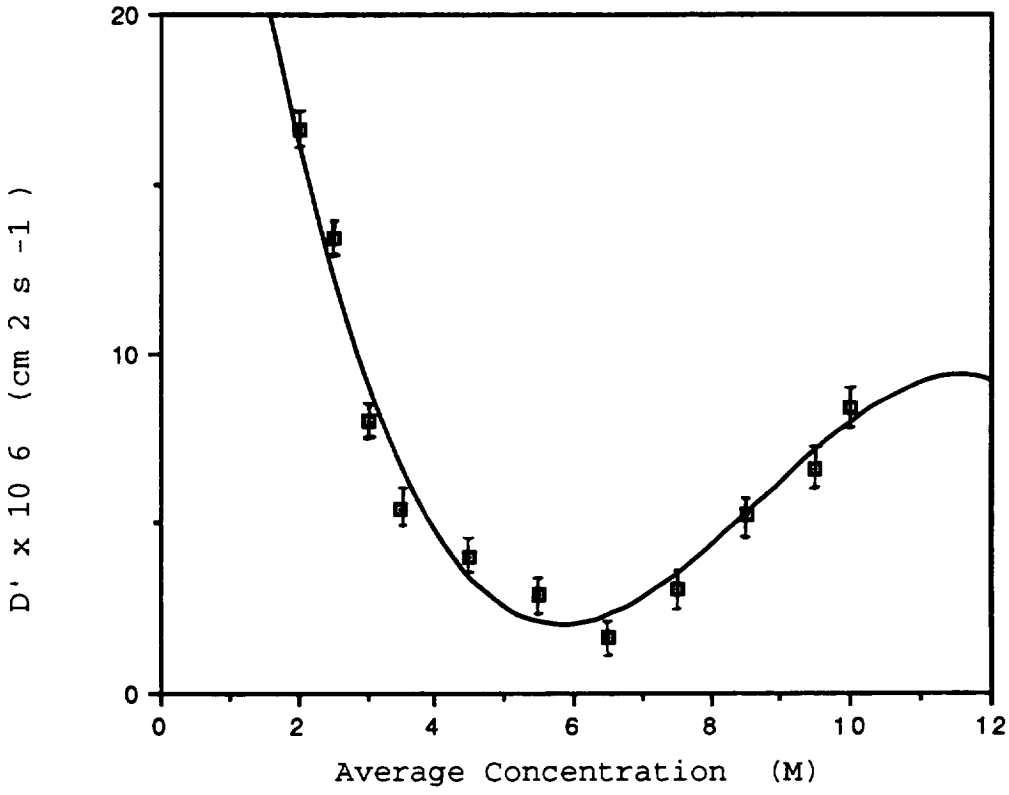

Figure 9. Diffusion Coefficients as a Function of Concentration

We attempted to extract D(c) from measured values of D' as a function of concentration by applying the Stokes method[9] to our data. Since our experiments did not begin with pure water in the top compartment, we had to make several approximations in order to arrive at diffusion coefficients corrected to zero time as Stokes had done. For example, the diffusion coefficient at a mean bottom concentration of 11.42M corrected to zero time was determined by using the following equation:

$$D'^{\circ}_{(CB=11.42)} = \frac{1}{11.42}\left[\int_{8.54}^{11.42} D\,dc + \int_{4.54}^{8.54} D\,dc + \int_{.54}^{4.54} D\,dc + \int_{0}^{.54} D\,dc \right] \qquad (4.3)$$

The first integral was substituted with (11.42 - 8.54) $D'_{(c'=10)}$ which represents an actual experiment. The last three integrals were substituted with $(C_T - C_B)\ D'_{(\frac{C_T+C_B}{2})}$ where the value of $D'_{(\frac{C_T+C_B}{2})}$ was approximated from the curve of D' versus c'. Table 4 lists the values used to calculate the curve for D'° at C_B using equation 2.23.

Table 4. Concentrations and Diffusion Coefficients

Top Concentrations			Bottom Concentrations			
initial	final	average	initial	final	average	D'
8.00	9.08	8.54	12.00	10.85	11.42	8.44
7.50	8.37	7.94	11.50	10.49	11.00	6.64
6.50	7.11	6.81	10.50	9.87	10.18	5.31
5.50	6.02	5.76	9.50	9.00	9.25	3.04
4.50	4.69	4.59	8.50	8.25	8.38	1.66
3.50	3.95	3.72	7.50	6.98	7.27	2.89
2.50	2.93	2.72	6.50	5.96	6.23	3.99
1.50	2.26	1.88	5.50	4.62	5.06	5.46
1.00	2.05	1.52	5.00	3.90	4.45	8.00
0.50	1.71	1.10	4.50	3.29	3.90	13.41
0.00	1.34	0.67	4.00	2.60	3.30	16.58

Once the values of D'° at C_B had been calculated, they were plotted against C_B. Figure 10 illustrates this result. The best fit third order equation for this curve is

$$D'^{\circ} = 52.6 - 13.1\ c + 1.33\ c^2 - 4.54\times10^{-2}\ c^3 \qquad (4.4)$$

Using this equation for the curve, it's first derivative was taken and used in equation 2.24 to arrive at values for D(c). The results of these calculations are shown graphically in Figure 10. This graph of D(c) is obviously incorrect since it yields negative values for D(c).

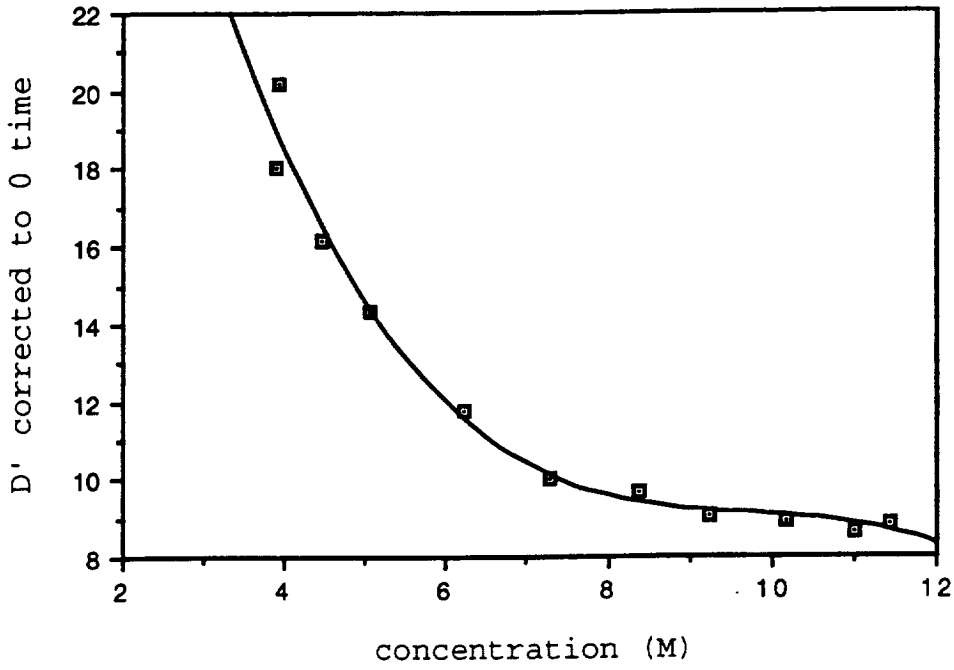

Figure 10. D'° Calculated by the Stokes Method

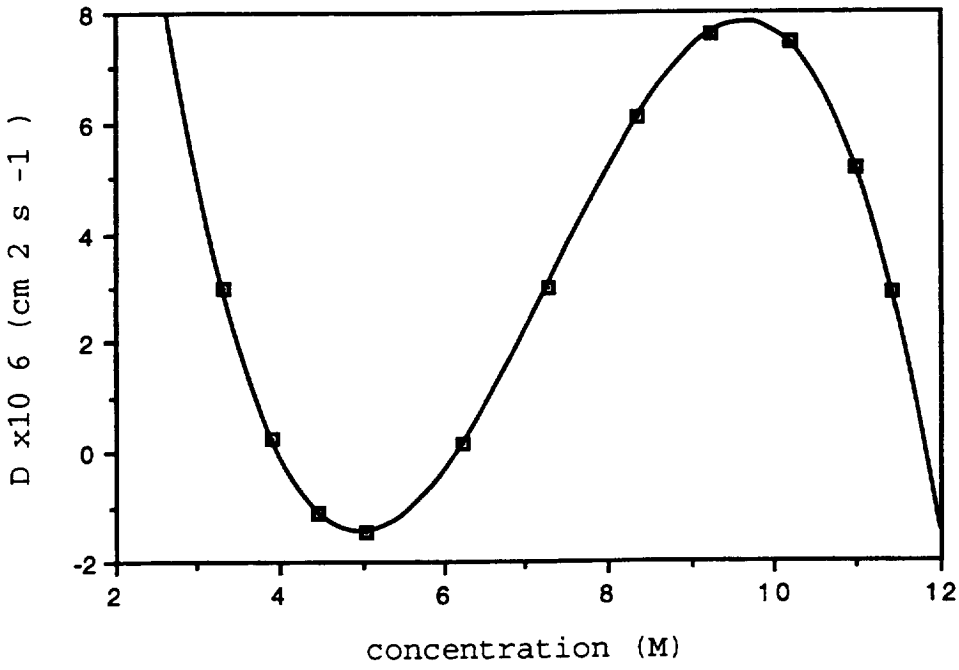

Figure 11. D(c) Calculated by the Stokes Method

One very likely cause of this error is the method used to calculate D'° at C_B. Our evaluation of equation 4.3 required several approximations as already mentioned. Stokes only made one such approximation; that is he assumed that $D'(C_T)$ could represent $D'^{\circ}(C_T)$. The more approximations, the greater the induced error in the final result, a weakness in the Stokes method which has been pointed out by Miller[26]. Although Miller concludes that the Stokes method be restricted to dilute solutions, we have attempted to apply the Stokes method to solutions with concentrations up to nearly 100% succinonitrile.

Although application of the Stokes method did not improve the accuracy of the diffusion coefficients, there are two reasons why we can assume that our measured diffusion coefficients, D', are a close approximation to the actual diffusion coefficients, D(c). First, the general form of the diffusion coefficients versus concentration agrees with previous studies near the critical point[27]. Second, corrections due to the second order effect when $\Delta C_{(0)}$ is 4M, and the average concentration is 5.9M, are less than 6 % of the differential diffusion coefficient as calculated by equation 4.1.

D. The Diffusion Coefficient as T^c is Approached

The last series of experiments were designed to determine the behavior of the diffusion coefficient at the consolute composition as T approaches T^c. Therefore, the variables affecting the apparent diffusion coefficient, namely initial concentration difference, concentration, and length of each diffusion run were held constant. The initial concentration difference was 4.0 M, each run lasted

approximately 4 days, and the average concentration was the critical composition, 5.904M. We also ran parallel diffusion experiments at an average composition of 6.5M so that we could compare results and determine if the diffusion experiments at the critical compositon exhibited any unusual behavior as compared to a non-critical composition. The results of the critical composition experiments are listed in Table 5.

Table 5. Diffusion Coefficients as the Consolute Temperature is Approached

Temperature/°C	D′ (10^{-6} cm^2 s^{-1})
60.0	2.02
60.0	2.14
59.0	1.95
58.0	1.73
57.0	2.09
56.5	1.18
56.3	1.89
56.2	1.32

If the results are plotted, there is some considerable scatter among the points. The results show, nevertheless, that the diffusion coefficient decreases as the critical temperature is approached. We also noted that the results of the comparison experiments at an average concentration of 6.5M showed the same general decrease in the integral diffusion coefficient, D', as the temperature was lowered.

In these experiments, we were trying to measure fine differences in the integral diffusion coefficient, D'. Much of the scatter we see in the data is a result of experimental error. Because

we chose to work with an initial concentration difference of 4M, we increased our experimental error. Although this will be discussed in the next section, had we used a larger initial concentration difference, we might have been able to determine the exact relationship between the measured diffusion coefficient and temperature.

E. Error Analysis

The error in determining the integral diffusion coefficient, D', has been examined by several authors. Mills and Woolf[8] have summarized these studies. Equation 2.16 is used to calculate the diffusion coefficient. When written again, where D' is solved for, we have

$$D' = \frac{1}{\beta t} \ln\left[\frac{(C_B(0) - C_T(0))}{(C_B(t) - C_T(t))}\right] \qquad (4.5)$$

There are errors in the measurement of β, t, and the concentrations. However, if the cell is carefully calibrated, the error involved in determining β is small and can be considered negligible in comparison with the error in determining concentrations. Likewise, the error associated with time is also negligible in comparison to the error in concentrations since the diffusion experiments usually lasted 4 days and the time was determined accurately to within a few seconds. The longer the diffusion experiment runs, the smaller the relative error in measuring the time.

The largest contributor to random error is the concentration measurement. Stokes[9] analyzed this error and found it to be greatest when the concentration ratio was smallest. Stokes

concluded that the optimal initial conditions occurred when the top compartment is filled with pure solvent, which serves to maximize the concentration ratio. He also noted that in an attempt to minimize the initial concentration difference, so that the differential (actual) diffusion coefficient is measured, there is a large increase in the error of D'.

In our experiments, we attempted to minimize the initial concentration difference so that our measured diffusion coefficient more accurately approximated the actual diffusion coefficient. In doing so, however, we thus increased the relative error. We realized this to some degree during the experiments and that is why we chose an initial concentration difference of 4M instead of smaller values we had also worked with. The error was greatest in the higher concentration ranges where our smallest initial concentration ratio was 1.5. Based on Stokes's calculations, this would have resulted in the error in D' being twenty times the error in measuring concentrations. Fortunately, at lower concentrations the error in D' would only have been three times the error in concentration measurements. Based on the calibration experiments, the uncertainty in determining concentrations by the distillation method was approximately 0.4 weight percent water at a concentration of 3.5M which equals an uncertainty of 0.05 M. Assuming the relative error in concentration was the same for all concentrations, then the uncertainty in the diffusion coefficient at an average concentration of 3.5 M would be nearly 7 x 10^{-7} cm^2s^{-1}. This means that at a concentration of 3.5M, the measured diffusion coefficient was within approximately 10% of the actual value of D'.

The error in D' can be reduced in several ways by changing the experimental techniques. One way to reduce the error is to increase the initial concentration ratio. This would mean that in many of the experiments, the value of D' measured is within the Stokes data analysis scheme less closely related to D(c'), however, the value of D' measured would be more accurate. A second method of reducing the error in D' is by using a quantitative analytical technique that has a higher degree of precision. We could not find such a method for the succinonitrile and water system. The last way to reduce the relative error in D' would be to perform several diffusion runs at an average concentration and take an average value of D' for that concentration.

Chapter V

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

A. Conclusions

We have demonstrated a second order effect which confirms the theory of Baird.[11,12] The second order effect experiments conducted at the critical composition while $\Delta C_{(o)}$ is varied, established the differential diffusion coefficient at that concentration and at 60.0°C. This method was useful in determining one diffusion coefficient value, but in order to determine the functional form of the differential diffusion coefficient, numerous runs at different average concentrations would have to be made. Therefore, although the second order effect method could be used to determine all differential diffusion coefficients, it would be extremely time consuming to do so.

We have determined the composition dependent nature of the interdiffusion coefficient at 60.0°C. That composition dependence demonstrates curvature as predicted by the Taylor series development of the Gibbs free energy. The experiments calculating D' at various concentrations are slightly inaccurate because of the experimental error involved in the analytical technique. We are confident, however, that the curve of D' versus c represents a close approximation to the actual form of D(c). As mentioned in the error analysis section, some of this error can be minimized by choosing the appropriate experimental conditions. The system of succinonitrile and water, however, will always have a significant

error in D' as long as azeotropic distillation remains the most accurate analytical method available.

As a result of experimental error, we were unable to determine the form of the diffusion coefficient's temperature dependence. There was a modest decrease in the diffusion coefficient as the critical temperature was approached, but we were unable to apply the thermodynamic theories to this result.

B. Suggestions for Future Work

Based on the conclusions listed above, any future experiments involving a fixed average concentration and varying temperature, should first be examined for a second order effect. Once the second order effect is established, the value of $\Delta C_{(o)}$ should be increased to a maximum and the second order effect used as a correction to the measured diffusion coefficient, D'. If possible, the top compartment should always be filled with pure solvent. This will minimize error and help resolve the temperature dependence of the diffusion coefficient.

Also, the temperatures at which the diffusion experiments were run could be varied more. In addition to the temperature runs at 60.0°C, runs at 65.0°C, and possibly 70.0°C, might help establish the temperature dependence of the diffusion coefficient.

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