

## CHAPTER I

### INTRODUCTION

Many chemical engineering processes involving mass transfer which is driven by phenomenon such as gas absorption, membrane separation, and heterogeneous reaction cannot be adequately modelled without accurate estimates of diffusion coefficients in the liquid phase. Still, very few measurements of diffusion coefficients in liquids at temperature and pressures above ambient have been published and theories to predict diffusion coefficients in liquids are not well established. Consequently, existing correlations often yield poor predictions of diffusion coefficients at the elevated temperatures and pressures where the majority of chemical processes operate. This research focuses on the measurement of diffusion coefficients which are required to model the Fischer-Tropsch Synthesis.

#### A. FISCHER-TROPSCH SYNTHESIS

The Fischer-Tropsch Synthesis is a process by which gasoline, diesel oil, wax, and alcohols are produced from hydrogen and carbon monoxide. Coal is usually gasified to supply the required hydrogen and carbon monoxide. Modern technology focuses on reacting these two gases in a liquid slurry containing a suspended catalyst. Previous conventional technology employed fixed bed and fluidized bed reactors. Literature on the process is voluminous. The interested reader is referred to Anderson (1984), Riekena et al. (1982), and Baird et al. (1980), as a starting point.

The Fischer-Tropsch synthesis reaction has been studied in many different types of reactors, at several different operating conditions, and with various catalysts. In

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order to evaluate mass transfer characteristics in these various systems, accurate estimates of liquid phase diffusion coefficients for products and reactants are critical. The task of estimating diffusion coefficients in a Fischer-Tropsch reactor is by no means elementary. The steady state liquid phase, often referred to as FT wax, is primarily a mixture of saturated hydrocarbons with an average carbon number of about 30, although it can range as high as 70. The melting point of the FT wax is typically in excess of 100°C, and reaction conditions of the normal process range from 473-573 K at 1 to 5 MPa. Prior to 1984, diffusion coefficients had not been measured in even the simplest pure low melting hydrocarbons at these conditions.

## B. OVERVIEW OF DIFFUSION RESEARCH PROGRAM

In 1984, a diffusion research program funded by the U. S. Department of Energy was started by Dr. Aydin Akgerman at Texas A&M University. The ultimate goal of this research program was to measure diffusion coefficients in an actual sample of Fischer-Tropsch reactor wax at typical reaction conditions. The experimental work was conducted in three phases.

Results of the first phase of the research have already been reported (Matthews and Akgerman, 1987a; Matthews et al., 1987a; and Matthews et al., 1987b). During the first phase of the project, a Taylor dispersion apparatus was constructed. This apparatus was then used to measure infinite dilution mutual diffusion coefficients of the normal alkane solutes octane, decane, dodecane, tetradecane, and hexadecane, and of the gases hydrogen, carbon monoxide, and carbon dioxide in the n-alkane solvents heptane ( $C_7$ ), dodecane ( $C_{12}$ ), and hexadecane ( $C_{16}$ ). Normal alkanes were chosen because they are a simple homologous series and are primary products of the FT synthesis. Hydrogen and carbon monoxide are reactants in the synthesis

and carbon dioxide is a product of the water-gas shift reaction. Measurements were made at temperatures between 298 and 573 K, and pressures from 0.1 to 3.45 MPa (14.7 to 500 psia). Prior to this work, the available data for alkane/alkane systems were primarily limited to the temperature range 290-343 K, and there were no data available for the diffusion of gases above 323 K.

Results from the first phase of the study indicated that the diffusion coefficients were a strong function of temperature, but only a very weak function of pressure over the range which was investigated. For this reason, all subsequent experiments were conducted at approximately 200 psia, a typical Fischer-Tropsch reactor pressure. During the first phase of the research program a new technique was developed for measuring solvent density using the Taylor dispersion apparatus. This technique was used throughout the entire research program to measure solvent density at each of the experimental conditions. The density data was eventually used to develop a correlation which predicts the diffusion coefficients.

This dissertation reports the results of the second and third phases of the diffusion research program. During the second phase of the program, extensive modifications were performed to the existing Taylor apparatus so that diffusion coefficients could be measured in molten solvents with melting points up to 400 K. Prior to these modifications, the apparatus could only be used with solvents which were liquids at ambient conditions. After the required modifications were completed, mutual diffusion coefficients at infinite dilution were measured for each of the selected alkane and gaseous solutes in the solvents n-eicosane ( $C_{20}$ ) and n-octacosane ( $C_{28}$ ) at temperatures from 373 to 533 K. Prior to this study, diffusion coefficients had never been measured in these solvents, which melt at 36 and 60°C respectively.

During the third and final phase of the experimental work, mutual diffusion coefficients at infinite dilution were measured for each of the selected solutes in an actual sample of FT wax which melted near 100°C. Measurements were made at 200 psia over the range 473–533 K, which are typical Fischer-Tropsch reactor conditions. The FT wax density was also measured at each experimental condition. Results indicated that estimates of diffusion coefficients currently being used to model the Fischer-Tropsch process are highly erroneous.

### C. ADDITIONAL ACCOMPLISHMENTS

Following the completion of the experimental work discussed in the previous section, a non-linear least squares computer model was developed to extract the diffusion coefficients from the raw Taylor dispersion data (see Chapters II and VI). The model, based on the analytical solution to the Taylor dispersion problem, proved to be superior to the simple approximate models used in previous Taylor dispersion research. The diffusion coefficients reported herein for the solvents n-eicosane, n-octacosane, and Fischer-Tropsch wax were determined using the new non-linear model.

Since the diffusion coefficients reported from the first phase of the study were extracted from the raw data using a more approximate method, all raw data from the first phase was reanalyzed with the new model. Significant errors were discovered in many of the diffusion coefficients which had been reported previously.

Once all of the diffusion coefficients had been extracted from the raw data using the new non-linear model, a correlation was developed based on the Rough Hard Sphere (RHS) theory for diffusion. In general, the RHS theory predicts that the ratio of the diffusion coefficient to the square root of temperature is proportional

to the molar volume of the solvent. Starting with this general form, a simple semi-empirical correlation was developed which predicts diffusion coefficients for the gaseous solutes hydrogen, CO, and CO<sub>2</sub> and alkane solutes ranging from n-octane (C<sub>8</sub>) to n-hexadecane (C<sub>16</sub>) in alkane solvents ranging from n-heptane (C<sub>7</sub>) to n-octacosane (C<sub>28</sub>). The correlation predicts the data accurately over the entire temperature range of the measurements. Recommendations are given for using the RHS correlation to predict diffusion coefficients in a Fischer-Tropsch wax mixture.

#### D. GENERAL OUTLINE

The dissertation follows in logical order. Chapter II begins with a description of the various types of diffusion coefficients which can be measured, explaining the reason why mutual diffusion coefficients at infinite dilution were measured for this study. Several different measurement techniques are also discussed, with an emphasis on Taylor dispersion. Chapter III summarizes previous studies which report measurements of diffusion in pure alkane solvents and alkane mixtures. In Chapter IV, predictive theories and correlations which have been applied to predict diffusion coefficients in liquid alkanes are reviewed. The Rough Hard Sphere theory is emphasized because it was chosen to correlate the reported data.

Chapters V through VII describe the specific accomplishments of this study. In Chapter V, the details of the specific apparatus and procedure are given. Chapter VI covers the development and validation of the new non-linear model for extracting diffusion coefficients from raw Taylor dispersion data. Finally, in Chapter VII, the results are presented and discussed. The Rough Hard Sphere correlation is also developed in Chapter VII. Chapter VIII presents the conclusions drawn from the research and Chapter IX contains several recommendations for future work.

## CHAPTER II

### MEASUREMENT OF DIFFUSION COEFFICIENTS

Measurements of diffusion data reported in the literature are often difficult to interpret due to inconsistent terminology and lack of clear definitions for the reported diffusion coefficients. Although several different terms are used, there are actually only two general classes of binary diffusion coefficients, the mutual diffusion coefficient and the tracer diffusion coefficient. Even though this study focuses on a special case of mutual diffusion, the mutual diffusion coefficient at infinite dilution, it is important to understand the relationship of the reported diffusion coefficients to other types of diffusion coefficients reported in the literature.

#### A. TYPES OF DIFFUSION COEFFICIENTS

The mutual diffusion coefficient,  $D_{12}$ , quantitatively describes diffusion of solute (1) and solvent (2) molecules interacting to equalize concentration gradients and depends only on type 1-2 molecular interactions. The tracer diffusion coefficients  $D_1^*$  and  $D_2^*$  measure the diffusion of a single species (1 or 2) interacting in a solution of solvent and solute molecules. Therefore, the tracer diffusion coefficient  $D_1^*$  depends on both types 1-2 and 1-1 molecular interactions, while  $D_2^*$  depends on types 1-2 and 2-2 interactions.

Figure 2.1 illustrates the typical qualitative behavior of both mutual and tracer diffusion as a function of concentration for a generic highly ideal binary system. Several important points can be noted from Figure 2.1;

1.  $(D_1^*)^S$  and  $(D_2^*)^S$ , often referred to as self diffusion coefficients, are limiting cases of the tracer diffusion coefficients, as noted. These quantities are also referred to as  $D_{11}$  and  $D_{22}$ .

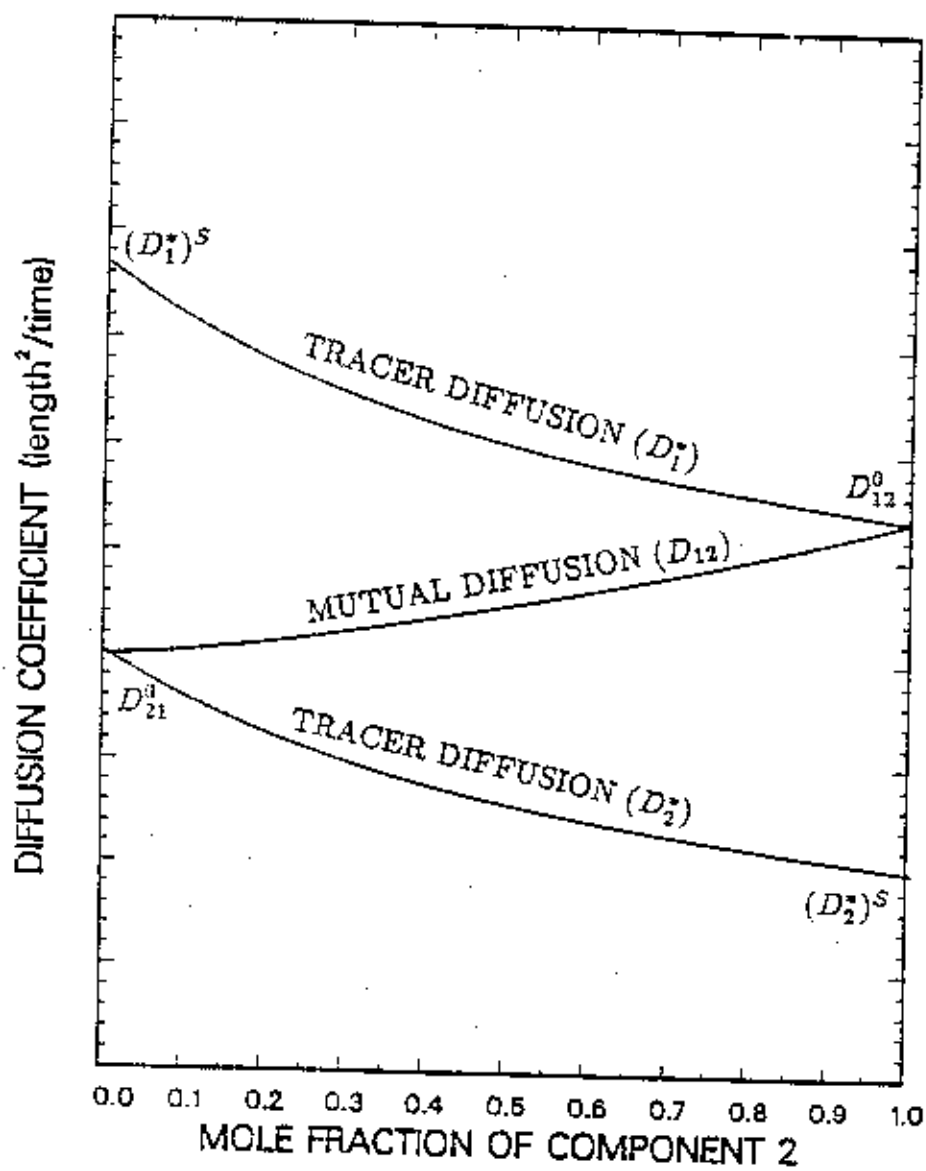


Figure 2.1. Qualitative behavior of diffusion coefficients for a highly ideal binary liquid system.

2. Tracer diffusion coefficients are actually strong functions of concentration, although the term 'tracer' is often mistakenly used in reference to only the limiting cases where tracer diffusion approaches mutual diffusion.

3. The mutual diffusion coefficient is also a function of concentration. For this study, we have measured several limiting cases of mutual diffusion, properly referred to as 'mutual diffusion coefficients at infinite dilution' or  $D_{12}^{\circ}$ . Throughout this report we will refer to these limiting cases as simply  $D_{12}$ , the diffusion coefficient, or the diffusivity. Except where stated otherwise, these terms have been used interchangeably.

The mutual diffusion coefficient,  $D_{12}$ , is the most commonly measured type of diffusion coefficient, and is the diffusion coefficient required for mass transfer calculations. Since most gases are only sparingly soluble in liquids, mutual diffusion coefficients for gases in liquids are always reported as being at infinite dilution. Since liquid-liquid mixtures can exist over the entire concentration range, the effect of concentration on the liquid-liquid mutual diffusion coefficient is often important. However, for the case of diffusion in the Fischer-Tropsch wax, the mutual diffusion coefficient at infinite dilution,  $D_{12}^{\circ}$ , is the proper diffusion coefficient for mass transfer calculations. In this case,  $D_{12}^{\circ}$  actually represents the diffusion of infinitely dilute solute, 1, through the FT wax mixture, 2. This is the situation that occurs as a product or reactant diffuses to or from the surface of the FT catalyst.

The next section is a general review of different classes of diffusion coefficient measurement techniques. Of the techniques which have been developed Taylor dispersion is the only method which can easily be extended to the temperatures and pressures required for this particular study. For this reason, the particular details of each technique are not elaborated.



## B. TECHNIQUES FOR MEASURING DIFFUSION COEFFICIENTS

Many different experimental methods have been used to measure diffusion coefficients in liquids. A comprehensive review of these techniques is given by Tyrrell and Harris (1984). The most common technique for measuring diffusion in liquids is the diaphragm cell. Since the diaphragm cell technique requires that steady state be attained in the cell, a single measurement may take days to complete. The technique is usually used to measure mutual diffusion, but may be used to measure tracer diffusion through the use of labelled radioactive tracers. Although diaphragm cells have been used successfully at high pressures, they are not amenable to high temperature measurements.

Several optical interference techniques have also been used to measure diffusion coefficients in liquids. These methods all rely on measuring interferometric fringe patterns which initially occur at a sharp boundary between two liquids. The fringe patterns are caused by gradients in the refractive index near the boundary. Optical interference methods are especially suited to measuring mutual diffusion coefficients over the entire concentration range in a single experiment. When a laser is used as a light source, highly accurate results may be obtained. However, due to inherent experimental difficulties associated with all interferometric techniques, these methods have not yet been extended to high temperatures and pressures.

The self diffusion coefficient, a special case of tracer diffusion is often measured due to its theoretical significance. Self diffusion can be measured using a radioactive tracer and any one of several standard techniques, but is most easily and accurately measured using a special nuclear magnetic resonance (NMR) method. The NMR spin echo technique requires only small quantities of sample and is easily extended to elevated temperatures and pressures. In the past, the technique has been used

primarily to measure self diffusion in pure liquids, but new Fourier transform techniques show promise of allowing the simultaneous determination of as many tracer diffusion coefficients as there are resolvable resonances.

Measuring diffusion of a dissolved gas in a liquid is a special case which presents major experimental difficulties. Malik and Hayduk (1968) devised a special capillary tube technique which has been used by many researchers. Another popular technique for measuring gas-liquid diffusion is the wetted wall column. Even the standard diaphragm cell has been used with some success. The major drawback to all of these methods is that they are highly dependent on accurate gas-liquid solubility data, which is rare, except for the simplest of systems at ambient conditions.

In recent years, the Taylor dispersion method has evolved into the most versatile method for quick and reliable measurements of diffusion coefficients in liquids. The method is a dynamic chromatography technique which has few of the limitations of the other methods. Taylor dispersion is especially amenable to elevated temperature and pressure measurements and can even be used to measure gas diffusivities in liquids without knowledge of gas solubility data. In the past, Taylor dispersion has been used almost exclusively to measure mutual diffusion, but could easily be extended to measure tracer diffusion as well. Since the Taylor dispersion technique was used for this study, it will now be discussed in detail.

### C. TAYLOR DISPERSION

In 1952, Sir Geoffrey Taylor was asked by a veterinarian to explain how the mean velocity of blood in the arteries of animals could be deduced from tracer studies (Taylor, 1954a). Sir Taylor answered the question in his classic paper

which explains a method to measure not only the mean velocity, but the diffusion coefficient of the tracer as well (Taylor, 1953). The method has become known as Taylor dispersion and has found widespread applications.

The idealized Taylor dispersion experiment can be described as follows. A pulse of solute is injected into a long uniform tube, in which a solvent is flowing in slow laminar flow. As the pulse is carried through the tube, it spreads due to the combined effects of laminar flow and molecular diffusion, although the peak center or maximum continues to flow at the mean velocity of the laminar profile. Eventually, the peak elutes from the end of the long tube, at which point the radially averaged concentration profile is measured as a function of time. From this recorded concentration vs. time data, the diffusion coefficient can be determined using the mathematics derived by Taylor.

The differential equation describing the solute concentration is given below in standard cylindrical coordinates.

$$D_{12} \left( \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial z^2} \right) = \frac{\partial C}{\partial t} + 2\bar{u} \left( 1 - \frac{r^2}{a^2} \right) \frac{\partial C}{\partial z} \quad (2.1)$$

In this equation,  $C$  is the concentration, which is a function of radial position  $r$ , and the axial position  $z$ .  $D_{12}$  is the mutual diffusion coefficient,  $a$  is the tube radius, and  $\bar{u}$  is the mean solvent velocity.

Applying several simplifying assumptions which are easily satisfied in practice, Taylor showed that Equation 2.1 could be reduced to the following simplified equation;

$$K \frac{\partial^2 C_a}{\partial Z^2} = \frac{\partial C_a}{\partial t} \quad (2.2)$$

where

$$Z = z - \bar{u}t \quad (2.3)$$

In Equation 2.2,  $C_a$  is the radially averaged concentration, and  $K$  is the effective Taylor dispersion coefficient.  $Z$  is the axial coordinate which moves with the mean solvent velocity  $\bar{u}$ . Aris (1956) used the method of moments to show that the definition for  $K$  given in Taylor's original work was not complete. Using straightforward calculus and algebra, Hunt (1976) verified that Aris's definition for  $K$  was indeed correct and is given by:

$$K = D_{12} + \frac{\bar{u}^2 a^2}{48D_{12}} \quad (2.4)$$

Taylor had neglected to include the first term on the right hand side of Equation 2.4. Taylor's assumption is often reasonable since in practice the first term is usually orders of magnitude smaller than the second term.

If  $D_{12}$  is assumed to be independent of concentration, Equation 2.2 can be solved analytically for at least three different initial conditions. The three different initial conditions correspond to the following types of experiments; (1) an impulse (delta) injection of concentrated solute at time zero; (2) a square-pulse injection at time zero; and (3) a step-change injection at time zero. The corresponding solutions to these three cases have been summarized by Baldauf and Knapp (1983). Taylor (1953) had originally presented the solutions for both the impulse injection and the step-change injection.

The step-change solution has not received much interest because the step-change injection is not as practical as the other types of injections. The impulse solution has received the greatest interest because it is much simpler than the square-pulse solution which contains a linear combination of terms containing the error function. Although a pure impulse cannot be achieved in practice, Evans and Kenney (1965) have shown that when the volume of the injected sample is less than 1% of the dispersion tube volume, the impulse solution and the square pulse

solution agree with extreme accuracy. Because this condition is easy to satisfy in a practical apparatus, all existing Taylor dispersion apparatuses have been operated so that the solute injection approximates an impulse injection.

For an impulse injection of mass  $M$  at time zero, injected into a flowing solvent stream which does not contain the solute, the radially averaged concentration at the end of the diffusion tube, distance  $L$  from the injection point, is given by;

$$C_a = \frac{M}{\pi a^2 (4\pi Kt)^{1/2}} \cdot \exp\left(\frac{-(L - \bar{u}t)^2}{4Kt}\right) \quad (2.5)$$

Surprisingly, even though this solution appeared in Taylor's (1953) original paper, it has not been used in its entirety to analyze data from any previous Taylor dispersion experiment.

Direct application of Equation 2.5 to determine  $K$  and hence  $D_{12}$  requires non-linear parameter estimation. Because much of the early Taylor dispersion work was completed prior to the advent of computers, non-linear techniques were considered impractical. Two general techniques have emerged as the most popular methods for Taylor dispersion data analysis. These techniques will be referred to as the "graphical method" and the "moment method." Both methods are approximate solutions to Equation 2.2 for the case of an impulse injection.

A graphical method was developed by chromatographers to calculate the diffusion coefficient directly from measurements of recording chart dispersion peaks. The method has been described with the greatest clarity by Grushka and Kikta (1974); but is actually based on the original work of Giddings and Seager (1962). Several researchers have used the method to calculate reported diffusion coefficients; the most recent example being Sun and Chen (1985). The graphical method is given

by the following equation;

$$D_{12} = \frac{\bar{u}}{4} \left[ H - \left( H^2 - \frac{a^2}{3} \right)^{1/2} \right] \quad (2.6)$$

where  $H$  is the theoretical plate height defined in terms of the spatial variance of the peak,  $\sigma_s^2$ ;

$$H = \sigma_s^2 / L \quad (2.7)$$

$H$  is determined experimentally from chart measurements by the following equation;

$$H = L(W_{1/2})^2 / (5.54t_{max}^2) \quad (2.8)$$

where  $W_{1/2}$  is the dispersion peak width measured at half height, and  $t_{max}$  is the time corresponding to the peak maximum. The method is termed the "graphical method" since the peak maximum and half width are usually measured from a recording chart with a ruler. The method has two obvious drawbacks; (1) the mathematics of the method are approximate, and (2) the method is subject to human measurement errors.

The moment method solution to Equation 2.2 was given by Aris (1956) and later explained more clearly by Alizadeh et al. (1980). In its simplest form, the solution is;

$$D_{12} = \frac{a^2 \bar{t}}{24\sigma_t^2} \quad (2.9)$$

where;

$$S = \int_0^{\infty} C_a(t) dt \quad (2.10)$$

$$\bar{t} = \frac{1}{S} \int_0^{\infty} t C_a(t) dt \quad (2.11)$$

$$\sigma_t^2 = \frac{1}{S} \int_0^{\infty} (t - \bar{t})^2 C_a(t) dt \quad (2.12)$$

Equations 2.10 through 2.12 are the zeroth, first, and second temporal moments of the dispersion peak. In practice, the moments are usually calculated from the raw peak data by finite summation using the trapezoidal rule. Close examination of Equation 2.12 reveals that the second temporal moment, or variance, is heavily weighted at the peak ends by the difference term. This weighting, where the measurement uncertainty is greatest, can result in large errors in the resulting diffusion coefficients calculated using Equation 2.9. The disadvantages of the moment method are discussed in detail by Radeke (1981).

Alizadeh and Wakeham (1982), two of the authors who developed the practical working moment method equations for Taylor dispersion, eventually abandoned the moment method. All of their reported diffusion coefficients were actually determined by fitting the raw peak data to a Gaussian equation which approximates Equation 2.5.

The moment method was originally used to analyze the data collected during the first phase of the diffusion research program at Texas A&M (Matthews (1986)). Since the calculated diffusion coefficients were found to be highly dependent on the selection of peak end points, one of the goals of this study was to develop an improved data analysis method.

In order to avoid the inherent errors associated with the moment and graphical methods, a new analysis method was developed based on the analytical solution to the Taylor dispersion problem. The development of this new method is discussed in Chapter VI. Several criteria which ensure that a practical Taylor apparatus is operated in accordance with the mathematical theory are also given in Chapter VI.

## CHAPTER III

## PREVIOUS EXPERIMENTAL WORK

Reported measurements of binary diffusion coefficients for alkane-alkane systems at ambient conditions are abundant in the literature. By contrast, diffusion coefficients at conditions far from ambient have been measured for only a few select alkane systems and even fewer measurements have been reported for gaseous solute diffusion in alkane solvents. Only a single study of diffusion in Fischer-Tropsch wax was located. In this chapter, the previous measurements which are particularly relevant to this study will be reviewed in chronological order. Although the data are not tabulated in this chapter, much of the data is used in later chapters to validate the results of this work.

Remarkably, much of the available temperature and pressure dependent diffusivity data for alkanes was collected nearly thirty years ago. In one of the only low temperature studies, Fishman (1955) measured the self diffusivities of n-pentane and n-heptane over the range -80 to 100°C. Fishman used tritium tagged tracers in a capillary type diffusion apparatus. Peter and Weinert (1956) also used a capillary method to measure diffusion coefficients for hydrogen in molten paraffin wax and Fischer-Tropsch reactor wax. The average molecular weights of these waxes were 250 and 340 respectively. Data were collected at 100 and 200°C at several pressures ranging up to 14,000 psi, but the accuracy of the data is uncertain because the technique relied upon solubility measurements at each experimental condition. (In an earlier study, Peter and Weinert (1955) reported solubility measurements for hydrogen, carbon monoxide, carbon dioxide, and water in similar samples of wax.)

Using the NMR spin-echo method, Douglass and McCall (1958) measured self diffusion coefficients of the normal alkane series  $C_5$  through  $C_{10}$ ,  $C_{18}$ , and  $C_{32}$



from temperatures near their melting points to approximately 100°C above their melting points. The study was especially unique in that it reported liquid phase self diffusion coefficients for C<sub>18</sub> and C<sub>32</sub>, two substances which are both solids at room temperature. McCall et al. (1959) also measured the pressure dependence of the self diffusion coefficient for n-C<sub>5</sub> through n-C<sub>10</sub> at pressures up to 8000 psi.

During the twenty year period from 1960 to 1980, several studies of mutual and tracer diffusion in alkane solvents were conducted. Nearly all of the data collected during this period was collected between 20-25°C, although some data was reported from 0-60°C for select systems.

Rossi and Bianchi (1961) measured  $D_{12}^{\circ}$ , the mutual diffusion coefficient at infinite dilution, for several normal alkane solutes between C<sub>10</sub> and C<sub>32</sub> in the solvent n-C<sub>7</sub>. Measurements were made in a diaphragm cell at 25°C. Using a diaphragm cell and the Guoy fringe technique, Van Geet and Adamson (1964) measured both tracer and mutual diffusion over the entire concentration range for the n-octane - n-dodecane system. Tracer diffusivities of n-octadecane (C<sub>18</sub>) were also obtained for the same system. All data was collected at both 25 and 60°C, making this one of the most thorough studies of its time.

Bidlack and Anderson (1964a) measured mutual diffusion over the entire concentration range for nC<sub>7</sub>-nC<sub>16</sub> and nC<sub>6</sub>-nC<sub>12</sub> at 25°C using an optical diffusimeter. In a separate study, Bidlack and Anderson (1964b) reported similar data for the nC<sub>8</sub>-nC<sub>16</sub> system. Bidlack et al. (1969) also measured  $D_{12}^{\circ}$  for several alkane solutes from n-pentane through n-octadecane in the solvent n-hexane at 25°C.

Shieh and Lyons (1969) measured concentration dependent mutual and tracer diffusion coefficients for several n-alkane systems at both 25 and 35°C. Diffusion coefficients were reported for C<sub>6</sub>-C<sub>12</sub>, C<sub>7</sub>-C<sub>16</sub>, and C<sub>8</sub>-C<sub>16</sub>, and C<sub>10</sub>-C<sub>16</sub>.

Diffusion coefficients for dissolved gases in alkane solvents were rarely measured prior to the late 1960's. In one of the first gaseous solute experiments, Davies et al. (1967) used a wetted wall column to measure the diffusion of carbon dioxide in n-heptane and other solvents at 25°C. As is typically the case for the diffusion of dissolved gases, results were assumed to represent mutual diffusion coefficients at infinite dilution.

Malik and Hayduk (1968) developed a capillary method which they used to measure the diffusivity of ethane ( $C_2$ ) in n-hexane and n-heptane at 30 and 40°C. These were the first measurements of diffusivity for a gaseous alkane solute in liquid alkane solvents. Previous research had not included methane, ethane, propane, or butane ( $C_1$  through  $C_4$ ), which are all gases at room temperature and atmospheric pressure.

The capillary technique described by Malik and Hayduk (1968) was used successfully by other researchers to measure diffusion in several additional binary systems containing gaseous alkane solutes. Hayduk and Cheng (1971) measured diffusivities for ethane in normal  $C_6$ ,  $C_7$ ,  $C_8$ ,  $C_{12}$ , and  $C_{16}$  at 25°C and diffusivities of carbon dioxide in  $C_{16}$  at both 25 and 50°C. Hayduk and Buckley (1972) measured ambient temperature diffusion coefficients for methane in the same normal alkane solvents  $C_6$  through  $C_{16}$ . Results at 0 and 50°C were also included for methane in dodecane. In a related study, Hayduk et al. (1973) reported diffusion coefficients for propane in the same set of normal alkane solvents.

Ertl and Dullien (1973) used the spin echo NMR technique to study self diffusion for several normal alkanes. Self diffusion coefficients were reported for  $C_7$ ,  $C_9$ ,  $C_{10}$ ,  $C_{12}$ ,  $C_{14}$ ,  $C_{16}$ , and  $C_{18}$  from temperatures very close to the melting point of each solvent up to near 165°C, where permissible ( $C_7$  and  $C_9$  boil lower

than 165°C). Data was also reported for several non-alkane liquids. The study covered the temperature range -90 through 166°C, which was a much larger range than covered by the self diffusion study of Douglass and McCall (1958).

Lo (1974) measured mutual diffusion over the entire concentration range for several normal alkane systems at 25°C. Data was obtained using a diaphragm cell for the following binary systems; C<sub>7</sub>-C<sub>10</sub>, C<sub>7</sub>-C<sub>12</sub>, C<sub>7</sub>-C<sub>14</sub>, and C<sub>8</sub>-C<sub>14</sub>. Moore and Welck (1974) used an unsteady state porous frit apparatus to measure isotope tracer diffusion at infinite dilution for the solutes C<sub>7</sub> and C<sub>10</sub> in each of the normal alkane solutes C<sub>6</sub> through C<sub>10</sub> at 25-40°C. Hayduk and Iokimidis (1976) constructed an unsteady state diaphragm cell which incorporated a bundle of capillary tubes as the 'diaphragm'. The apparatus was used to measure infinite dilution diffusion coefficients for n-tetracosane (C<sub>24</sub>) and n-dotriacontane (C<sub>32</sub>) in C<sub>6</sub>, C<sub>7</sub>, and C<sub>12</sub> at 25°C.

Evans et al. (1979) were the first to use a Taylor dispersion apparatus to measure diffusion coefficients in alkane solvents. They reported mutual diffusion coefficients at infinite dilution for the gases argon, krypton, xenon, and methane in hexane, decane, and tetradecane at 25°C. Diffusion coefficients for several non-gaseous solutes were also reported. All dispersion peaks were analyzed by the simple graphical method discussed previously.

Prior to 1982, the only alkane solvent diffusion data above 60°C were the self diffusion coefficients measured using the NMR spin echo method. Using a Taylor dispersion apparatus, Chen et al. (1982) collected the first high temperature mutual diffusion data in alkane solvents. Mutual diffusion coefficients at infinite dilution were reported for the solutes argon, krypton, xenon, methane, carbon tetrachloride, and several tetraalkyltins in normal octane, decane, and tetradecane

for temperatures ranging from 25 to 160°C. Diffusion coefficients were determined from Taylor dispersion peak data using the simple graphical method.

Alizadeh and Wakeham (1982) also used the Taylor dispersion method to study diffusion in alkanes. Mutual diffusion coefficients were measured for all possible binary combinations of normal hexane, heptane, and octane. The measurements were performed between 20 and 70°C over the entire concentration range for each binary mixture. The authors originally determined the diffusion coefficients using the moments of the Taylor peak distributions. Peak moments were calculated by direct numerical integration of the concentration versus time data. This method proved to be not as precise as an alternative method. Instead, peak data were fitted to a simple gaussian distribution and the resulting best fit parameters were then used to calculate the reported diffusion coefficients.

The recent investigations in our laboratory at Texas A&M have greatly extended the range of available diffusion data for alkane systems. Using a Taylor dispersion apparatus, a large volume of data were collected over the temperature range 50-291°C at pressures of 1380 and 3450 kPa (200 and 500 psi). Mutual diffusion coefficients for several solutes at infinite dilution, solvent density, and solvent viscosity were measured over the entire range of temperatures and at each pressure. Diffusion coefficients were calculated using the moment method, with the peak moments calculated by direct numerical integration of computer recorded peak data. Results for the various systems were published in three separate papers.

In the first paper, Matthews and Akgerman (1987a) reported the mutual diffusion coefficients at infinite dilution for normal  $C_8$ ,  $C_{10}$ ,  $C_{12}$ ,  $C_{14}$ , and  $C_{16}$  in the solvents  $C_7$  and  $C_{12}$ . Matthews et al. (1987a) reported similar data for normal  $C_8$ ,  $C_{10}$ ,  $C_{12}$ , and  $C_{14}$  in normal hexadecane ( $C_{16}$ ). Finally, Matthews et

al. (1987b) reported data for hydrogen, carbon monoxide, and carbon dioxide in the solvents normal heptane, dodecane, and hexadecane. For the gaseous solute study, samples of solvent, saturated under pressure with the gas, were injected into the diffusion tube. Later in this dissertation, a new alternative method of collecting gas-liquid diffusion data will be presented. The method involves injecting pure gas bubbles into the diffusion tube and therefore eliminates the need for a saturator.

## CHAPTER IV

## THEORY OF PREDICTING DIFFUSION IN LIQUIDS

The theory of diffusion in solids is fairly well defined since a solid is a structured form of crystals or amorphous materials. Diffusion in gases can be understood since a gas is a totally random distribution of particles. However, diffusion in liquids is difficult to describe theoretically because liquids exhibit properties of both gases and solids, with some randomness and some structure. For this reason, an accurate theory for diffusion in liquids has yet to be developed, although several theories have been proposed. This chapter contains a review of the following four general classes of liquid diffusion theories; hydrodynamic theory, activated state theory, free volume theory, and kinetic theory. The kinetic theory is expounded in greatest detail since it was used as the basis for the correlation developed in this work.

## A. HYDRODYNAMIC THEORY

For a single particle moving in a solution by Brownian motion, Einstein (1905; cf. Rossi and Bianchi, 1961) showed that the diffusion coefficient is given by;

$$D = \frac{kT}{f} \quad (4.1)$$

where  $f$  is the frictional coefficient of the diffusing particle. For spherical and rigid particles much larger than the solvent molecules, Stokes (1851; cf. Rossi and Bianchi, 1961) found;

$$f = 3\pi\eta\sigma \quad (4.2)$$

which when combined with Equation 4.1 gives the Stokes-Einstein equation:

$$D = \frac{kT}{(3\pi\eta\sigma)} \quad (4.3)$$

The Stokes-Einstein equation accurately predicts diffusion for only a limited number of systems and even for these systems fails miserably at elevated temperatures. Still, the fact that the equation predicts that  $D\eta/T$  is a constant has been used as the starting point for several well-known correlations including the equation developed by Wilke and Chang (1955). Correlations which relate the diffusion coefficient to viscosity have become known as hydrodynamic models, even though many such correlations are primarily empirical.

## B. ACTIVATION THEORY

Several liquid diffusion theories have been based on the extension of the Arrhenius concept of chemical kinetics to diffusion. In its simplest form, the activation theory is given by;

$$\frac{D}{T} = A \exp\left(\frac{-E}{RT}\right) \quad (4.4)$$

where  $E$  is the energy of activation. For diffusion, the energy of activation has been described as the total energy required to form a void or hole into which the diffusing molecule can jump (Glasstone et al., 1941).

Using theoretical arguments, many researchers have disputed the validity of the activation theory for diffusion. Tyrrell and Harris (1984) summarize the overwhelming evidence which indicates that the energy of activation for diffusion is of little physical significance. Nonetheless, the activation theory has been used successfully as the basis for correlating binary diffusivity data for several different systems. Akgerman and Gainer (1972) used the theory to develop one of the few correlations for predicting diffusion coefficients of dissolved gas solutes in liquid solvents.

### C. FREE VOLUME THEORY

The free volume theory is the simplest theory to explain physically. The theory was originally proposed by Batchinski (1913) for viscosity. Batchinski observed that the following relationship accurately predicts viscosity for many liquids;

$$\frac{1}{\eta} = B \cdot \frac{V - V_{\eta}}{V_{\eta}} \quad (4.5)$$

In this equation  $B$  is a different constant for each liquid.  $V$  is the liquid molar volume, and  $V_{\eta}$  is simply the value of the liquid molar volume where viscosity becomes infinite. Experiments have shown that Equation 4.5 is obeyed when  $V_{\eta}$  is taken to be the molar volume of either the liquid or the solid at the fluid's melting point. The difference  $(V - V_{\eta})$  can be explained physically as the free volume available between the fluids actual volume and the limiting volume of the close-packed fluid at its melting point.

Hildebrand (1971) observed that the self diffusion coefficient may also be described by a similar free volume expression:

$$D = B' \cdot \frac{V - V_D}{V_D} \quad (4.6)$$

In this expression,  $V_D$  is the molar volume where diffusion ceases, which in theory should be equivalent to  $V_{\eta}$ . Hildebrand (1971) found that Equation 4.6 fit experimental data well for self diffusion of benzene and tetrachloromethane. The free volume expression was also shown to fit mutual diffusion data at infinite dilution for iodine in tetrachloromethane. Although the free volume theory is rarely used in its simplest form as given by Equation 4.6, several empirical correlations are based on the free volume theory of diffusion.



## D. KINETIC THEORY

Kinetic theories for liquids and dense gases are actually modifications of the well established kinetic theory for low pressure gases. The kinetic theory for gases is commonly referred to as Chapman-Enskog theory and is discussed in detail by Chapman and Cowling (1970). Remarkably, Chapman and Enskog developed the theory at the same time while working independently in different countries; Chapman in England, and Enskog in Sweden. Both men first published their early works on kinetic theory between 1915 and 1920. Although both used radically different mathematical techniques, their resulting expressions for mass flux, heat flux, and momentum flux, and the corresponding transport coefficients were identical. Chapman admitted that Enskog's mathematical approach was more eloquent and adopted it in his own book (Chapman and Cowling (1970)), which was first published in 1939.

Chapman and Cowling (1970) is still considered the primary source of information about kinetic theory, even though Chapman himself compared reading the book to "chewing glass" (cf. Brush, 1972). In order to avoid the same criticism of this work, the mathematical details of the kinetic theory are not included in this chapter. Instead, only the results, as they apply to the diffusion coefficient are summarized.

Most approaches to diffusion in liquids which are based on kinetic theory start with the first order approximation for self diffusion in a dilute gas of smooth hard spheres or the analogous expression for mutual diffusion. Both equations were given by Chapman and Cowling (1970) as follows. For self diffusion:

$$(nD^{CE})_0 = \frac{3}{8\sigma^2} \left( \frac{kT}{\pi m} \right)^{1/2} \quad (4.7)$$

where  $(nD^{CE})_0$  is the product of the number density and the Chapman-Enskog smooth hard sphere self diffusion coefficient at the low pressure limit of the gas,  $\sigma$  is the molecular diameter, and  $m$  is the molecular mass. For mutual diffusion the analogous equation is;

$$(nD_{12}^{CE})_0 = \frac{3}{8\sigma_{12}^2} \left[ \frac{kT}{2\pi} \frac{(m_1 + m_2)}{m_1 m_2} \right]^{1/2} \quad (4.8)$$

where  $\sigma_{12}$  is the average molecular diameter, often referred to as the collision diameter.

The following assumptions were made in the development of Equations 4.7 and 4.8;

1. Molecules are smooth hard spheres which collide instantaneously.
2. The gas is dilute (the mean free path is much larger than the molecular diameter).
3. Only binary molecular collisions occur.
4. No attractive or repulsive force fields affect the molecules.
5. The assumption of molecular randomness applies. There is no correlation between positions and velocities of the molecules.

As the density of a low pressure gas is increased, these assumptions become more and more unrealistic. Enskog (cf. Chapman and Cowling, 1970) relaxed only the assumption of uncorrelated molecular positions and concluded that self diffusion in dense gases could be predicted by scaling the low pressure diffusion coefficient as follows;

$$\frac{nD}{(nD)_0} = \frac{1}{g(\sigma)} \quad (4.9)$$

where  $g(\sigma)$  is the radial distribution function. Thorne (cf. Chapman and Cowling (1970)) derived the analogous expression for mutual diffusion;

$$\frac{nD_{12}}{(nD_{12})_0} = \frac{1}{g(\sigma_{12})} \quad (4.10)$$

where  $g(\sigma_{12})$  is the pair radial distribution function. The radial distribution functions account for the fact that the local density near a collision is greater than the average density of the solution.

An approximate form for  $g(\sigma_{12})$  given by Lebowitz (1964) has been used by many researchers, but Dymond and Woolf (1982) noted that the Lebowitz approximation fails for the normal range of liquid densities. The correct form for  $g(\sigma_{12})$  when component 1 is present in trace concentration was given by Dymond and Woolf (1982);

$$g(\sigma_{12}) = \frac{1}{(1-\xi)^3} \left[ 1 + \frac{(\sigma_1 - 2\sigma_2)\xi}{(\sigma_1 + \sigma_2)} + \frac{(2\sigma_2 - \sigma_1)(\sigma_2 - \sigma_1)\xi^2}{2\sigma_2(\sigma_1 + \sigma_2)} \right] \quad (4.11)$$

where the solvent packing fraction,  $\xi$ , is given by;

$$\xi = \frac{\pi n \sigma_2^3}{6} \quad (4.12)$$

In these equations,  $n$  is the number density of the solvent,  $\sigma_1$  is the hard sphere diameter of the solute, and  $\sigma_2$  is the hard sphere diameter of the solvent.

Before proceeding with an explanation of how Equations 4.9 and 4.10 have been applied for liquids, it is appropriate to recall some subtle limitations of Equations 4.7 and 4.8. Since these equations were based on the assumption that the spheres are

smooth, the equations do not account for coupling of the rotational and translational velocities of the molecules. The rough hard sphere model accounts mathematically for the coupling of rotational and translational velocities as molecules collide. Chapman and Cowling (1970) presented expressions analogous to Equations 4.7 and 4.8 for rough spheres. The resulting expressions for self diffusion and mutual diffusion are;

$$D^{RHS} = D^{CE} \cdot A(m_2, \sigma_2, I_2) \quad (4.13)$$

and

$$D_{12}^{RHS} = D_{12}^{CE} \cdot A_{12}(m_1, \sigma_1, I_1, m_2, \sigma_2, I_2) \quad (4.14)$$

Expressions were given by Chapman and Cowling (1970) for the rotational-translational coupling functions,  $A$ , which depend on the molecular masses, diameters, and moments of inertia,  $I$ . The  $A$  functions are unity in the limit of no translational-rotational coupling, and are bounded by zero and one. Thus the effect of such coupling is to decrease the diffusion coefficient. Chandler (1975) noted that the coupling effect can be very significant for collisions of polyatomic molecules.

Until this point in the discussion, there has been no mention of the concentration dependence of the mutual diffusion coefficient. The Chapman-Enskog result given by Equation 4.8 is a first order approximation (Chapman and Cowling (1970)), and is independent of concentration. Higher order approximations are discussed by Chapman and Cowling (1970) and include the effect of concentration. These higher order approximations are also influenced by the relative ratio of  $m_1/m_2$  to a greater

degree than the first order approximation. The second order approximation for the infinite dilution diffusion coefficient approaches the first order approximation given by Equation 4.8 as  $m_2/m_1$  approaches zero, where subscript 2 refers to the solvent and subscript 1 to the infinitely dilute solute. For the opposite case, where the solute molecules are much lighter than the solvent molecules, ( $m_1/m_2$  approaches zero), the infinite dilution diffusion coefficient given by the second order approximation is approximately 13/12 larger than the first order approximation given by Equation 4.8.

Obviously, an exact formula for the diffusion coefficient is not even available for simple gaseous systems. However, due to the lack of a better theory for diffusion in liquids, Equations 4.7 through 4.10 have been used as a starting point for many recent theoretical investigations of liquid phase diffusion.

Rather than trying to extract complicated analytical solutions of higher order, the most popular recent approach has been to use computer simulations to correct the Chapman-Enskog first order approximation. Molecular dynamics computer simulations carried out by Alder et al. (1970) determined the ratio of the "true" smooth hard sphere self diffusion coefficient to the Chapman-Enskog first order approximation, by relating the ratio to the molecular velocity autocorrelation function. Alder et al. (1974) and Esteal et al. (1983) determined the analogous ratio for infinite dilution mutual diffusion coefficients. The molecular dynamics ratios were reported as a function of  $V/V_0$ ,  $m_1/m_2$ , and  $\sigma_1/\sigma_2$ , where  $V$  is the

solvent molar volume and  $V_o$  is the theoretical close-packed solvent molar volume spheres given by;

$$V_o = N\sigma^3/\sqrt{2} \quad (4.15)$$

Unfortunately, molecular dynamics ratios were calculated for very limited ranges of  $V/V_o$ ,  $m_1/m_2$ , and  $\sigma_1/\sigma_2$ , precluding their use for predicting many experimentally determined diffusion coefficients.

Following Dymond and Woolf (1982), the rough hard sphere diffusion coefficients, corrected by the ratio determined from molecular dynamics calculations, can be written for self diffusion as;

$$D^{RHS} = \frac{3}{8n\sigma^2} \left[ \frac{kT}{\pi m} \right]^{1/2} \cdot \frac{A}{g(\sigma)} \left[ \frac{D^{SHS}}{D^{CE}} \right]_{MD} \quad (4.16)$$

and for mutual diffusion as;

$$D_{12}^{RHS} = \frac{3}{8n\sigma_{12}^2} \left[ \frac{kT(m_1 + m_2)}{2\pi m_1 m_2} \right]^{1/2} \cdot \frac{A_{12}}{g(\sigma_{12})} \left[ \frac{D_{12}^{SHS}}{D_{12}^{CE}} \right]_{MD} \quad (4.17)$$

The ratios denoted by the subscripts MD are the ratios of the molecular dynamics smooth hard sphere diffusion coefficients to the Chapman-Enskog first order approximations for the smooth hard sphere diffusion coefficients given by Equations 4.7 and 4.8.

Using the available molecular dynamics calculations of Alder et al. (1970) for self diffusion, Dymond (1974) used simple linear regression to develop the following relationship;

$$\frac{1}{g(\sigma)} \left[ \frac{D^{SHS}}{D^{CE}} \right]_{MD} = 1.271 \left( 1 - 1.384 \frac{V}{V_o} \right) \quad (4.18)$$

Substituting this expression into Equation and rearranging the terms yields;

$$10^9 D_{RHS}/\sqrt{T} = A \cdot \frac{2.527 R_g^{1/2}}{V_o^{2/3} M^{1/2}} \cdot (V - 1.384V_o) \quad (4.19)$$

where  $R_g$  is the universal gas constant, and  $M$  is the molecular weight of the liquid. Dymond did not develop an analogous expression for mutual diffusion.

#### E. CORRELATION OF EXPERIMENTAL DATA WITH THE RHS THEORY

There have not been enough molecular dynamics studies covering wide ranges of  $\sigma_1/\sigma_2$ ,  $m_1/m_2$ , and  $V/V_o$  to allow for the development of a general RHS correlation for liquid phase diffusion coefficients. Since the required molecular dynamics data are not available, there has not even been a comprehensive study of the behavior of either of the rotational-translational coupling parameters,  $A$  or  $A_{12}$ . Furthermore, since most experimental diffusion coefficients have been measured over a limited range of conditions near ambient, the data required to verify any such studies is not yet available.

It is only recently that the possibility of developing a practical correlation based on the rough hard sphere theory has been considered seriously in the literature. Chen et al. (1982) tested the hypothesis that the following general equation, based on Equation 4.19 for self diffusion, would also apply to mutual diffusion at infinite dilution;

$$D_{12}^o/\sqrt{T} = \beta(V - V_D) \quad (4.20)$$

In this equation  $\beta$  is the slope of  $D_{12}^o/\sqrt{T}$  versus  $V$ , and  $V_D$  is the intercept where diffusion goes to zero. Chen plotted data for several solutes in the solvents  $C_8$ ,  $C_{10}$ , and  $C_{12}$  at temperatures up to  $160^\circ\text{C}$  and found that  $D_{12}^o/\sqrt{T}$  versus the solvent molar volume,  $V$ , was highly linear in every case. Expressions for  $\beta$  and  $V_D$  were not given.

Using the data from our previous study, Matthews and Akgerman (1987b) tested several of the existing correlations for predicting mutual diffusion coefficients at infinite dilution. None of the existing correlations accurately predicted the data at elevated temperatures. However, the data was found to closely match the form of Equation 4.20. Using least squares analysis, the following equations were developed to predict diffusion in the normal alkane solvents  $C_7$  through  $C_{18}$ :

$$\frac{10^9 D_{12}^o}{\sqrt{T}} = aM_1^b \left( \frac{\sigma_1}{\sigma_2} \right)^3 (V - V_D) \quad (4.21.a)$$

where, for n-alkane solutes;

$$V_D = 0.308V_c, \quad b = -1.56, \quad a = 15.8 \quad (4.21.b)$$

and for dissolved gases;

$$V_D = 0.302V_c, \quad b = -0.76, \quad a = 1.65 \quad (4.21.c)$$

In these equations,  $D_{12}$  is in the  $\text{m}^2/\text{s}$ ,  $T$  in  $\text{K}$ ,  $M$  in  $\text{g}/\text{mol}$ , and molar volumes in  $10^{-6} \text{ m}^3/\text{mol}$ . The hard sphere diameters were calculated using the group



contribution method of Bondi (1964). This was the first attempt to develop a practical predictive equation using the RHS theory.

Although Equations 4.21.a through 4.21.c accurately predict the data which were used in their development, the form of the correlations raises some important theoretical questions. The fact that the molecular diameters appear only as the ratio  $\sigma_1/\sigma_2$  indicates that the slope  $\beta$ , is independent of molecular diameter for the special case of self diffusion. This is in direct contradiction with the molecular dynamics results of Dymond (1974) as represented by Equation 4.19. Despite this contradiction, the equations predict the data well, most likely because  $\sigma$  is approximately proportional to  $M$  for the homologous series of alkanes. The contradiction between Equation 4.21.a and Dymond's (1974) results explains why a separate correlation was required for the gaseous solute data. If theoretically correct, one equation should be sufficient for describing the diffusion of both gaseous and liquid solutes.

Equation 4.21.a through 4.21.c also suggest that  $V_D$ , the molar volume where diffusion approaches zero, is a function of the solute properties. This phenomenon was also verified by the data of Chen et al. (1982) and Hildebrand (1977), but has yet to be explained.

Using data from this study, together with previous data from the first phase of the Texas A&M diffusion program, a single correlation was developed for predicting the diffusion coefficients of both gaseous and liquid solutes in the entire range of

alkane solvents from  $C_7 - C_{25}$ . This correlation is discussed in Chapter VII and guidelines are given for applying the correlation to predict diffusion coefficients in Fischer-Tropsch reactor wax, which typically contains a high percentage of alkanes.