PREDICTION OF SELF-DIFFUSION AND INFINITE DILUTION DIFFUSION COEFFICIENTS IN LIQUIDS

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PREFACE

Two models, based on the Bearman equation, are developed for predicting infinite dilution diffusion coefficients for liquid metals. One of the models is theoretical and the second one is semi-empirical in nature. Both models are equally good; the semi-empirical equation is, however, easier to use. The semi-empirical equation is combined with the Stokes-Einstein temperature correction equation to obtain an equation for predicting infinite dilution diffusion coefficients for organic systems at various temperatures.

A second type model is developed for predicting self-diffusion coefficients for organic liquids, based on the Arrhenius equation. A group contribution technique represented by a geometric series is used to determine the predictive constants. This predictive method was tested for the homologous series of n-alkanes and n-alcohols and was found to be better than the existing models. The proposed method is promising and its application to other homologous series is recommended.

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NOMENCLATURE

a	activity
A	constant for a particular liquid, defined by Equation (2-13)
AAPD	average absolute percent deviation
C	concentration
Calc.	calculated diffusion coefficient
d	interatomic distance
D	self-diffusion coefficient
D_o	pre-exponential factor
D_A^*	tracer diffusion coefficient of A in the mixture
D_{BB}	self-diffusion coefficient of B
D_{AB}	mutual diffusion coefficient
D_{AB}^o	diffusion coefficient of A at infinite dilution in B
$\Delta \ln D$	difference of natural logarithmic self-diffusion coefficient between two neighboring members of the n-alkane series
e	electronic charge
E	activation energy for self-diffusion
E_c	coulombic interaction energy
E_s	activation energy for self-diffusion
E_i	activation energy for impurity diffusion
Exp.	experimental diffusion coefficient
$G(n)$	fitted value of a certain parameter as a function of n
$\Delta^{o\text{-}xs}\bar{G}_A$	partial molar excess Gibbs free energy of A at infinite dilution in B
ΔH	latent heat of vaporization at the normal boiling point, cal/g
ΔH_v	latent heat of vaporization at the normal boiling point, cal/mol

j	fluctuation distance
K	constant in Reddy-Doraiswamy equation
K'	constant in Scheibel equation
k_f	force constant
M	molecular weight
$[M]$	additive and constitutive parameter for self-diffusion coefficient, defined by Equation (1-8)
n	number of carbon atoms in a compound
N	number of carbon atoms in n-alkane
N_o	Avogadro's number
NPTS	total number of data points
PD	percent deviation
$\|PD\|$	absolute value of percent deviation
q	screening constant
r	geometric ratio for n-alkane series
r_1	geometric ratio for n-alcohol series
R	gas constant
Δr	predictive constant for a functional group
T	absolute temperature
v	molar volume
V	molar volume at the normal boiling point
x	predictive constant for n-alkane series
x_1	predictive constant for n-alcohol series
x_A	mole fraction of A
Δx	predictive constant for a functional group
y	predictive constant for n-alkane series
y_1	predictive constant for n-alcohol series

Δy	predictive constant for a functional group
z	excess valence of the solute
Z_B	coordination number of solvent B
Z°_{AB}	coordination number of A at infinite dilution in B

Greek Symbols

β	slowly varying function of z
γ	activity coefficient
γ°_A	activity coefficient of A at infinite dilution in B
λ	interaction energy
Λ	Wilson parameter, defined by Equation (B-2)
μ	viscosity
ρ	density
ϕ	association factor of solvent B
ω	accentric factor

Subscripts

A	solute
B	solvent
c	at critical temperature
m	at melting point
r	in reduced form

Superscripts

o	infinite dilution

CHAPTER I

INTRODUCTION

Molecular diffusion is encountered in practically all branches of chemical engineering. Knowledge of diffusion coefficients is useful in the design of chemical reactors and equipment for unit operations, such as distillation, extraction, absorption, and adsorption. On a theoretical basis, knowledge of diffusion coefficients is useful in the understanding of the mechanism of diffusion transport in liquids.

Molecular diffusion is caused by a chemical potential gradient, which results in the diffusion of a species from a region of higher chemical potential to a region of lower chemical potential. However, due to the difficulty of experimentally measuring a chemical potential gradient, the diffusion coefficient is defined in terms of the concentration gradient. The term intra-diffusion (or tracer-diffusion) coefficient is used when the diffusion of a labeled component is followed in a chemically homogeneous mixture. Self-diffusion is the special case of tracer-diffusion for a system that consists of only one chemical component. The term inter-diffusion (or mutual-diffusion) coefficient is used to describe the diffusion of one constituent in a binary system. Inter-diffusion at infinite dilution (or infinite dilution diffusion) is the special case of inter-diffusion for a system in which the species being followed is present in very low concentrations.

At present, no general correlation is available for predicting self-diffusion coefficients for organic liquids with reasonable accuracy. One of the objectives of this work was to develop a general method for predicting self-diffusion coefficients. The method developed in this work is based on the corresponding states principle and the group contribution technique. The group contributions were obtained by correlating self-diffusion coefficients for n-alkanes and n-alcohols. Subsequently, the group contributions were used to predict self-diffusion coefficients for n-alkanes and n-alcohols not used during the correlating process.

A second objective of this research was to develop models for predicting infinite dilution diffusion coefficients for liquid metals and for organic systems. A theoretical model was developed for predicting infinite dilution diffusion coefficients by using the solvent self-diffusion coefficients and thermodynamic properties of the system. This model was tested by predicting infinite dilution diffusion coefficients for liquid metals. Subsequently, the theoretical model was empirically modified in order to obtain a simple equation. The semi-empirical equation was then combined with the temperature correction equation to predict infinite dilution diffusion coefficients for organic systems at various temperatures.

CHAPTER II

LITERATURE REVIEW

A large number of correlations are available in the literature for the prediction of self-diffusion and infinite dilution diffusion coefficients in liquids. Most of these correlations are either semi-empirical or empirical in nature, and they all have certain limitations regarding the classes of liquids and/or the temperature ranges in which they are applicable. Ertl, Ghai, and Dullien (1,2) reviewed the theories and correlations that were developed for predicting self-diffusion, infinite dilution diffusion, mutual-diffusion, and intra-diffusion coefficients through 1972. Some of the important correlations will be reviewed in this chapter in order to show the present status of the equations that can be used for predicting self-diffusion and infinite dilution diffusion coefficients.

Correlations for Self-Diffusion Coefficients

Most of the correlations for predicting infinite dilution diffusion coefficients for organic systems can also be used to predict self-diffusion coefficients. These correlations will be presented in the section on infinite dilution diffusion coefficients. The correlations used exclusively for the prediction of self-diffusion coefficients in liquids will be reviewed in this section.

Van Geet and Adamson (3) proposed an empirical equation to predict self-diffusion coefficients for n-alkanes, which was based on the

regularities in this class of liquids. They noted that the self-diffusion coefficient for any single hydrocarbon obeyed the Arrhenius exponential equation quite well. The Arrhenius equation is written as

$$D = D_o \exp\left(-\frac{E}{RT}\right) \qquad (1\text{-}1)$$

where

D = self-diffusion coefficient, cm^2/s

D_o = pre-exponential factor, cm^2/s

E = activation energy for self-diffusion, Kcal/mol

T = absolute temperature, K

In addition, the values of self-diffusion coefficient at a given temperature were found to vary with the chain length in a regular way, and a simple relationship was observed between the pre-exponential factor and the activation energy. This relationship is expressed as

$$\log D_o = -3.28 + 0.179\ E \qquad (1\text{-}2)$$

where log is used to represent the logarithm to the base 10. They combined Equations (1-1) and (1-2) to obtain the following equation

$$\log D = -3.28 - E\left(\frac{1000}{2.3RT} - 0.179\right) \qquad (1\text{-}3)$$

The authors constructed a nomograph for the prediction of self-diffusion coefficients for n-alkanes based on Equation (1-3). The only informa-

tion needed is the number of carbon atoms in the n-alkane. They estimated an average error of 5 percent for n-alkanes which had carbon numbers ranging from 5 to 32, and for a temperature range of -50 to 300°C. However, the correlation was tested for the available experimental data, which did not cover the entire range of conditions set forth in the model. Ghai et al. (2) reported that the nomograph gave higher errors at high temperatures.

Dullien (4) derived an equation to predict self-diffusion coefficients of liquids by using a general relationship between transport coefficients of pure fluids and a molecular kinetic model of liquids. The constant was empirically modified to correlate experimental data for 32 liquids with an average deviation of 4 percent. This equation is written as

$$\frac{\mu v D}{RT} = 0.124 \times 10^{-6} v_c^{2/3} \qquad (1\text{-}4)$$

where

μ = viscosity, cp

v = molar volume, cm^3/mol

v_c = critical volume, cm^3/mol

However, this correlation failed to correlate experimental data for methanol and ethanol with reasonable accuracy.

Vadovic and Colver (5) developed an expression, equivalent to Dullien's equation (4), for predicting self-diffusion coefficients. They developed the equation from a consideration of the rigid sphere

model and modified the constant by a least squares fit of the experimental data for 20 liquids. The empirically modified correlation is

$$\frac{D\mu M}{\rho T} = 0.216 \times 10^{-8} \, v_m^{2/3} \qquad (1\text{-}5)$$

where

M = molecular weight

ρ = density, g/cm^3

v_m = molar volume at the melting point, cm^3/mol

This equation predicted self-diffusion coefficients for 20 liquids, including liquid metals, with an average deviation of 6 percent. The advantage of this expression over the Dullien equation is that the molar volume at the melting point is readily available for liquid metals and other high boiling substances, whereas the critical volume is not generally available.

Ertl and Dullien (6) correlated self-diffusion coefficients for n-alkanes by using the Arrhenius exponential equation. They also found a correlation between activation energy and the number of carbon atoms for n-alkanes:

$$E = -6.11 + 8.04 \ln (N) \qquad (1\text{-}6)$$

where

ln = natural logarithm

E = activation energy for self-diffusion, KJ/mol

N = number of carbon atoms in the n-alkane

This equation was found to apply to systems containing carbon numbers ranging from 5 to 20; but, it became invalid for systems with smaller carbon numbers. The authors pointed out that a decreasing influence of chain length on the diffusion process was implied by Equation (1-6).

Tyn and Calus (7) correlated the self-diffusion coefficients for liquids by using additive and constitutive parameters. They derived the following equation for the self-diffusion coefficient:

$$D = T \left(\frac{v}{[M]} \right)^{7.7} \qquad (1\text{-}7)$$

where

[M] = additive and constitutive parameter for the self-diffusion coefficient

$$= v\,(T/D)^{3/23},\ (Ks/cm^2)^{3/23}\ (cm^3/mol) \qquad (1\text{-}8)$$

v = molar volume, cm^3/mol

Contributions to the parameter [M] were computed for various bonds present in alkanes, aromatics, cycloparaffins, alcohols, organic halides, and ethers by using experimental self-diffusion data. The bond and structural contributions were used to calculate the parameter [M] for 46 liquids. Subsequently, self-diffusion coefficients were reproduced with an average deviation of 12 percent for 46 liquids.

Tyn (8) presented a simple graphical correlation for predicting self-diffusion coefficients for 38 liquids in the temperature range of 0 to 100°C. The principle is analogous to the Duhring rule, which correlates the properties of compounds with those of a reference compound. A linear relationship was assumed between the temperature at which a particular liquid would have a given self-diffusion coefficient and the temperature at which pure water would have the same self-diffusion coefficient. The author reported an average error of 2 percent for the liquids correlated. However, this method has the disadvantage that self-diffusion coefficients at two temperatures must be known in order to apply the same principle to liquids not used during the correlating process.

The most recent correlation for predicting self-diffusion coefficients in liquids is due to Riazi and Daubert (9). They used the corresponding states principle to correlate reduced self-diffusion coefficients of pure liquids with reduced temperature and an accentric factor. The reduced self-diffusion coefficients were correlated as

$$D_r = \frac{D}{D_c} = (0.4-\omega)D_r^{(1)} + (0.2-\omega)\, D_r^{(2)} \qquad (1\text{-}9)$$

where

D_c = self-diffusion coefficient at the critical temperature, cm^2/s

D_r, $D_r^{(1)}$, $D_r^{(2)}$ = reduced self-diffusion coefficients

ω = accentric factor

The critical self-diffusion coefficients were evaluated relative to that of benzene, which was obtained by extrapolation to the critical temperature. The authors presented a graph of reduced self-diffusion coefficients $D_r^{(1)}$ and $D_r^{(2)}$ as a function of reduced temperature, T_r. They reported an average error of 4.5 percent for 16 liquids. However, this correlation failed to predict the self-diffusion coefficient of ethanol with reasonable accuracy.

In this study the Tyn graphical correlation, the Tyn and Calus group contribution method, and the Wilke-Chang equation will be used as a basis of comparison for the proposed method.

Correlations for Infinite Dilution Diffusion Coefficients

Diffusion coefficient of a solute at infinite dilution in a solvent implies that each solute atom or molecule is in an environment of essentially pure solvent. In engineering work, however, infinite dilution diffusion coefficients are assumed to be applicable for concentrations of the solute up to approximately 5 mole percent. From an engineering point of view, equations relating infinite dilution diffusion coefficients to self-diffusion coefficients are most desirable. Only a few such equations have been presented, and these are all restricted to liquid metal systems and the homologous series of n-alkanes. Some of the important correlations for infinite dilution diffusion coefficients will be reviewed separately in the following sections for liquid metals and for organic systems.

Liquid Metal Systems

Self-diffusion coefficients for liquid metals can be predicted with high accuracy by using the hydrodynamical and the fluctuation theories. The models which can be used to predict self-diffusion coefficients for liquid metals were developed by Swalin (10), Walls and Upthegrove (11), Hines, Walls, and Arnold (12), and Hines and Walls (13). However, the development of models that can be used to predict infinite dilution diffusion coefficients has met with less success. The fluctuation, the critical fluctuation, and the hole theories for self-diffusion have been extended by several investigators to predict infinite dilution diffusion coefficients in liquid metal systems.

For the case of tin diffusing into silver, Leak and Swalin (14) attributed the enhancement in diffusion to the coulombic contribution that resulted from the solute having a higher valence than the solvent. They proposed a model based on Swalin's (10) fluctuation theory for self-diffusion, but with the Thomas-Fermi model being used to represent the coulombic interaction energy. The Thomas-Fermi model was combined with the Morse potential in order to account for the presence of the solute. The fluctuation theory equation is

$$\frac{D^{\circ}_{AB}}{D_{BB}} = 1 + \frac{q^2 E_c}{k_f}\left(1 + \frac{2}{qd} + \frac{2}{q^2 d^2}\right) \qquad (1\text{-}10)$$

where

D°_{AB} = diffusion coefficient of A at infinite dilution in B, cm^2/s

D_{BB} = self-diffusion coefficient of B, cm^2/s

q = screening constant, Å^{-1}

d = interatomic distance, Å

k_f = force constant, Mdyne/cm

The coulombic interaction term is defined as

$$E_c = \frac{\beta z e^2}{d} \exp(-qd) \qquad (1\text{-}11)$$

where

e = electronic charge, e.s.u.

z = excess valence of the solute

The quantity β is a slowly varying function of z. Alfred and March (15) estimated the value of β from solute diffusion in solid metals.

Swalin and Leak (16) proposed two models to relate infinite dilution diffusion (or impurity diffusion) coefficients to solvent self-diffusion coefficients. In one model they modified the fluctuation theory of Swalin (10) to incorporate a critical fluctuation volume. They used the Thomas-Fermi model to calculate the coulombic interaction between the solute and the solvent and the Morse potential to evaluate the activation energy of the solvent. The critical fluctuation theory expression is

$$\frac{D^{\circ}_{AB}}{D_{BB}} = \exp\left(\frac{E_s - E_i}{RT}\right) \qquad (1\text{-}12)$$

where

E_s = activation energy for self-diffusion, cal/g atom

E_i = activation energy for impurity diffusion, cal/g atom

The difference in activation energies for self-diffusion and impurity diffusion was defined as the coulombic interaction energy, E_c, where

$$E_c = E_s - E_i$$

$$= \frac{N_o \beta z e^2}{4.185 \times 10^7 (d+j)} \exp [- q (d+j)] \qquad (1\text{-}13)$$

and

N_o = Avogadro's number

j = fluctation distance, Å

In the second model, Swalin and Leak (16) used the Thomas-Fermi model along with the hole theory to derive an equation for the ratio of the impurity diffusion coefficient to the solvent self-diffusion coefficient. They proposed that the energy of hole formation would be reduced by a coulombic interaction term. The hole theory expression is given by Equation (1-12) with the following modification.

$$E_c = E_s - E_i$$

$$= \frac{N_o \beta z e^2}{4.185 \times 10^7 d} \exp (-qd) \qquad (1\text{-}14)$$

Swalin and Leak (16) tested Equations (1-10) through (1-14) for systems in which the solute and the solvent differed only in their valences.

Gupta (17) modified the critical fluctuation theory expression for the coulombic interaction term and obtained the following equation:

$$E_c = \frac{N_o \beta z e^2}{4.185 \times 10^7 (d+j)} \exp\left[-q\left(d+\frac{1}{2}j\right)\right] \qquad (1\text{-}15)$$

Gupta (17) tested the fluctuation, the critical fluctuation, and the hole theory expressions for systems similar to those evaluated by Swalin and Leak (16). These studies reported combined average errors of 18 and 28 percent for seven systems when compared with the fluctuation and the critical fluctuation theory models, respectively. The hole theory gave an average error of 18 percent for four systems. All systems tested were for silver as the solvent.

Gupta (18) modified the fluctuation and the critical fluctuation theories to account for the inequality of the jump frequency of the solute and the solvent. He tested these equations for eight solutes in solvent tin and six solutes in solvent silver. The modified fluctuation theory gave an average error of 68 percent for solvent tin and 33 percent for solvent silver. The modified critical fluctuation theory predicted impurity diffusion coefficients with an average error of 78 percent for solvent tin and 30 percent for solvent silver. The hole theory gave an average error of 80 percent for solvent tin and 33 percent for solvent silver.

Wang and Gupta (19) modified the expressions proposed by Gupta (18) for the fluctuation and the critical fluctuation theories by using the Thomas-Fermi and the Hartree potentials to calculate the additional

coulombic interaction term due to the excess solute charge. Wang and Gupta (19), and Gupta and Wang (20) tested these equations for five solutes in solvent silver. The modified expressions gave an average error of 15 percent for the fluctuation theory and 50 percent for the critical fluctuation theory.

From a review of the existing correlations it is clear that most of the expressions do not predict infinite dilution diffusion coefficients in liquid metals with reasonable accuracy. Only one each of the fluctuation and the hole theory equations predict infinite dilution diffusion coefficients with average errors less than 20 percent. However, it is important to note that these expressions have been tested for only two solvent systems - silver and tin. Besides, some of the terms in these expressions were adjusted to fit the experimental data. Consequently, none of the existing correlations is truly predictive in nature.

Organic Systems

The Wilke-Chang (21) equation is one of the most widely used correlation for predicting infinite dilution diffusion and self-diffusion coefficients in non-electrolytes at low viscosities. The Wilke-Chang equation is an empirical modification of the Stokes-Einstein equation and is expressed as

$$D^{\circ}_{AB} = 7.4 \times 10^{-8} \frac{(\phi M_B)^{1/2} T}{\mu_B (V_A)^{0.6}} \qquad (1\text{-}16)$$

where

D°_{AB} = diffusion coefficient of A at infinite dilution in B, cm^2/s

M_B = molecular weight of solvent B

V_A = molar volume of solute A at its normal boiling point, cm^3/mol

μ_B = viscosity of solvent B, cp

T = absolute temperature, K

ϕ = association factor of solvent B

Wilke and Chang (21) recommended a value of 2.6 for the association factor for water, 1.9 for methanol, 1.5 for ethanol, and 1.0 for unassociated solvents such as benzene, ether, and the aliphatic hydrocarbons. According to Reid et al. (22), the Wilke-Chang equation predicts diffusion coefficients to within 11 percent of experimental values for water as a solvent and to within 23 percent for organic solvents. The Wilke-Chang equation is not recommended when water is the solute, since the prediction errors may be as high as 200 percent.

The chief disadvantage of the Wilke-Chang correlation is the necessity to evaluate the association factor for a particular solvent before it can be used to predict diffusion coefficients. Consequently, a number of correlations have been presented as modifications of the Wilke-Chang equation by eliminating the association factor. The equations of Sitaraman et al. (23) and Reddy and Doraiswamy (24) are the results of two such efforts.

Sitaraman et al. (23) eliminated the association factor in the Wilke-Chang equation by introducing the latent heats of vaporization of the solute and solvent at their normal boiling points. Sitaraman et al.'s equation is

$$D_{AB}^{\circ} = 5.4 \times 10^{-8} \left(\frac{M_B^{1/2} \Delta H_B^{1/3} T}{\mu_B V_A^{1/2} \Delta H_A^{1/3}}\right)^{0.93} \qquad (1\text{-}17)$$

where ΔH_A and ΔH_B are the latent heats of vaporization of the solute and solvent, respectively, at the normal boiling points, with units of cal/g. The Sitaraman et al. (23) equation is less restrictive than the Wilke-Chang equation, and is recommended when water is the solute (25). The Sitaraman et al. equation gives about 12 percent error for water as a solute, whereas the Wilke-Chang equation gives about 200 percent error. Both equations give the same magnitude of errors for water and organic solvents.

Reddy and Doraiswamy (24) modified the Wilke-Chang equation by replacing the solvent association factor with the cube root of the solvent molar volume. Their equation is expressed as

$$D_{AB}^{\circ} = \frac{K M_B^{1/2} T}{\mu_B (V_A V_B)^{1/3}} \qquad (1\text{-}18)$$

where V_B is the molar volume of the solvent at the normal boiling point, with units of cm^3/mol. Reddy and Doraiswamy (24) recommended the following values of the constant K: (1) if $V_B/V_A \leq 1.5$, $K = 10 \times 10^{-8}$; and (2) if $V_B/V_A \geq 1.5$, $K = 8.5 \times 10^{-8}$. They reported average errors of less than 20 percent for 96 binary systems. Infinite dilution diffusion coefficients were predicted with an average error of 25 percent for water as a solute in organic solvents.

Scheibel (26) modified an earlier equation proposed by Wilke (27) to eliminate the diffusion factor, which was given in the form of a family of curves. Scheibel represented the curves by an empirical equation and combined it with the Wilke equation to obtain the following equation:

$$D_{AB}^{\circ} = \frac{K' T}{\mu_B V_A^{1/3}} \qquad (1\text{-}19)$$

where

$$K' = 8.2 \times 10^{-8} \left[1 + \left(\frac{3V_B}{V_A}\right)^{2/3}\right] \qquad (1\text{-}20)$$

Scheibel (26) made the following recommendations as exceptions to the general form of K' represented by Equation (1-20): (1) for water as a solvent, $K' = 25.2 \times 10^{-8}$ if $V_A < V_B$; (2) for benzene as a solvent, $K' = 18.9 \times 10^{-8}$ if $V_A < 2V_B$; and (3) for other solvents, $K' = 17.5 \times 10^{-8}$ if $V_A < 2.5V_B$. Reid et al. (22) reported that the Scheibel equation predicts infinite dilution diffusion coefficients with an average error of 11 percent for water as a solvent, and to within 20 percent for organic solvents.

King et al. (28) reported that the self-diffusion coefficient should be dependent upon variables representing the molecular size, intermolecular forces and the number of nearest neighbors. Based on the empirical observation that the group $D\mu/T$ was nearly constant for self-diffusion, King et al. (28) developed an empirical equation for the prediction of infinite dilution diffusion coefficients. King et al's equation is

$$D_{AB}^{\circ} = 4.4 \times 10^{-8} \frac{T}{\mu_B} \left(\frac{V_B}{V_A}\right)^{1/6} \left(\frac{\Delta H_{vB}}{\Delta H_{vA}}\right)^{1/2} \qquad (1\text{-}21)$$

where ΔH_{vA} and ΔH_{vB} are the latent heats of vaporization of the solute and solvent, respectively, at their normal boiling points, with units of cal/mol. The King et al. equation predicts infinite dilution diffusion coefficients with an average error of 20 percent. However, this equation is not recommended for viscous solvents. The recommended upper limit for $D^{\circ}_{AB}\ \mu_B/T$ is $1.5\ X10^{-7}$ cp cm^2/Ks.

Lo (29) observed that the infinite dilution diffusion coefficient in a binary n-alkane system is a linear function of the logarithm of the number of carbon atoms in the solute for a particular solvent. Lo (29) developed an analytical expression for the infinite dilution diffusion coefficient in terms of the self-diffusion coefficient of the solvent and the number of carbon atoms in the solute and solvent. Lo's equation is

$$D^{\circ}_{AB} = D_{BB} + \frac{1\ X\ 10^{-5}}{0.1964 - 0.06785N_B} \log \left(\frac{N_A}{N_B}\right) \qquad (1\text{-}22)$$

where

D_{BB} = self diffusion coefficient of solvent B, cm^2/s

N_A, N_B = number of carbon atoms in solute A and solvent B, respectively

Reid et al. (22) recommended that the Scheibel equation be used to predict infinite dilution diffusion coefficients for solutes diffusing into organic solvents. The equations of Wilke-Chang, Sitaraman et al., and Scheibel will be used for comparisons with predictions of the present work.

CHAPTER III

DEVELOPMENT OF MODELS

Infinite Dilution Diffusion Coefficients

Bearman (30) derived an equation to show the concentration dependence of diffusion coefficients in liquids by using the statistical mechanical theory. As shown by Bearman (30), the concentration dependent diffusion coefficient for regular solutions is given by

$$D_{AB} = D_A^* \left(\frac{\partial \ln a_A}{\partial \ln C_A}\right)_{T,P} \tag{2-1}$$

where D_{AB} is the mutual diffusion coefficient, D_A^* is the tracer diffusion coefficient of A in the mixture at the same composition, a_A is the activity of A, and C_A is the concentration of A. An alternate expression for the concentration dependent mutual diffusion coefficient is

$$D_{AB} = D_A^* \left(\frac{x_A v_A + x_B v_B}{v_B}\right) \left(\frac{\partial \ln a_A}{\partial \ln x_A}\right)_{T,P} \tag{2-2}$$

where v_A and v_B are the molar volumes, and x_A and x_B are the mole fractions of A and B. Writing the activity in terms of the mole fraction and the activity coefficient, Equation (2-2) can be written as

$$D_{AB} = D_A^* \left(\frac{x_A v_A + x_B v_B}{v_B}\right) \left[1 + \left(\frac{\partial \ln \gamma_A}{\partial \ln x_A}\right)_{T,P}\right] \tag{2-3}$$

Proposed Models

As defined by Bearman (30), regular solution theory is based on the assumption that the molar volumes are mole fraction additive, and the radial distribution functions are independent of concentration at constant temperature and pressure. The former assumption is approximately met for liquids in general, and the latter assumption is valid when the solute and solvent molecules are of similar size and shape. The latter assumption is also met approximately in infinitely dilute solutions. If A is infinitely dilute in B, x_A can be equated to zero and x_B can be equated to one in the above model. In addition, the diffusion of a solute may be visualized as the diffusion of an impurity through the solvent. In infinitely dilute solutions the diffusivity of the solute should be equal to the diffusivity of the solvent except for a correction factor associated with the non-ideal effects caused by the presence of the solute. For this limiting case the tracer diffusion coefficient in the Bearman (30) equation can be replaced by the self-diffusion coefficient of the solvent, and Equation (2-3) can be expressed as

$$D^{\circ}_{AB} = D_{BB} \left[1 + \left(\frac{\partial \ln \gamma^{\circ}_A}{\partial \ln x_A}\right)_{T,P}\right] \qquad (2\text{-}4)$$

where

D°_{AB} = diffusion coefficient of A at infinite dilution in B, cm^2/s

D_{BB} = self-diffusion coefficient of solvent B, cm^2/s

γ°_A = activity coefficient of A at infinite dilution in B

Equation (2-4) shows that the correction to be applied to the solvent self-diffusion coefficient is related to the term $(\partial \ln \gamma_A^\circ / \partial \ln x_A)$. If the solute and solvent form an ideal solution, the diffusion coefficient of the solute would be equal to that of the solvent, as expected. Since the solute moves through an approximately uniform environment for the case of infinite dilution, the gradient of the activity coefficient provides a small but finite contribution to the diffusion coefficient of the solute. Equation (2-4) was used to predict infinite dilution diffusion coefficients for liquid metal systems.

Application of Equation (2-4) to organic systems is not practical since activity coefficient data are not readily available for dilute solutions at the temperatures of the reported diffusion data. Consequently, Equation (2-4) was modified empirically in order for it to apply to organic systems.

Since the activity coefficient of the solute is related to the partial molar excess Gibbs free energy, Equation (2-4) can be written as

$$D_{AB}^\circ = D_{BB} \left(1 + \frac{1}{RT} \frac{\partial \Delta^\circ \bar{G}_A^{xs}}{\partial \ln x_A}\right) \qquad (2\text{-}5)$$

where $\Delta^\circ \bar{G}_A^{xs}$ is the partial molar excess Gibbs free energy of A at infinite dilution in B. In the expression above, the difference between the solute and solvent diffusion coefficients is due to the partial molar excess Gibbs free energy that results from the non-ideality of the solution due to the presence of the solute. This energy may be described simply as an additional binding energy associated with the presence of the solute in the solvent. This additional binding energy, in turn, can be related to the number of nearest neighbor bonds that must be broken before diffusion of the solute can occur.

Diffusion of a solute at infinite dilution in a solvent may be visualized as the diffusion of an impurity. The number of nearest neighbors of solute A at infinite dilution in solvent B may be represented by Z^{o}_{AB}. Before an atom or molecule can travel from one equilibrium position to another, one-half of the near neighbor bonds must be broken. For the case of impurity diffusion, the number of bonds that must be broken is $Z^{o}_{AB}/2$. The partial molar excess Gibbs free energy, $\Delta^{o}\bar{G}^{xs}_{A}$, is the energy necessary to break $Z^{o}_{AB}/2$ nearest neighbor bonds with the solute. Thus, the correction term to the solvent self-diffusion coefficient is related to the partial molar excess Gibbs free energy, $\Delta^{o}\bar{G}^{xs}_{A}$, and the number of nearest neighbors, Z^{o}_{AB}. In order to simplify Equation (2-5), the correction term to the solvent self-diffusion coefficient, $(\partial\, \Delta^{o}\bar{G}^{xs}_{A}/\partial \ln x_{A})$, is replaced by the term $(-\Delta^{o}\bar{G}^{xs}_{A}.\ 2/Z^{o}_{AB})$ as an approximation. In effect, this substitution implies that the energy needed to break one near neighbor bond of the solute is $(-\Delta^{o}\bar{G}^{xs}_{A}.\ 2/Z^{o}_{AB})$. The negative sign of this term is based on empirical observations made for liquid metal systems investigated in this work. Thus Equation (2-5) can be written as

$$D^{o}_{AB} = D_{BB}\left(1 - \frac{\Delta^{o}\bar{G}^{xs}_{A}}{RT}\,\frac{2}{Z^{o}_{AB}}\right) \qquad (2\text{-}6)$$

Although Equation (2-6) is relatively easy to use, it still does not solve the problem of non-availability of activity coefficient data in infinitely dilute solutions at the temperatures of interest. However, activity coefficients at infinite dilution can be calculated near the boiling points by using the Wilson equation. Equation (2-6) can be written for any reference temperature, in this case the boiling point BP, as

$$(D^{\circ}_{AB})_{BP} = (D_{BB})_{BP} \left(1 - \frac{\Delta\, {}^{\circ}\bar{G}^{XS}_{A}}{RT} \frac{2}{Z^{\circ}_{AB}}\right)_{BP} \qquad (2\text{-}7)$$

The reference temperature is taken as the boiling point of the lower boiling component in the binary system.

Application of the Stokes-Einstein equation (25) to diffusion at two temperatures, T_1 and T_2, gives an equation for the temperature correction to the diffusion coefficient, as

$$\left(\frac{D^{\circ}_{AB}\,\mu_B}{T}\right)_{T_1} = \left(\frac{D^{\circ}_{AB}\,\mu_B}{T}\right)_{T_2} \qquad (2\text{-}8)$$

where μ_B is the viscosity of the solvent. Combining Equations (2-7) and (2-8) the following correlation is obtained for the prediction of infinite dilution diffusion coefficients at any temperature:

$$D^{\circ}_{AB} = \left(\frac{D_{BB}\mu_B}{T}\right)_{BP} \frac{T}{\mu_B} \left(1 - \frac{\Delta\, {}^{\circ}\bar{G}^{XS}_{A}}{RT} \frac{2}{Z^{\circ}_{AB}}\right)_{BP} \qquad (2\text{-}9)$$

Equation (2-9) can be written in an alternate form in terms of the activity coefficient, as

$$D^{\circ}_{AB} = \left(\frac{D_{BB}\,\mu_B}{T}\right)_{BP} \frac{T}{\mu_B} \left(1 - \frac{2 \ln \gamma^{\circ}_{A}}{Z^{\circ}_{AB}}\right)_{BP} \qquad (2\text{-}10)$$

Infinite dilution diffusion coefficients at the temperatures of interest can be predicted by using the solvent self-diffusion coefficient at the reference temperature, the solvent viscosity at the reference temperature and at the temperature of interest, the activity coefficient of the solute at the reference temperature and the number of nearest neighbors of the solute at infinite dilution in the solvent.

Self-Diffusion Coefficients

Group Contribution Method

The temperature dependence of experimental self-diffusion coefficients is widely reported in the form of an Arrhenius equation

$$D = D_o \exp\left(-\frac{E}{RT}\right) \tag{2-11}$$

where

D = self-diffusion coefficient, cm^2/s

D_o = pre-exponential factor, cm^2/s

E = activation energy for self-diffusion, cal/mol

T = absolute temperature, K

Equation (2-11) can be written as a reduced equation if comparison is made at constant pressure. Thus

$$\ln D = \ln D_c + A\left(1 - \frac{1}{T_r}\right) \tag{2-12}$$

where

$\ln$ = natural logarithm

D_c = self-diffusion coefficient at critical temperature, cm^2/s

$A = \frac{E}{RT_c}$ = constant for a particular liquid (2-13)

$T_r = T/T_c$ = reduced temperature

T_c = critical temperature, K

Equation (2-12) has the form of a corresponding states type correlation. This equation was used for the correlation and prediction of self-diffusion coefficients for n-alkanes and n-alcohols. The experimental values of the critical temperature, T_c, were fitted to an analytical equation. Subsequently, T_c was treated as a reference temperature, which was obtained from the analytical equation. D_c was defined as the self-diffusion coefficient at the critical temperature T_c. However, since $\ln D_c$ was obtained by fitting Equation (2-12) to experimental data, $\ln D_c$ was treated as an empirical constant.

The parameters $\ln D_c$, A, and T_c were correlated with the number of carbon atoms in the molecule of the diffusing species. The most general form of the equation, that can be used to correlate the parameters $\ln D_c$, A, and T_c with the carbon number n, has a geometric form expressed as

$$G(n) = x + y\,(1 + r + r^2 + r^3 + \ldots\ldots\ldots + r^{n-1}) \qquad (2\text{-}14)$$

$$= x + y\,\frac{(1-r^n)}{(1-r)} \quad \text{for } r \neq 1 \qquad (2\text{-}15)$$

$$= x + yn \quad \text{for } r = 1 \qquad (2\text{-}16)$$

$$= x + y \quad \text{for } r = 0 \qquad (2\text{-}17)$$

where the function G(n) represents the parameters $\ln D_c$, A, and T_c. The term n is the number of carbon atoms in the compound, and x, y, and r are adjustable constants. The contributions due to the successive addition of methylene groups to a carbon skeleton with one carbon atom are yr, yr^2, yr^3, ..., yr^{n-1}. This implies that each methylene group contribution differs from the preceding one by a constant ratio r.

A plot of critical temperature versus carbon number for n-alkanes is shown in Figure 1. The increment in the critical temperature

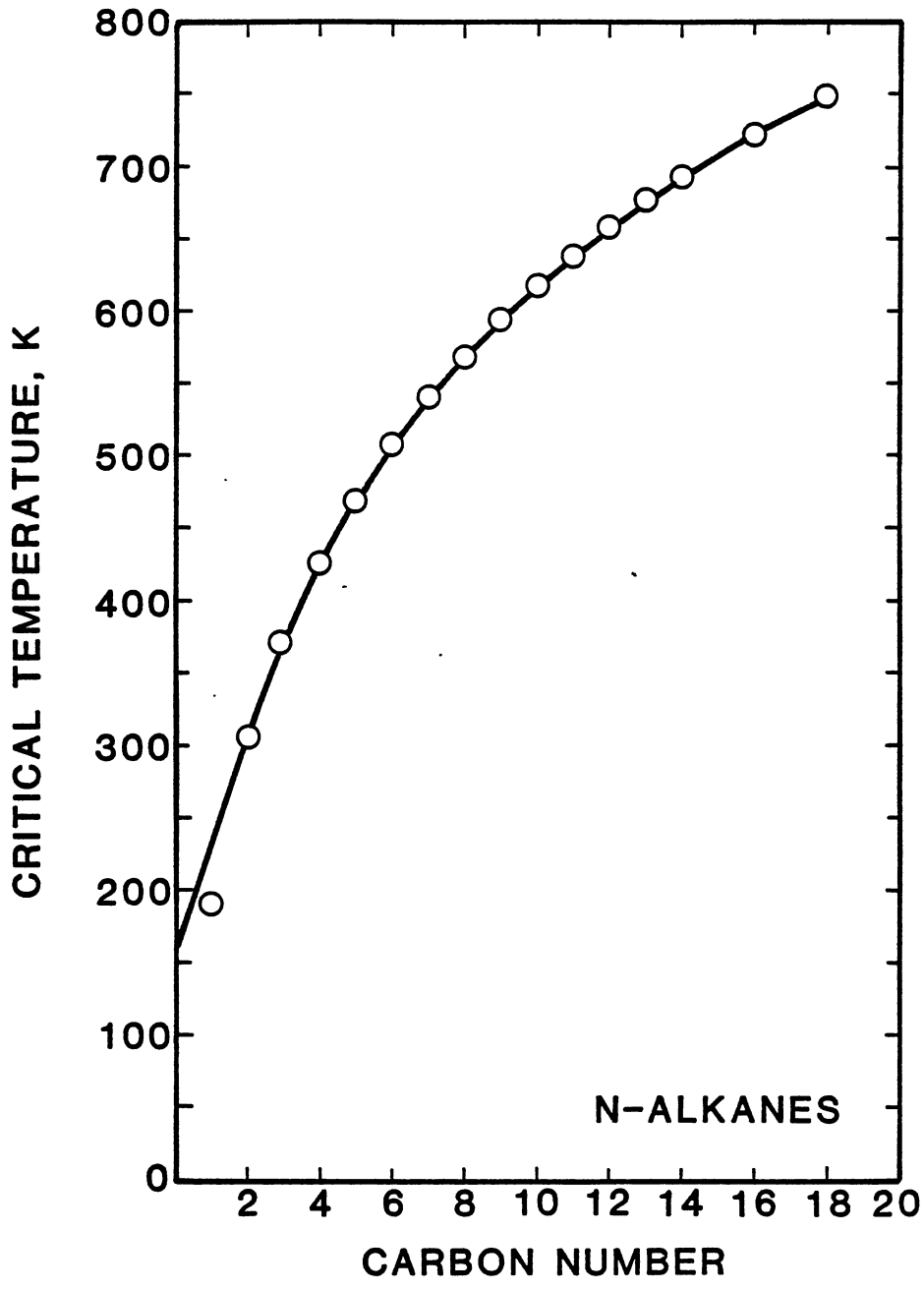

Figure 1. Critical Temperature Versus Carbon Number for n-Alkanes

associated with the successive addition of methylene groups to the carbon skeleton is shown in Figure 2. The increment in the critical temperature due to the addition of successive methylene groups decreases with increasing carbon number. This behavior is represented by a geometric series with "r" less than 1. For the case of the geometric ratio "r" less than 1, the group contribution due to the addition of a methylene group to any carbon skeleton decreases progressively in going from a low carbon compound to a higher carbon compound. The difference in the natural logarithm of the self-diffusion coefficient for n-alkanes with increasing carbon number, at a fixed value of the reduced temperature, is shown in Figure 3. It follows the same trend as that observed for the critical temperature. In analogy, all three parameters $\ln D_c$, A, and T_c were represented by a decreasing geometric series with the geometric ratio "r" less than 1. The geometric series type group contribution was proposed by Chen (31). Ertl and Dullien (6) also observed that the activation energy for self-diffusion, E, for n-alkanes was a decreasing function of the number of carbon atoms in the diffusing molecule.

The functional form of the parameters $\ln D_c$, A, and T_c is the same for any homologous series. However, the adjustable constants include the contribution due to the addition of a particular functional group, such as a hydroxyl group, to the carbon skeleton of the n-alkane homologous series. Thus

$$G(n) = x_1 + y_1 \frac{(1-r_1^{\,n})}{(1-r_1)} \quad \text{for } r_1 \neq 1 \qquad (2\text{-}18)$$

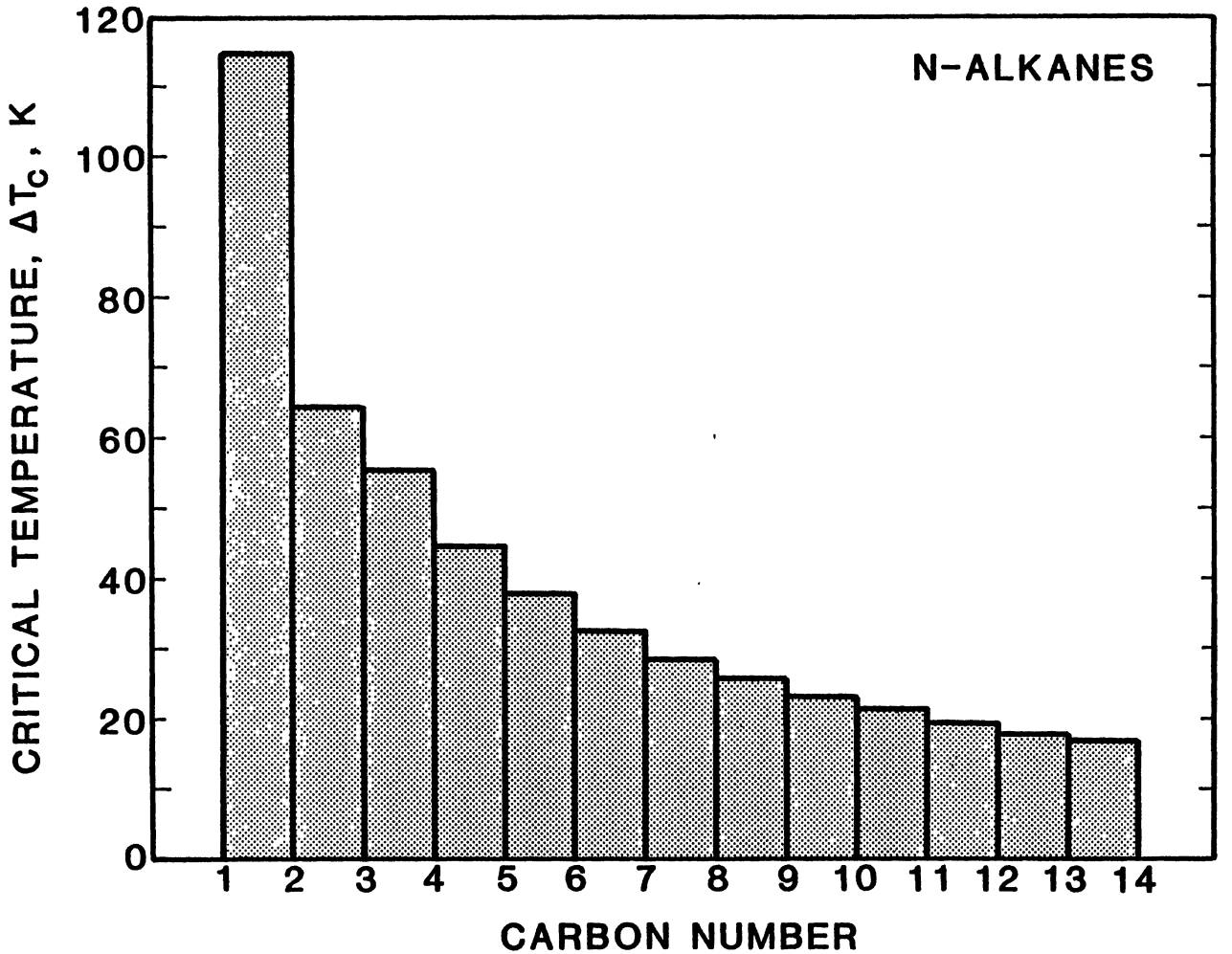

Figure 2. Contribution of nth Methylene Group to the Critical Temperature for n-Alkanes

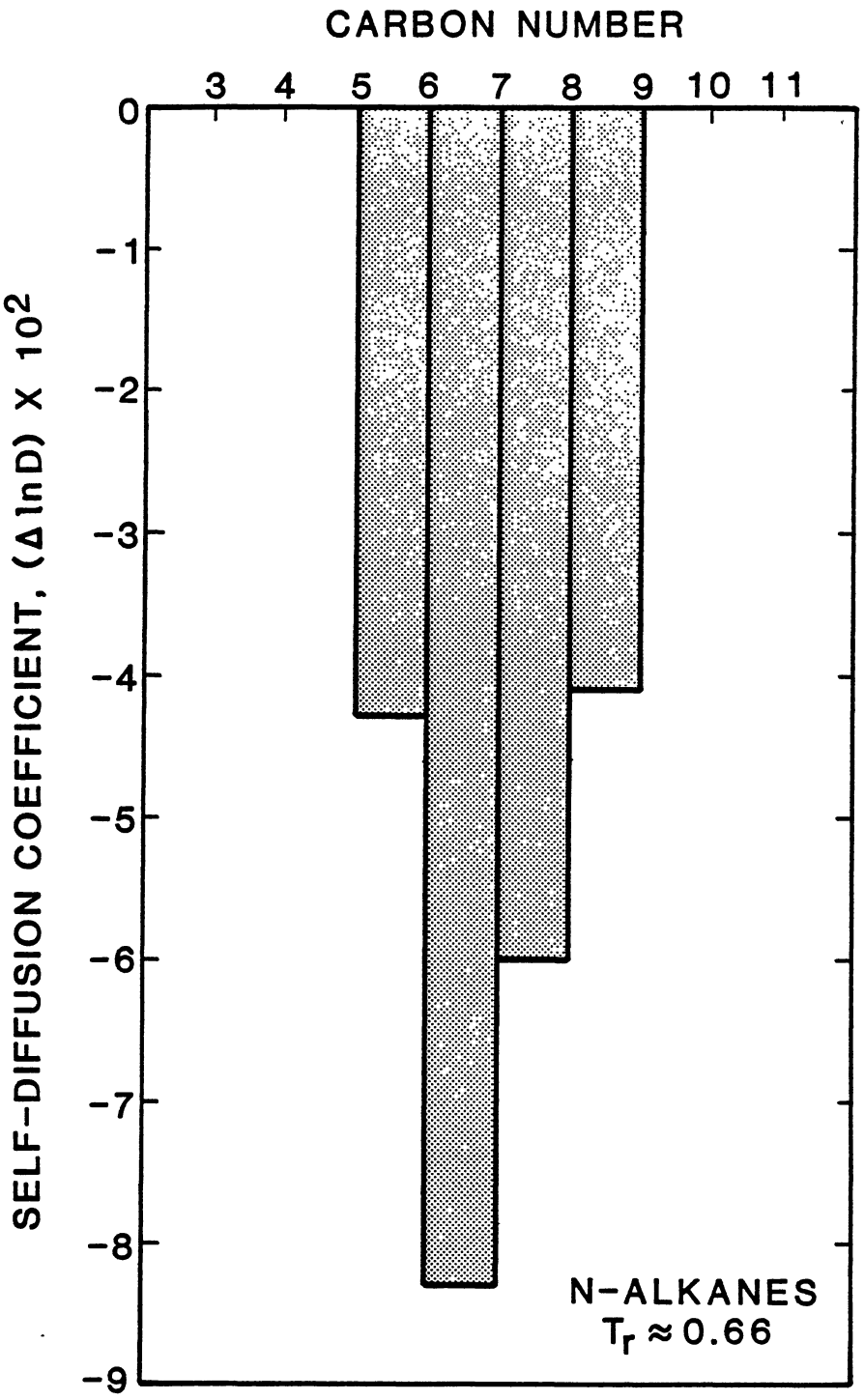

Figure 3. Contribution of nth Methylene Group to the Natural Logarithm of the Self-Diffusion Coefficient for n-Alkanes at $T_r \approx 0.66$

where

$$x_1 = x + \Delta x \tag{2-19}$$

$$y_1 = y + \Delta y \tag{2-20}$$

$$r_1 = r + \Delta r \tag{2-21}$$

The group contributions x, y, and r are the same as those for the n-alkane series, while the constants Δx, Δy, and Δr are contributions due to the addition of a functional group at the end of the carbon chain of the n-alkane homologous series.

Equations (2-15) and (2-18) were used to generate each of the three parameters $\ln D_c$, A, and T_c in Equation (2-12). The three constants for critical temperature were first obtained for the homologous series of n-alkanes and n-alcohols. Subsequently, the remaining six constants for both homologous series were obtained by using the available self-diffusion data for n-alkanes and n-alcohols. Thus, there are nine constants required to predict self-diffusion coefficients for n-alkanes. In order to predict self-diffusion coefficients for n-alcohols, another nine constants are to be added to the nine n-alkane constants. The predictive capability of the group contribution method was tested by using the method to obtain self-diffusion coefficients for compounds not included in the regression.

CHAPTER IV

RESULTS AND COMPARISONS WITH OTHER METHODS

Infinite Dilution Diffusion Coefficients

Liquid Metal Systems

Diffusion coefficient computations at infinite dilution were made for 20 systems by using Equations (2-4) and (2-6). The systems were chosen at temperatures above the melting points of the solute and solvent. Failure to observe this precaution introduces the effect of solute dissolution in the solvent, and hence predicts diffusion coefficients which may be in error by as much as an order of magnitude. The selected systems were restricted to those for which thermodynamic data were available. Thermodynamic data that had been evaluated at a consistent standard state were obtained from Hultgren et al. (32). The solvent self-diffusion coefficients and coordination numbers are given in Table X (Appendix). At infinite dilution the number of nearest neighbors of the solute in the solvent can be represented by the coordination number of the solvent, Z_B. This substitution is justified since the solute is present in very low concentrations and does not alter the structure of the solvent significantly. Diffusion coefficients and thermodynamic data at infinite dilution are given in Table XI (Appendix). Experimental impurity diffusion and self-diffusion coefficients were obtained from the Arrhenius equations reported by the original investigators, unless their values were reported at the temperature

for which thermodynamic data were available. In a few cases the Arrhenius equations for experimental self-diffusion coefficients were applied slightly outside the temperature range of the actual measurements.

The partial molar excess Gibbs free energy $\Delta \bar{G}_A^{xs}$ was correlated in terms of mole fraction by using the α-function defined by Hultgren et al. (32).

$$\alpha_A = \frac{\Delta \bar{G}_A^{xs}}{(1-x_A)^2} \tag{4-1}$$

A graph of α_A versus x_A was constructed to obtain values of α_A in the mole fraction range of 0 to 0.05. These α_A values were then used to calculate partial molar excess Gibbs free energies and activity coefficients. Activity coefficients at mole fractions of 0.01 and 0.02 were used to calculate values of the term $(\partial \ln \gamma_A^{\circ}/\partial \ln x_A)$. The calculated values are given in Table XI (Appendix).

The experimental and predicted diffusion coefficients at infinite dilution and the deviations between the predicted and experimental values are given in Table I. The diffusion coefficients were predicted with average absolute deviations of less than 18 percent by using Equations (2-4) and (2-6). The proposed models give better results than most of the existing models. The predictions are comparable to the fluctuation theory and the hole theory predictions, but the present models are much easier to use.

Comparison of the terms $(\partial \ln \gamma_A^{\circ}/\partial \ln x_A)$ and $\Delta^{\circ}\bar{G}_A^{xs}$ in Table XI (Appendix) shows that the numerical values of these two terms have opposite signs except in one case. This empirical observation was used to modify Equation (2-5) in order to obtain the simpler Equation (2-6) for the prediction of infinite dilution diffusion coefficients.

TABLE I

COMPARISON OF EXPERIMENTAL AND PREDICTED
INFINITE DILUTION DIFFUSION COEFFICIENTS
FOR LIQUID METAL SYSTEMS

		Exp.	Pred. Eqn. (2-4)		Pred. Eqn. (2-6)	
Solute (A) -	Temp.	D°_{AB} x10^5	D°_{AB} x10^5	Dev.	D°_{AB} x10^5	Dev.
Solvent (B)	K	cm^2/s	cm^2/s	%	cm^2/s	%
Ag-Sn	1250	14.89	11.76	-21.0	14.83	-0.4
Sb-Sn	905	6.47	6.77	4.6	7.93	22.6
Tl-Sn	723	3.09	4.30	39.2	3.58	15.9
Cu-Ag	1423	3.55	3.70	4.2	2.85	-19.7
Ag-Cu	1423	4.15	4.54	9.4	3.61	-13.0
Au-Ag	1350	3.12	3.47	11.2	4.08	30.8
Ge-Ag	1250	3.91	2.82	-27.9	3.15	-19.4
Bi-Sb	1200	8.33	9.41	13.0	10.94	31.3
Cd-Ga	700	6.44	8.41	30.6	4.97	-22.8
Sn-Ag	1250	3.88	2.42	-37.6	2.43	-37.4
Cd-Pb	773	4.83	4.89	1.2	3.57	-26.1
Ag-Sb	1250	9.82	9.85	0.3	11.08	12.8
Sn-Cd	773	5.10	4.10	-19.6	3.68	-27.8
Pb-In	673	3.99	4.60	15.3	4.16	4.3
K-Na	384	4.23	4.54	7.3	3.82	-9.7
Na-K	384	5.85	5.27	-9.9	4.44	-24.1
Bi-Pb	700	5.16	3.76	-27.1	4.37	-15.3
Sb-Ag	1250	4.09	3.09	-24.4	4.30	5.1
Bi-Sn	600	2.75	3.14	14.2	2.96	7.6
Sn-In	700	5.39	5.29	-1.9	6.05	12.2
		AAPD:		16.0		17.9
	No. of Systems = 20					

Organic Systems

Infinite dilution diffusion coefficients were predicted for organic systems by using Equation (2-10). Diffusion coefficients, activity coefficients, and coordination numbers at infinite dilution are given in Table XII (Appendix). The coordination numbers at infinite dilution were obtained by the method of Alukhanov et al. (33). Some of the activity coefficients were obtained by using the Wilson parameters slightly outside their temperature range. The experimental and predicted infinite dilution diffusion coefficients, and deviations between the experimental and predicted values are given in Table II. The infinite dilution diffusion coefficients were predicted with an average absolute deviation of 16 percent.

Infinite dilution diffusion coefficients predicted by the methods of Wilke-Chang (21), Sitaraman et al. (23), and Scheibel (26) are also given in Table II for comparison. It is clear from Table II that the predictions of the proposed method are comparable to the predictions of Wilke-Chang and Scheibel. In addition, the present correlation performs better than the correlation of Sitaraman et al.

The data used for the prediction of infinite dilution diffusion coefficients by the Wilke-Chang, Sitaraman et al., and Scheibel correlations are given in Table XIII (Appendix). The viscosity data were obtained from API Research Project 44 (34) for hydrocarbons, and from TRC Data Project (35) for n-alcohols. The viscosity data for chloroform and CCl_4 were taken from CRC Handbook (36) and for MEK from Timmermans (37). Latent heats of vaporization at NBP (normal boiling point) were obtained from Perry (38). The molar volume at NBP was calculated by the LeBas method (22).

TABLE II

COMPARISON OF EXPERIMENTAL AND PREDICTED INFINITE DILUTION DIFFUSION COEFFICIENTS FOR ORGANIC SYSTEMS

Solute (A) - Solvent (B)	Temp. K	Exp. $D^{\circ}_{AB_2} \times 10^5$ cm^2/s	This Work $D^{\circ}_{AB_2} \times 10^5$ cm^2/s	This Work Dev. %	Wilke-Chang $D^{\circ}_{AB_2} \times 10^5$ cm^2/s	Wilke-Chang Dev. %	Sitaraman et al. $D^{\circ}_{AB_2} \times 10^5$ cm^2/s	Sitaraman et al. Dev. %	Scheibel $D^{\circ}_{AB_2} \times 10^5$ cm^2/s	Scheibel Dev. %
n-Hexane-Benzene	278.0	1.78	1.39	-21.9	1.14	-36.0	1.11	-37.6	1.23	-30.9
	284.0	1.89	1.56	-17.5	1.28	-32.3	1.24	-34.4	1.38	-27.0
	288.0	2.15	1.69	-21.4	1.39	-35.3	1.34	-37.7	1.50	-30.2
Benzene-n-Hexane	288.0	3.70	3.28	-11.4	3.92	5.9	3.09	-16.5	3.37	-8.9
	298.0	4.64	3.72	-19.8	4.45	-4.1	3.48	-25.0	3.83	-17.5
n-Heptane-n-Hexane	298.0	3.78	4.19	10.8	3.24	-14.3	2.88	-23.8	3.21	-15.1
Cyclohexane-Toluene	298.0	2.42	2.11	-12.8	2.20	-9.1	1.93	-20.2	1.93	-20.2
	313.0	3.069	2.63	-14.3	2.74	-10.5	2.37	-22.5	2.41	-21.2
	328.0	3.80	3.21	-15.5	3.34	-12.1	2.86	-24.7	2.94	-22.6
Toluene-Cyclohexane	298.0	1.569	1.16	-26.1	1.29	-17.8	1.17	-25.4	1.19	-24.2
	313.0	1.913	1.55	-19.0	1.73	-9.6	1.53	-20.0	1.59	-16.9
	328.0	2.409	2.02	-16.1	2.26	-6.2	1.97	-18.2	2.08	-13.7
Toluene-n-Heptane	279.9	2.95	2.14	-27.5	2.45	-16.9	2.05	-30.5	2.07	-29.8
	298.0	3.72	2.79	-25.0	3.19	-14.2	2.62	-29.6	2.69	-27.7
	313.0	4.33	3.39	-21.7	3.87	-10.6	3.14	-27.5	3.27	-24.5
n-Heptane-Benzene	298.0	1.785	1.82	2.0	1.53	-14.3	1.50	-16.6	1.72	-3.6
	313.0	2.279	2.33	2.2	1.96	-14.0	1.90	-16.6	2.21	-3.0
	318.0	2.75	2.52	-8.4	2.12	-22.9	2.04	-25.8	2.39	-13.1
	338.0	3.65	3.36	-7.9	2.83	-22.7	2.67	-26.8	3.18	-12.9
	348.0	4.07	3.84	-5.7	3.23	-20.6	3.02	-25.8	3.63	-10.8
	353.1	4.25	4.08	-4.0	3.43	-19.3	3.19	-24.9	3.86	-9.2
	358.0	4.60	4.35	-5.4	3.66	-20.4	3.39	-26.3	4.12	-10.4

TABLE II (Continued)

Solute (A) - Solvent (B)	Temp. K	Exp. $D^{\circ}_{AB_2} \times 10^5$ cm^2/s	This Work $D^{\circ}_{AB_2} \times 10^5$ cm^2/s	This Work Dev. %	Wilke-Chang $D^{\circ}_{AB_2} \times 10^5$ cm^2/s	Wilke-Chang Dev. %	Sitaraman et al. $D^{\circ}_{AB_2} \times 10^5$ cm^2/s	Sitaraman et al. Dev. %	Scheibel $D^{\circ}_{AB_2} \times 10^5$ cm^2/s	Scheibel Dev. %
Benzene-n-Heptane	298.0	3.40	2.75	-19.1	3.61	6.2	2.82	-17.1	2.88	-15.3
	318.0	4.40	3.56	-19.1	4.67	6.1	3.58	-18.6	3.73	-15.2
	328.0	5.616	4.01	-28.6	5.26	-6.3	4.00	-28.8	4.20	-25.2
	338.0	6.05	4.50	-25.6	5.91	-2.3	4.46	-26.3	4.72	-22.0
	348.0	6.55	5.04	-23.1	6.61	0.9	4.95	-24.4	5.27	-19.5
	358.0	7.30	5.61	-23.2	7.36	0.8	5.47	-25.1	5.87	-19.6
	371.4	8.40	6.44	-23.3	8.45	0.6	6.22	-26.0	6.74	-19.8
Cyclohexane-Benzene	298.0	2.09	2.00	-4.3	1.85	-11.5	1.69	-19.1	1.91	-8.6
	298.0	2.101	2.00	-4.8	1.85	-11.9	1.69	-19.6	1.91	-9.1
	313.0	2.65	2.58	-2.6	2.38	-10.2	2.14	-19.2	2.46	-7.2
	333.0	3.445	3.46	0.4	3.20	-7.1	2.81	-18.4	3.30	-4.2
Benzene-Cyclohexane	298.0	1.88	1.26	-33.0	1.46	-22.3	1.26	-33.0	1.27	-32.4
	298.0	1.883	1.26	-33.1	1.46	-22.5	1.26	-33.1	1.27	-32.6
	298.0	1.896	1.26	-33.5	1.46	-23.0	1.26	-33.5	1.27	-33.0
	308.0	2.207	1.53	-30.7	1.78	-19.3	1.51	-31.6	1.55	-29.8
	313.0	2.45	1.68	-31.4	1.96	-20.0	1.65	-32.7	1.70	-30.6
	333.0	3.285	2.39	-27.2	2.78	-15.4	2.29	-30.3	2.42	-26.3
Toluene-Benzene	298.0	1.847	2.10	13.7	1.85	0.2	1.68	-9.0	1.91	3.4
	313.0	2.385	2.71	13.6	2.38	-0.2	2.13	-10.7	2.46	3.1
Benzene-Toluene	298.0	2.545	2.37	-6.9	2.49	-2.2	2.07	-18.7	2.07	-18.7
	313.0	3.24	2.95	-9.0	3.10	-4.3	2.54	-21.6	2.58	-20.4
Cyclohexane -n-Hexane	298.0	3.77	3.97	5.3	3.93	4.2	3.24	-14.1	3.57	-5.3
CCl_4-n-Hexane	298.0	3.70	3.81	3.0	4.03	8.9	3.92	5.9	3.62	-2.2
	298.0	3.86	3.81	-1.3	4.03	4.4	3.92	1.6	3.62	-6.2
CCl_4-n-Heptane	298.0	3.17	2.83	-10.7	3.27	3.2	3.18	0.3	2.73	-13.9
CCl_4-Toluene	298.0	2.19	2.18	-0.5	2.25	2.7	2.34	6.8	1.96	-10.5
CCl_4-Cyclohexane	298.0	1.486	1.19	-19.9	1.32	-11.2	1.42	-4.4	1.20	-19.2

TABLE II (Continued)

Solute (A) - Solvent (B)	Temp. K	Exp. $D^{\circ}_{AB} \times 10^5$ cm^2/s	This Work $D^{\circ}_{AB} \times 10^5$ cm^2/s	This Work Dev. %	Wilke-Chang $D^{\circ}_{AB} \times 10^5$ cm^2/s	Wilke-Chang Dev. %	Sitaraman et al. $D^{\circ}_{AB} \times 10^5$ cm^2/s	Sitaraman et al. Dev. %	Scheibel $D^{\circ}_{AB} \times 10^5$ cm^2/s	Scheibel Dev. %
CCl_4-Cyclohexane	313.0	1.915	1.59	-17.0	1.77	-7.6	1.86	-2.9	1.61	-15.9
	328.0	2.415	2.08	-13.9	2.32	-3.9	2.39	-1.0	2.11	-12.6
CCl_4-Benzene	293.0	1.76	1.73	-1.7	1.74	-1.1	1.88	6.8	1.77	0.6
	298.0	1.922	1.90	-1.1	1.90	-1.1	2.05	6.7	1.94	0.9
	298.0	2.00	1.90	-5.0	1.90	-5.0	2.05	2.5	1.94	-3.0
Benzene-CCl_4	298.2	1.419	1.39	-2.0	1.95	37.4	1.36	-4.2	1.26	-11.2
	313.0	1.775	1.78	0.3	2.51	41.4	1.72	-3.1	1.62	-8.7
Toluene-n-Hexane	298.0	4.21	3.60	-14.5	3.93	-6.7	3.23	-23.3	3.57	-15.2
Benzene-Methanol	300.0	2.76	1.86	-32.6	2.09	-24.3	1.84	-33.3	2.11	-23.6
Toluene-Methanol	298.0	2.56	1.76	-31.3	1.78	-30.5	1.66	-35.2	1.77	-30.9
CCl_4-Methanol	288.0	1.70	1.43	-15.9	1.52	-10.6	1.70	0.0	1.52	-10.6
	298.0	2.248	1.72	-23.5	1.83	-18.6	2.01	-10.6	1.82	-19.0
	298.0	2.30	1.72	-25.2	1.83	-20.4	2.01	-12.6	1.82	-20.9
Chloroform-Methanol	288.0	2.07	1.72	-16.9	1.72	-16.9	1.75	-15.5	1.75	-15.5
MEK-Benzene	303.0	2.086	2.03	-2.7	2.28	9.3	1.90	-8.9	2.23	6.9
Chloroform-Benzene	298.0	2.50	2.03	-18.8	2.15	-14.0	2.10	-16.0	2.07	-17.2
MEK-Toluene	303.0	2.21	2.20	-0.5	2.68	21.3	2.15	-2.7	2.23	0.9
Benzene-Ethanol	298.0	1.81	0.889	-50.9	1.09	-39.8	1.04	-42.5	1.05	-42.0
Toluene-Ethanol	288.0	1.60	0.682	-57.4	0.772	-51.8	0.787	-50.8	0.784	-51.0
Methylcyclohexane	298.0	2.21	2.07	-6.3	1.98	-10.4	1.84	-16.7	1.82	-17.6
-Toluene	318.0	3.09	2.76	-10.7	2.64	-14.6	2.40	-22.3	2.43	-21.4
	333.0	3.66	3.36	-8.2	3.21	-12.3	2.88	-21.3	2.96	-19.1
		AAPD:		15.8		14.0		20.1		17.1

No. of systems = 30

No. of data points = 71

Self-Diffusion Coefficients Using the Group Contribution Method

A non-linear least squares fitting subroutine MARQ written by Chandler (39) was used to obtain the optimal group contributions (or predictive constants). The group contributions for the reference temperature, T_c, were first obtained for the homologous series of n-alkanes and n-alcohols by fitting the experimental critical temperature data with the proposed model represented by Equations (2-15) and (2-18). Subsequently, the remaining six predictive constants for both homologous series were obtained by fitting the available self-diffusion data for n-alkanes and n-alcohols with Equations (2-12), (2-15) and (2-18). Thus, nine constants were generated for the homologous series of n-alkanes, and another nine constants for the hydroxyl group. The nine constants for the hydroxyl group are to be added to the nine constants for n-alkanes in order to predict self-diffusion coefficients for n-alcohols.

The proposed method was applied to 10 n-alkanes and 5 n-alcohols. The deviations between the correlated self-diffusion coefficients and the experimental data for n-alkanes are given in Table III. The predicted self-diffusion coefficients and deviations from the experimental values for n-alkanes are given in Table IV. The compounds listed in Table IV were not included in the regression. The experimental, correlated, and predicted self-diffusion coefficients for n-alcohols are given in Table V. The deviations of the correlated and predicted self-diffusion coefficients from the experimental values are also given in Table V. The compound marked with asterisk (n-octanol) was not included in the regression and thereby constitutes prediction by the proposed

TABLE III

CORRELATION OF SELF-DIFFUSION COEFFICIENTS FOR N-ALKANES
AND COMPARISON WITH OTHER METHODS

		Exp.	This Work		Wilke-Chang		Tyn		Tyn-Calus	
	Temp.	D x10^5	D x10^5	Dev.	D x10^5	Dev.	D x10^5	Dev.	D x10^5	Dev.
Compound	K	cm^2/s	cm^2/s	%	cm^2/s	%	cm^2/s	%	cm^2/s	%
n-Pentane	250.1	2.97	3.08	3.7	2.56	-13.8	-	-	2.59	-12.8
	273.0	4.14	4.17	0.7	3.52	-15.0	4.20	1.4	3.62	-12.6
	298.0	5.62	5.52	-1.8	4.77	-13.0	5.55	-1.3	5.30	-3.3
	308.5	6.29	6.13	-2.5	5.37	-14.6	6.10	-3.0	6.27	-0.3
n-Hexane	273.0	3.00	3.02	0.7	2.54	-15.3	3.05	1.7	2.77	-7.7
	293.0	3.85	3.91	1.6	3.32	-13.8	3.90	1.3	3.65	-5.2
	298.0	4.12	4.15	0.7	3.54	-14.1	4.15	0.7	3.92	-4.9
	313.0	4.80	4.91	2.3	4.24	-12.0	4.90	1.7	4.85	0.6
	333.0	6.00	5.99	-0.2	5.31	-11.5	6.00	0.0	6.50	8.3
	353.0	7.30	7.14	-2.2	-	-	7.35	0.7	8.81	20.7
n-Heptane	185.4	0.310	0.295	-4.8	0.188	-39.4	-	-	-	-
	210.0	0.634	0.613	-3.3	0.460	-27.4	-	-	1.02	60.9
	220.7	0.827	0.801	-3.1	0.623	-24.7	-	-	1.17	41.5
	240.2	1.275	1.23	-3.5	0.989	-22.4	-	-	1.50	17.6
	250.1	1.52	1.48	-2.6	1.21	-20.4	-	-	1.71	12.5
	260.3	1.866	1.78	-4.6	1.46	-21.8	-	-	1.95	4.5
	273.0	2.08	2.19	5.3	1.82	-12.5	2.15	3.4	2.29	10.1
	288.4	2.647	2.74	3.5	2.30	-13.1	2.60	-1.8	2.80	5.8
	293.0	2.80	2.92	4.3	2.45	-12.5	2.85	1.8	2.97	6.1
	297.5	3.036	3.10	2.1	2.61	-14.0	2.95	-2.8	3.15	3.8
	299.0	3.230	3.16	-2.2	2.66	-17.6	3.10	-4.0	3.22	-0.3
	300.0	3.279	3.21	-2.1	2.70	-17.7	3.15	-3.9	3.26	-0.6
	305.1	3.368	3.42	1.5	2.89	-14.2	3.30	-2.0	3.49	3.6
	308.0	3.572	3.54	-0.9	3.00	-16.0	3.45	-3.4	3.62	1.3

TABLE III (Continued)

		Exp.	This Work		Wilke-Chang		Tyn		Tyn-Calus	
	Temp.	D x10^5	D x10^5	Dev.	D x10^5	Dev.	D x10^5	Dev.	D x10^5	Dev.
Compound	K	cm^2/s	cm^2/s	%	cm^2/s	%	cm^2/s	%	cm^2/s	%
n-Heptane	315.6	3.978	3.88	-2.5	3.30	-17.0	3.80	-4.5	4.00	0.6
	318.5	4.123	4.01	-2.7	3.42	-17.1	3.95	-4.2	4.16	0.9
	327.3	4.500	4.42	-1.8	3.80	-15.6	4.38	-2.7	4.68	4.0
	327.5	4.569	4.43	-3.0	3.81	-16.6	4.40	-3.7	4.70	2.9
	335.6	4.804	4.83	0.5	4.19	-12.8	4.75	-1.1	5.24	9.1
	337.3	4.990	4.91	-1.6	4.27	-14.4	4.90	-1.8	5.37	7.6
	346.6	5.391	5.39	-0.02	4.74	-12.1	5.45	1.1	6.10	13.2
	354.4	5.522	5.80	5.0	5.16	-6.6	5.90	6.8	6.81	23.3
	360.5	6.240	6.13	-1.8	5.50	-11.9	6.30	1.0	7.42	18.9
	368.8	6.56	6.59	0.5	6.00	-8.5	6.80	3.7	8.37	27.6
	373.0	7.030	6.82	-3.0	6.26	-11.0	7.15	1.7	8.89	26.5
n-Nonane	235.1	0.509	0.519	2.0	0.379	-25.5	-	-	0.905	78.0
	263.5	0.948	0.979	3.3	0.789	-16.8	-	-	1.27	34.0
	280.2	1.309	1.34	2.4	1.11	-15.2	1.25	-4.5	1.55	18.4
	298.0	1.70	1.80	5.9	1.52	-10.6	1.75	2.9	1.92	12.9
	299.5	1.790	1.84	2.8	1.56	-12.8	1.80	0.6	1.95	8.9
	320.2	2.388	2.48	3.9	2.14	-10.4	2.40	0.5	2.50	4.7
	339.2	3.092	3.16	2.2	2.77	-10.4	3.00	-3.0	3.15	1.9
	357.7	3.832	3.90	1.8	3.47	-9.4	3.80	-0.8	3.96	3.3
	372.6	4.308	4.56	5.8	4.10	-4.8	4.50	4.5	4.77	10.7
	385.8	4.991	5.18	3.8	4.73	-5.2	-	-	5.64	13.0
	403.6	6.004	6.06	0.9	5.68	-5.4	-	-	7.13	18.8
	421.8	6.984	7.03	0.7	6.77	-3.1	-	-	9.12	30.6
n-Decane	247.7	0.480	0.502	4.6	0.371	-22.7	-	-	0.983	104.8
	247.9	0.499	0.504	1.0	0.374	-25.1	-	-	0.986	97.6
	263.3	0.707	0.716	1.3	0.565	-20.1	-	-	1.17	65.5
	275.3	0.878	0.917	4.4	0.747	-14.9	0.85	-3.2	1.35	53.8

TABLE III (Continued)

		Exp.	This Work		Wilke-Chang		Tyn		Tyn-Calus	
	Temp.	D x10^5	D x10^5	Dev.	D x10^5	Dev.	D x10^5	Dev.	D x10^5	Dev.
Compound	K	cm^2/s	cm^2/s	%	cm^2/s	%	cm^2/s	%	cm^2/s	%
n-Decane	293.0	1.29	1.27	-1.6	1.07	-17.1	1.25	-3.1	1.64	27.1
	298.0	1.31	1.38	5.3	1.17	-10.7	1.40	6.9	1.74	32.8
	298.5	1.360	1.40	2.9	1.18	-13.2	1.42	4.4	1.75	28.7
	299.0	1.388	1.41	1.6	1.19	-14.3	1.44	3.7	1.76	26.8
	313.0	1.749	1.76	0.6	1.52	-13.1	1.80	2.9	2.06	17.8
	328.8	2.267	2.21	-2.5	1.93	-14.9	2.30	1.5	2.48	9.4
	355.3	3.184	3.10	-2.6	2.75	-13.6	3.10	-2.6	3.37	5.8
	355.5	3.219	3.10	-3.7	2.76	-14.3	3.12	-3.1	3.38	5.0
	373.3	4.017	3.79	-5.7	3.42	-14.9	-	-	4.17	3.8
	395.4	5.069	4.74	-6.5	4.36	-14.0	-	-	5.48	8.1
	420.0	6.190	5.91	-4.5	5.60	-9.5	-	-	7.52	21.5
	440.0	7.299	6.94	-4.9	6.79	-7.0	-	-	9.86	35.1
n-Tetradecane	279.2	0.368	0.364	-1.1	0.284	-23.8	0.40	8.7	-	-
	286.3	0.442	0.428	-3.2	0.346	-21.7	0.46	4.1	0.358	-19.0
	303.0	0.637	0.611	-4.1	0.522	-18.1	0.80	25.6	0.425	-33.3
	317.6	0.815	0.808	-0.9	0.712	-12.6	0.85	4.3	0.493	-39.5
	330.1	1.050	1.01	-3.8	0.901	-14.2	1.10	4.8	0.559	-46.8
	346.2	1.371	1.31	-4.4	1.19	-13.2	1.40	2.1	0.658	-52.0
	359.2	1.685	1.58	-6.2	1.45	-13.9	1.60	-5.0	0.750	-55.5
	374.3	2.035	1.95	-4.2	1.80	-11.5	-	-	0.874	-57.1
	393.4	2.505	2.47	-1.4	2.30	-8.2	-	-	1.01	-59.7
	416.0	3.227	3.19	-1.1	2.99	-7.3	-	-	1.34	-58.5
	433.6	3.868	3.82	-1.2	3.62	-6.4	-	-	1.61	-58.4
n-Octadecane	301.7	0.297	0.297	0.0	-	-	0.30	1.0	0.366	23.2
	304.8	0.320	0.319	-0.3	0.263	-17.8	0.35	9.4	0.378	18.1
	313.0	0.383	0.382	-0.3	0.326	-14.9	0.42	9.7	0.411	7.3
	323.0	0.460	0.470	2.2	0.413	-10.2	0.50	8.7	0.455	-1.1

TABLE III (Continued)

		Exp.	This Work		Wilke-Chang		Tyn		Tyn-Calus	
	Temp.	D x10^5	D x10^5	Dev.	D x10^5	Dev.	D x10^5	Dev.	D x10^5	Dev.
Compound	K	cm^2/s	cm^2/s	%	cm^2/s	%	cm^2/s	%	cm^2/s	%
n-Octadecane	323.6	0.479	0.476	-0.6	0.418	-12.7	0.52	8.6	0.457	-4.6
	347.7	0.763	0.747	-2.1	0.685	-10.2	0.70	-8.3	0.579	-24.1
	374.5	1.141	1.15	0.8	1.08	-5.3	-	-	0.747	-34.5
	396.2	1.528	1.57	2.7	1.47	-3.8	-	-	0.914	-40.2
	416.0	1.938	2.02	4.2	1.90	-2.0	-	-	1.10	-43.2
	426.0	2.135	2.28	6.8	2.15	0.7	-	-	1.20	-43.8
	438.6	2.533	2.63	3.8	2.48	-2.1	-	-	1.35	-46.7
		AAPD:		2.7		13.7		3.8		23.2

No. of compounds = 7

No. of data points = 85

TABLE IV

PREDICTION OF SELF-DIFFUSION COEFFICIENTS FOR N-ALKANES
AND COMPARISON WITH OTHER METHODS

		Exp.	This Work		Wilke-Chang		Tyn		Tyn-Calus	
	Temp.	D x10^5	D x10^5	Dev.	D x10^5	Dev.	D x10^5	Dev.	D x10^5	Dev.
Compound	K	cm^2/s	cm^2/s	%	cm^2/s	%	cm^2/s	%	cm^2/s	%
n-Octane	273.0	1.47	1.60	8.8	1.33	-9.5	1.50	2.0	1.59	8.2
	293.0	2.10	2.19	4.3	1.85	-11.9	2.05	-2.4	2.03	-3.3
	298.0	2.25	2.36	4.9	2.00	-11.1	2.20	-2.2	2.16	-4.0
	313.0	2.73	2.90	6.2	2.48	-9.2	2.70	-1.1	2.60	-4.8
	333.0	3.57	3.70	3.6	3.21	-10.1	3.40	-4.8	3.34	-6.4
	343.0	3.80	4.14	8.9	3.63	-4.5	3.85	1.3	3.80	0.0
	353.0	4.15	4.60	10.8	4.05	-2.4	4.25	2.4	4.33	4.3
	373.0	5.20	5.58	7.3	5.05	-2.9	5.30	1.9	5.64	8.5
n-Dodecane	264.0	0.419	0.412	-1.7	0.310	-26.0	-	-	1.05	150.6
	278.7	0.568	0.576	1.4	0.463	-18.5	0.50	-12.0	1.23	116.5
	298.0	0.814	0.851	4.5	0.722	-11.3	0.80	-1.6	1.51	85.7
	300.5	0.900	0.891	-1.0	0.759	-15.7	0.85	-5.6	1.55	72.2
	314.3	1.151	1.14	-1.0	0.990	-14.0	1.20	4.3	1.80	56.4
	329.9	1.448	1.47	1.5	1.30	-10.2	1.40	-3.3	2.13	47.1
	345.4	1.834	1.84	0.3	1.65	-10.0	1.80	-1.9	2.52	37.4
	361.6	2.298	2.29	-0.3	2.07	-9.9	2.20	-4.3	3.01	31.0
	380.9	2.925	2.90	-0.9	2.65	-9.4	-	-	3.74	27.9
	406.4	3.714	3.82	2.9	3.55	-4.4	-	-	5.00	34.6
	434.6	4.871	4.99	2.4	4.76	-2.3	-	-	7.00	43.7
n-Hexadecane	291.7	0.352	0.327	-7.1	-	-	0.40	13.6	0.351	-0.3
	299.7	0.426	0.392	-8.0	0.327	-23.2	0.45	5.6	0.382	-10.3
	318.3	0.580	0.577	-0.5	0.509	-12.2	0.65	12.1	0.462	-20.3
	332.9	0.773	0.759	-1.8	0.687	-11.1	0.80	3.5	0.533	-31.0

TABLE IV (Continued)

		Exp.	This Work		Wilke-Chang		Tyn		Tyn-Calus	
	Temp.	D x10^5	D x10^5	Dev.	D x10^5	Dev.	D x10^5	Dev.	D x10^5	Dev.
Compound	K	cm^2/s	cm^2/s	%	cm^2/s	%	cm^2/s	%	cm^2/s	%
n-Hexadecane	343.7	1.002	0.916	-8.6	0.839	-16.3	0.95	-5.2	0.595	-40.6
	368.0	1.400	1.34	-4.3	1.25	-10.7	1.35	-3.6	0.763	-45.5
	382.8	1.663	1.65	-0.8	1.55	-6.8	-	-	0.898	-46.0
	397.4	2.083	2.00	-4.0	1.88	-9.7	-	-	-	-
	399.6	2.141	2.05	-4.3	1.93	-9.9	-	-	-	-
	419.8	2.655	2.61	-1.7	2.46	-7.3	-	-	-	-
	434.6	2.894	3.07	6.1	2.91	0.6	-	-	-	-
		AAPD:		4.0		10.4		4.5		36.1

No. of compounds = 3

No. of data points = 30

TABLE V

CORRELATION AND PREDICTION OF SELF-DIFFUSION COEFFICIENTS
FOR N-ALCOHOLS AND COMPARISON WITH OTHER METHODS

		Exp.	This Work		Wilke-Chang		Tyn		Tyn-Calus	
	Temp.	D x10^5	D x10^5	Dev.	D x10^5	Dev.	D x10^5	Dev.	D x10^5	Dev.
Compound	K	cm^2/s	cm^2/s	%	cm^2/s	%	cm^2/s	%	cm^2/s	%
Methanol	268.0	1.26	1.10	-12.7	-	-	-	-	1.86	47.6
	278.0	1.55	1.44	-7.1	2.47	59.4	1.50	-3.2	2.11	36.1
	288.0	1.91	1.84	-3.7	2.98	56.0	1.85	-3.1	2.39	25.1
	298.0	2.44	2.31	-5.3	3.58	46.7	2.25	-7.8	2.71	11.1
	308.0	2.90	2.86	-1.4	4.25	46.6	2.80	-3.4	3.07	5.9
	313.0	3.01	3.18	5.6	4.62	53.5	3.00	-0.3	3.27	8.6
	318.0	3.43	3.50	2.0	5.01	46.1	3.25	-5.2	3.47	1.2
	328.0	3.97	4.23	6.5	5.87	47.9	3.80	-4.3	3.92	-1.3
	338.0	4.50	5.05	12.2	6.84	52.0	4.50	0.0	4.45	-1.1
Ethanol	279.8	0.618	0.651	5.3	0.964	56.0	0.60	-2.9	0.975	57.8
	288.0	0.770	0.804	4.4	1.17	51.9	0.75	-2.6	1.07	39.0
	298.0	1.01	1.03	2.0	1.46	44.6	1.00	-1.0	1.21	19.8
	308.0	1.30	1.29	-0.8	1.82	40.0	1.35	3.8	1.36	4.6
	318.0	1.66	1.59	-4.2	2.23	34.3	1.65	-0.6	1.53	-7.8
	328.0	2.06	1.94	-5.8	2.72	32.0	2.00	-2.9	1.72	-16.5
	338.0	2.61	2.35	-10.0	3.30	26.4	2.40	-8.0	1.94	-25.7
n-Propanol	288.0	0.504	0.510	1.2	0.473	-6.2	0.50	-0.8	0.625	24.0
	297.0	0.512	0.643	25.6	0.610	19.1	0.65	27.0	0.690	34.8
	298.0	0.646	0.659	2.0	0.628	-2.8	0.70	8.4	0.698	8.0
	308.0	0.814	0.836	2.7	0.821	0.9	0.80	-1.7	0.780	-4.2
	318.0	1.03	1.05	1.9	1.06	2.9	1.00	-2.9	0.873	-15.2
	328.0	1.37	1.29	-5.8	1.34	-2.2	1.25	-8.8	0.981	-28.4
	338.0	1.74	1.57	-9.8	1.69	-2.9	1.45	-16.7	1.10	-36.8

TABLE V (Continued)

		Exp.	This Work		Wilke-Chang		Tyn		Tyn-Calus	
	Temp.	D x10^5	D x10^5	Dev.	D x10^5	Dev.	D x10^5	Dev.	D x10^5	Dev.
Compound	K	cm^2/s	cm^2/s	%	cm^2/s	%	cm^2/s	%	cm^2/s	%
n-Butanol	297.0	0.426	0.449	5.4	-	-	0.50	16.3	0.511	20.0
	298.0	0.504	0.461	-8.5	0.456	-9.5	0.55	9.1	0.516	2.4
	308.0	0.649	0.591	-8.9	0.606	-6.6	0.65	0.2	0.574	-11.6
	318.0	0.822	0.747	-9.1	0.793	-3.5	0.80	-2.7	0.638	-22.4
n-Octanol*	297.0	0.138	0.136	-1.4	0.137	-0.7	-	-	0.242	75.4
		AAPD:		6.1		28.9		5.5		21.2

No. of compounds = 5

No. of data points = 28

* not included in regression

method. The proposed group contribution method gave average absolute deviations of 2.7 and 4.0 percent for correlation and prediction of self-diffusion coefficients for n-alkanes. The average absolute deviation for n-alcohols was 6.1 percent. The results are equally good for compounds which were excluded from the regression. Only one point for n-propanol gave a deviation of 25 percent. Similar deviations were obtained for this data point by other prediction methods. This indicates that the experimental value may be in error.

The percent deviation is defined as

$$PD = [(Calc. - Exp.)/Exp.] \times 100 \qquad (4\text{-}2)$$

where Calc. is the calculated value and Exp. is the experimental value. The average absolute percent deviation is defined as

$$AAPD = \Sigma \, |PD| \, / \, NPTS \qquad (4\text{-}3)$$

where $|PD|$ is the absolute value of percent deviation and NPTS is the total number of data points.

Self-diffusion coefficients predicted by the Wilke and Chang equation, the Tyn and Calus group contribution technique, and the graphical correlation of Tyn are given in Tables III, IV and V for the purpose of comparison. The results obtained by the proposed method are as good as those obtained by the graphical correlation of Tyn. In addition, the present method performs significantly better than the methods of Wilke and Chang, and Tyn and Calus. The Tyn graphical correlation cannot predict self-diffusion coefficient for n-octanol,

since two self-diffusion coefficients are needed for each compound in order to obtain a correlating line on the graph and only one experimental value is available for n-octanol. Furthermore, the Tyn correlation cannot be applied outside the temperature range of 0 to 100°C.

The results of critical temperature correlation for n-alkanes and n-alcohols are given in Tables VI and VII. The experimental critical temperatures were obtained from Ambrose (40). The group contribution values for n-alkanes and the hydroxyl group are given in Tables VIII and IX. These constants should be used with Equations (2-12), (2-15), and (2-18).

The sources of experimental self-diffusion data are given in Table XIV (Appendix). The data used to predict self-diffusion coefficients for n-alkanes and n-alcohols by the methods of Wilke and Chang, and Tyn and Calus are given in Table XV (Appendix). The molar volumes were calculated from the density data. The viscosity and density data for n-alkanes were obtained from the API Research Project 44 report (34, 41). The density data for n-alcohols were obtained from the MCA Research Project report (42), and viscosity data were taken from the TRC Data Project report (35). The viscosity of n-octanol was obtained by interpolation of the data given by Lange (43). The molar volume at the normal boiling point was calculated by the LeBas method (22).

TABLE VI

CORRELATION OF CRITICAL TEMPERATURES FOR N-ALKANES

	Critical Temperature, T_c		
Compound	Exp., K	Eqn. (2-15)	Percent Dev.
n-Pentane	469.5	471.2	0.36
n-Hexane	507.3	506.4	-0.18
n-Heptane	540.1	538.4	-0.31
n-Octane	568.68	567.4	-0.23
n-Nonane	594.4	593.9	-0.08
n-Decane	617.5	617.9	0.06
n-Undecane	638.7	639.7	0.16
n-Dodecane	658.1	659.5	0.21
n-Tridecane	676.0	677.5	0.22
n-Tetradecane	693.0	693.8	0.12
n-Hexadecane	722.0	722.2	0.03
n-Octadecane	748.0	745.6	-0.32
		AAPD:	0.19

TABLE VII

CORRELATION OF CRITICAL TEMPERATURES FOR N-ALCOHOLS

	Critical Temperature, T_c		
Compound	Exp., K	Eqn. (2-18)	Percent Dev.
Ethanol	513.77	512.1	-0.33
n-Propanol	536.63	538.8	0.40
n-Butanol	562.9	564.0	0.20
n-Pentanol	588.0	587.9	-0.02
n-Hexanol	611.0	610.4	-0.10
n-Heptanol	633.0	631.6	-0.22
n-Octanol	652.4	651.7	-0.11
n-Nonanol	671.0	670.6	-0.06
n-Decanol	687.0	688.5	0.22
		AAPD:	0.18

TABLE VIII

GROUP CONTRIBUTIONS FOR THE N-ALKANE SERIES

	A	$\ln D_c$	T_c
x	1.1731	-8.9103	234.2
y	0.18227	0.06785	56.884
r	0.90992	0.80501	0.90857

TABLE IX

GROUP CONTRIBUTIONS FOR THE HYDROXYL GROUP

	A	$\ln D_c$	T_c
Δx	2.9005	3.0712	219.6
Δy	-0.1841	-2.36605	-26.911
Δr	0.08998	-0.61933	0.03572

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Infinite Dilution Diffusion Coefficients

Infinite dilution diffusion coefficients are predicted for liquid metals and organic systems starting from the pure component self-diffusion coefficients of the solvents. Thus, infinite dilution diffusion coefficients can be predicted for any number of systems by using a few self-diffusion coefficients. The number of systems for which the infinite dilution diffusion coefficients can be predicted are restricted only by the availability of thermodynamic data for the systems. The other data required for the predictions are readily available in the literature. The following conclusions can be drawn based on the results of this work:

1. The Bearman equation can be modified to predict diffusion coefficients at infinite dilution for liquid metals with reasonable accuracy.
2. The theoretical model developed from the Bearman equation was modified empirically to obtain a simple equation which can be used to predict infinite dilution diffusion coefficients for liquid metals with reasonable accuracy.
3. Predictions of the theoretical and the semi-empirical models developed from the Bearman equation are comparable to those of the

fluctuation and the hole theory models for liquid metals. In addition, the new models are easier to use than other currently existing models.

4. The semi-empirical equation developed from the Bearman equation was combined with the Stokes-Einstein temperature correction to predict infinite dilution diffusion coefficients for organic systems at any temperature with reasonable accuracy.
5. Predictions of the semi-empirical equation for organic systems, obtained by combining the Stokes-Einstein temperature correction with the semi-empirical equation developed from the Bearman equation, are comparable to those of the Wilke and Chang, and Scheibel equations, and better than the predictions of Sitaraman et al.

Self-Diffusion Coefficients

Self-diffusion coefficients are correlated and predicted for n-alkanes and n-alcohols over a wide range of temperature. The only information required for predicting the self-diffusion coefficients is the structure of the compound. The following conclusions can be drawn from the results of this work:

1. The Arrhenius equation in the corresponding states form can be used to represent adequately the temperature dependence of self-diffusion coefficients.
2. The constants of the reduced Arrhenius equation can be represented by a geometric series.
3. The constants of the group contribution technique for predicting self-diffusion coefficients were generated for both non-polar (n-alkanes) and polar (n-alcohols) compounds.

4. The proposed method correlates and predicts self-diffusion coefficients with a higher accuracy than any other currently existing method.

Recommendations

Infinite Dilution Diffusion Coefficients

1. A comprehensive experimental program should be undertaken to measure infinite dilution diffusion coefficients for organic and aqueous systems over a wide temperature range.
2. These consistent experimental data should be used to test the predictive capability of the proposed equation.
3. The available experimental self-diffusion data for water show large variations. Hence, self-diffusion coefficients for water should be measured. The measured self-diffusion coefficients should be used to test the proposed equation for aqueous systems.

Self-Diffusion Coefficients

1. A study should be undertaken to measure self-diffusion coefficients for higher carbon number n-alcohols and other homologous series.
2. The new self-diffusion data for n-alcohols should be used to test the reproducibility of the present group contributions for the hydroxyl group.
3. The new self-diffusion data should be used to generate group contributions for other functional groups and for the effect of position of the functional group.

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APPENDIX A

TABULATION OF DATA USED FOR CALCULATIONS

TABLE X

SELF-DIFFUSION COEFFICIENTS AND COORDINATION NUMBER DATA FOR LIQUID METALS

Element	Self-Diffusion Coefficient			Coordination Number	
	Temp. K	$D_{BB} \times 10^5$ cm^2/s	Ref.	Z_B	Ref.
Sn	600	3.18	44	8.8	45
	723	4.42	46	8.8	45
	905	6.60	46	8.8	45
	1250	10.74	46	8.8	45
Cu	1400	4.45	47	10.4	45
	1423	4.71	47	10.4	45
Sb	1200	9.26	48	8.8	45
	1250	9.94	48	8.8	45
Na	384	4.69	49	11.1	45
K	384	5.38	49	10.2	45
Ga	700	9.12	50	9.0	45
Ag	1250	2.65	14	9.4	45
	1350	3.34	14	9.4	45
	1423	3.86	14	9.4	45
In	673	4.70	51	9.8	45
	700	5.04	51	9.8	45
Cd	750	3.94	52	10.4	45
	773	4.21	52	10.4	45
Pb	700	3.73	53	8.3	45
	773	5.05	53	8.3	45

TABLE XI

DIFFUSION COEFFICIENTS AND THERMODYNAMIC DATA AT INFINITE DILUTION FOR LIQUID METAL SYSTEMS

Solute (A) - Solvent (B)	Temp. K	Infinite Dilution Diffusion Coefficient D°_{AB} x10^5 cm^2/s	Ref.	$\Delta^{\circ}\bar{G}^{xs}_A$ at Infinite Dilution cal/g atom	$\frac{\partial \ln \gamma^{\circ}_A}{\partial \ln x_A}$
Ag-Sn	1250	14.89	46	-4160	0.095
Sb-Sn	905	6.47	46	-1600	0.025
Tl-Sn	723	3.09	54	1200	-0.028
Cu-Ag	1423	3.55	55	3465	-0.041
Ag-Cu	1423	4.15	55	3440	-0.036
Au-Ag	1350	3.12	17	-2782	0.039
Ge-Ag	1250	3.91	20	-2200	0.064
Bi-Sb	1200	8.33	56	-1900	0.016
Cd-Ga	700	6.44	50	2850	-0.078
Sn-Ag	1250	3.88	14	990	-0.087
Cd-Pb	773	4.83	57	1869	-0.032
Ag-Sb	1250	9.82	58	-1250	-0.009
Sn-Cd	773	5.10	59	1008	-0.025
Pb-In	673	3.99	60	750	-0.022
K-Na	384	4.23	61	790	-0.033
Na-K	384	5.85	61	680	-0.021
Bi-Pb	700	5.16	53	-993	0.008
Sb-Ag	1250	4.09	16	-7265	0.165
Bi-Sn	600	2.75	62	363	-0.013
Sn-In	700	5.39	63	-1362	0.049

TABLE XII

DIFFUSION COEFFICIENTS, ACTIVITY COEFFICIENTS, AND COORDINATION NUMBER DATA AT INFINITE DILUTION FOR ORGANIC SYSTEMS

Solute (A) - Solvent (B)	Infinite Dilution Diffusion Coefficient Temp. K	$D^{\circ}_{AB} \times 10^5$ cm^2/s	Ref.	Infinite Dilution Activity Coefficient Temp. K	$\ln\gamma^{\circ}_A$	Ref.	Infinite Dilution Coordination Number Z°_{AB}
n-Hexane-	278.0	1.78	64	338	0.4191	65	11.4
Benzene	284.0	1.89	64				
	288.0	2.15	64				
Benzene-	288.0	3.70	21	333	0.3107	65	8.9
n-Hexane	298.0	4.64	66				
n-Heptane-							
n-Hexane	298.0	3.78	66	333	-0.2561	65	10.6
Cyclohexane-	298.0	2.420	67	353	0.2274	65	10.0
Toluene	313.0	3.069	67				
	328.0	3.800	67				
Toluene-	298.0	1.569	67	353	0.2377	65	10.0
Cyclohexane	313.0	1.913	67				
	328.0	2.409	67				
Toluene-	279.9	2.95	68	373	0.2577	65	9.1
n-Heptane	298.0	3.72	68				
	313.0	4.33	68				
n-Heptane-	298.0	1.785	67	353	0.4033	65	12.0
Benzene	313.0	2.279	67				
	318.0	2.75	69				
	338.0	3.65	69				
	348.0	4.07	69				
	353.1	4.25	69				
	358.0	4.60	69				
Benzene-	298.0	3.40	69	353	0.2155	65	8.5
n-Heptane	318.0	4.40	69				
	328.0	5.616	67				
	338.0	6.05	69				
	348.0	6.55	69				
	358.0	7.30	69				
	371.4	8.40	69				
Cyclohexane-	298.0	2.090	67	353	-0.1626	70	10.7
Benzene	298.0	2.101	71				
	313.0	2.650	67				
	333.0	3.445	67				
Benzene-	298.0	1.880	71	353	-0.1592	70	9.3
Cyclohexane	298.0	1.883	72				
	298.0	1.896	67				

TABLE XII (Continued)

Solute (A) - Solvent (B)	Infinite Dilution Diffusion Coefficient: Temp. K	$D^{\circ}_{AB_2} \times 10^5$ cm^2/s	Ref.	Infinite Dilution Activity Coefficient: Temp. K	$\ln\gamma^{\circ}_A$	Ref.	Infinite Dilution Coordination Number Z°_{AB}
Benzene-	308.0	2.207	66				
Cyclohexane	313.0	2.450	67				
	333.0	3.285	67				
Toluene-	298.0	1.847	67	353	-0.4369	65	10.8
Benzene	313.0	2.385	67				
Benzene-	298.0	2.545	67	353	-0.3276	65	9.3
Toluene	313.0	3.240	67				
Cyclohexane-							
n-Hexane	298.0	3.77	66	333	0.0375	73	9.5
CCl_4-	298.0	3.70	74	333	0.2162	70	9.0
n-Hexane	298.0	3.86	66				
CCl_4-							
n-Heptane	298.0	3.17	21	353	0.0955	70	8.7
CCl_4-							
Toluene	298.0	2.19	21	353	0.0611	70	9.5
CCl_4-	298.0	1.486	67	353	0.1086	70	9.5
Cyclohexane	313.0	1.915	67				
	328.0	2.415	67				
CCl_4-	293.0	1.76	75	353	0.1228	70	10.2
Benzene	298.0	1.922	76				
	298.0	2.00	21				
Benzene-	298.2	1.419	64	333	0.0856	77	9.7
CCl_4	313.0	1.775	64				
Toluene-							
n-Hexane	298.0	4.21	68	333	0.4777	70	9.5
Benzene-							
Methanol	300.0	2.76	78	328	1.7893	73	13.9
Toluene-							
Methanol	298.0	2.56	79	328	2.0364	73	15.0
CCl_4-	288.0	1.70	23	328	2.0390	73	14.1
Methanol	298.0	2.248	80				
	298.0	2.30	74				
Chloroform-							
Methanol	288.0	2.07	23	328	0.9630	73	13.1
MEK-							
Benzene	303.0	2.086	81	353	0.2265	70	10.0
Chloroform-							
Benzene	298.0	2.50	38	333	-0.1389	77	9.5
MEK-							
Toluene	303.0	2.21	81	353	0.3603	70	9.3
Benzene							
Ethanol	298.0	1.81	82	338	1.3631	73	11.8

TABLE XII (Continued)

Solute (A) - Solvent (B)	Infinite Dilution Diffusion Coefficient: Temp. K	$D^{\circ}_{AB_2} \times 10^5$ cm^2/s	Ref.	Infinite Dilution Activity Coefficient: Temp. K	$\ln\gamma^{\circ}_A$	Ref.	Infinite Dilution Coordination Number Z°_{AB}
Toluene							
Ethanol	288.0	1.60	83	338	1.6854	77	12.9
Methylcyclohexane	298.0	2.21	84	373	0.2698	73	10.7
-Toluene	318.0	3.09	84				
	333.0	3.66	84				

TABLE XIII

DATA FOR THE PREDICTION OF INFINITE DILUTION DIFFUSION COEFFICIENTS BY THE WILKE-CHANG, SITARAMAN ET AL., AND SCHEIBEL CORRELATIONS

Compound	Molar Volume at NBP cm^3/mol	Latent Heat of Vaporization at NBP cal/g	Temp. K	Viscosity cp
n-Hexane	140.6	80.48	288.0	0.3265
n-Heptane	162.8	76.45	279.9	0.4827
			298.0	0.3955
			313.0	0.3416
			318.0	0.3262
			328.0	0.2984
			338.0	0.2739
			348.0	0.2522
			353.0	0.2424
			358.0	0.2330
			371.4	0.2105
Benzene	96.0	94.14	278.0	0.8235
			280.3	0.7931
			284.0	0.7456
			288.0	0.6983
			293.0	0.6468
			298.0	0.6010
			303.0	0.5604
			313.0	0.4908
			318.0	0.4615
			333.0	0.389
			338.0	0.368
			348.0	0.332
			353.0	0.317
			358.0	0.301
Toluene	118.2	86.80	298.0	0.5500
			303.0	0.5187
			313.0	0.4636
			318.0	0.4398
			328.0	0.398
			333.0	0.379
			353.0	0.316
			373.0	0.268
Cyclohexane	118.2	85.60	298.0	0.895
			308.0	0.759
			313.0	0.702
			328.0	0.563
			333.0	0.526
			353.0	0.410

TABLE XIII (Continued)

Compound	Molar Volume at NBP cm^3/mol	Latent Heat of Vaporazation at NBP cal/g	Temp. K	Viscosity cp
Methanol	37.0	262.79	300.0	0.5362
Ethanol	59.2	204.26	298.0	1.0826
Chloroform	92.3	59.01	298.0	0.542
MEK	96.2	105.93	303.0	0.365
Methylcyclohexane	140.4	76.90	298.0	0.683
CCl_4	113.2	46.42	298.0	0.906
			313.0	0.739
			323.0	0.651
			333.0	0.585

TABLE XIV

SELF-DIFFUSION COEFFICIENT DATA FOR ORGANIC COMPOUNDS

Compound	Temp. K	Self-Diffusion Coefficient D x10^5 cm^2/s	Ref.
n-Pentane	250.1	2.97	85
	273.0	4.14	85
	298.0	5.62	85
	308.5	6.29	85
n-Hexane	273.0	3.00	86
	293.0	3.85	87
	298.0	4.12	86
	313.0	4.80	86
	333.0	6.00	86
	353.0	7.30	86
n-Heptane	185.4	0.310	88
	210.0	0.634	88
	220.7	0.827	88
	240.2	1.275	88
	250.1	1.52	85
	260.3	1.866	88
	273.0	2.08	85
	288.4	2.647	88
	293.0	2.80	86
	297.5	3.036	88
	299.0	3.230	88
	300.0	3.279	88
	305.1	3.368	88
	308.0	3.572	88
	315.6	3.978	88
	318.5	4.123	88
	327.3	4.500	88
	327.5	4.569	88
	335.6	4.804	88
	337.3	4.990	88
	346.6	5.391	88
	353.0	5.60	86
	354.4	5.522	88
	360.5	6.240	88
	368.8	6.56	85
	373.0	7.030	88
n-Octane	273.0	1.47	86
	293.0	2.10	87
	298.0	2.25	4
	313.0	2.73	87
	333.0	3.553	89

TABLE XIV (Continued)

Compound	Temp. K	Self-Diffusion Coefficient D x10^5 cm^2/s	Ref.
n-Octane	343.0	3.80	87
	353.0	4.15	86
	373.0	5.20	86
n-Nonane	235.1	0.509	88
	263.5	0.948	88
	280.2	1.309	88
	298.0	1.70	4
	299.5	1.790	88
	320.2	2.388	88
	339.2	3.092	88
	357.7	3.832	88
	372.6	4.308	88
	385.8	4.991	88
	403.6	6.004	88
	421.8	6.984	88
n-Decane	247.7	0.480	88
	247.9	0.499	88
	263.3	0.707	88
	275.3	0.878	88
	293.0	1.29	86
	298.0	1.31	4
	298.5	1.360	88
	299.0	1.388	88
	313.0	1.749	88
	328.8	2.267	88
	355.3	3.184	88
	355.5	3.219	88
	373.3	4.017	88
	395.4	5.069	88
	420.0	6.190	88
	440.0	7.299	88
n-Dodecane	264.0	0.419	88
	278.7	0.568	88
	298.0	0.814	89
	300.5	0.900	88
	314.3	1.151	88
	329.9	1.448	88
	345.4	1.834	88
	361.6	2.298	88
	380.9	2.925	88
	406.4	3.714	88
	434.6	4.871	88
n-Tetradecane	279.2	0.368	88
	286.3	0.442	88

TABLE XIV (Continued)

Compound	Temp. K	Self-Diffusion Coefficient D x10^5 cm^2/s	Ref.
n-Tetradecane	303.0	0.637	88
	317.6	0.815	88
	330.1	1.050	88
	346.2	1.371	88
	359.2	1.685	88
	374.3	2.035	88
	393.4	2.505	88
	416.0	3.227	88
	433.6	3.868	88
n-Hexadecane	291.7	0.352	88
	299.7	0.426	88
	318.3	0.580	88
	332.9	0.773	88
	343.7	1.002	88
	368.0	1.400	88
	382.8	1.663	88
	397.4	2.083	88
	399.6	2.141	88
	419.8	2.655	88
	434.6	2.894	88
n-Octadecane	301.7	0.297	88
	304.8	0.320	88
	313.0	0.383	88
	323.0	0.46	4
	323.6	0.479	88
	347.7	0.763	88
	374.5	1.141	88
	396.2	1.528	88
	416.0	1.938	88
	426.0	2.135	88
	438.6	2.533	88
Methanol	268.0	1.26	90
	278.0	1.55	90
	288.0	1.91	90
	298.0	2.44	91
	308.0	2.90	91
	313.0	3.01	90
	318.0	3.43	91
	328.0	3.97	91
	338.0	4.50	91
Ethanol	279.8	0.618	90
	288.0	0.77	90
	298.0	1.01	90
	308.0	1.30	90

TABLE XIV (Continued)

Compound	Temp. K	Self-Diffusion Coefficient D x10^5 cm^2/s	Ref.
Ethanol	318.0	1.66	90
	328.0	2.06	90
	338.0	2.61	90
n-Propanol	288.0	0.504	92
	297.0	0.512	93
	298.0	0.646	92
	308.0	0.814	92
	318.0	1.03	91
	328.0	1.37	91
	338.0	1.74	91
n-Butanol	297.0	0.426	93
	298.0	0.504	92
	308.0	0.649	92
	318.0	0.822	92
n-Octanol	297.0	0.138	93
Benzene	333.0	3.40	86
	338.0	4.07	90
	353.0	4.37	86
Toluene	353.0	4.56	86
	373.0	5.60	86
Cyclohexane	353.0	3.14	86
CCl_4	323.0	2.00	90
	333.0	2.44	90

TABLE XV

DATA FOR THE PREDICTION OF SELF-DIFFUSION COEFFICIENTS BY THE WILKE-CHANG AND TYN-CALUS CORRELATIONS

Compound	Molar Volume at NBP cm^3/mol	Temp. K	Viscosity cp	Molar Volume cm^3/mol
n-Pentane	118.4	250.1	0.350	108.24
		273.0	0.278	111.79
		298.0	0.224	116.15
		308.5	0.206	118.18
n-Hexane	140.6	273.0	0.3799	127.26
		293.0	0.3117	130.71
		298.0	0.2976	131.62
		313.0	0.2611	134.45
		333.0	0.2216	138.54
		353.0	-	143.04
n-Heptane	162.8	185.4	3.44	-
		210.0	1.591	133.14
		220.7	1.236	134.68
		240.2	0.8477	137.64
		250.1	0.7215	139.21
		260.3	0.6211	140.87
		273.0	0.5246	143.00
		288.4	0.4381	145.70
		293.0	0.4169	146.54
		297.5	0.3976	147.38
		299.0	0.3916	147.66
		300.0	0.3877	147.84
		305.1	0.3685	148.82
		308.0	0.3581	149.37
		315.6	0.3336	150.86
		318.5	0.3248	151.43
		327.3	0.3003	153.23
		327.5	0.2998	153.28
		335.6	0.2796	154.99
		337.3	0.2756	155.37
		346.6	0.2551	157.42
		354.4	0.2398	159.20
		360.5	0.2287	160.65
		368.8	0.2146	162.69
		373.0	0.2080	163.73
n-Octane	185.0	273.0	0.7104	158.93
		293.0	0.5450	162.55
		298.0	0.5136	163.49
		313.0	0.4355	166.43
		333.0	0.3576	170.55

TABLE XV (continued)

Compound	Molar Volume at NBP cm^3/mol	Temp. K	Viscosity cp	Molar Volume cm^3/mol
n-Octane		343.0	0.3264	172.75
		353.0	0.3005	175.02
		373.0	0.2547	179.87
n-Nonane	207.2	235.1	2.12	168.06
		263.5	1.141	173.08
		280.2	0.8613	176.22
		298.0	0.6676	179.68
		299.5	0.6551	179.99
		320.2	0.5112	184.27
		339.2	0.4189	188.46
		357.7	0.3524	192.77
		372.6	0.3102	196.46
		385.8	0.2787	199.89
		403.6	0.2427	204.84
		421.8	0.2127	210.28
n-Decane	229.4	247.7	2.257	186.30
		247.9	2.244	186.35
		263.3	1.576	189.15
		275.3	1.248	191.42
		293.0	0.9256	194.87
		298.0	0.8588	195.88
		298.5	0.8529	195.99
		299.0	0.8469	196.09
		313.0	0.6989	198.99
		328.8	0.5771	202.45
		355.3	0.4365	208.62
		355.5	0.4357	208.68
		373.3	0.3694	213.12
		395.4	0.3068	219.16
		420.0	0.2538	226.56
		440.0	0.2193	233.25
n-Dodecane	273.8	264.0	2.832	221.44
		278.7	2.003	224.44
		298.0	1.374	228.58
		300.5	1.318	229.13
		314.3	1.057	232.22
		329.9	0.8466	235.85
		345.4	0.6969	239.67
		361.6	0.5813	243.78
		380.9	0.4788	249.02
		406.4	0.3810	256.48
		434.6	0.3043	265.56
n-Tetradecane	318.2	279.2	3.225	-
		286.3	2.718	258.61
		303.0	1.904	262.46

TABLE XV (continued)

Compound	Molar Volume at NBP cm^3/mol	Temp. K	Viscosity cp	Molar Volume cm^3/mol
n-Tetradecane		317.6	1.465	265.92
		330.1	1.203	268.95
		346.2	0.9581	273.03
		359.2	0.8133	276.37
		374.3	0.6841	280.40
		393.4	0.5616	285.73
		416.0	0.4562	292.29
		433.6	0.3936	297.73
n-Hexadecane	362.6	291.7	-	292.36
		299.7	2.974	294.55
		318.3	2.027	299.55
		332.9	1.571	303.44
		343.7	1.329	306.48
		368.0	0.9556	313.75
		382.8	0.8028	318.83
		397.4	0.6861	-
		399.6	0.6709	-
		419.8	0.5526	-
		434.6	0.4850	-
n-Octadecane	407.0	301.7	-	327.77
		304.8	3.724	328.68
		313.0	3.084	331.17
		323.0	2.508	334.18
		323.6	2.481	334.36
		347.7	1.628	341.58
		374.5	1.116	349.66
		396.2	0.862	356.31
		416.0	0.701	362.61
		426.0	0.637	365.84
		438.6	0.568	369.99
Methanol	37.0	268.0	-	39.33
		278.0	0.746	39.78
		288.0	0.639	40.25
		298.0	0.5513	40.73
		308.0	0.4793	41.22
		313.0	0.4481	41.47
		318.0	0.4196	41.71
		328.0	0.3696	42.20
		338.0	0.327	42.74
Ethanol	59.2	279.8	1.5429	57.54
		288.0	1.3096	58.05
		298.0	1.0826	58.68
		308.0	0.902	59.33
		318.0	0.757	59.99
		328.0	0.640	60.67

TABLE XV (continued)

Compound	Molar Volume at NBP cm^3/mol	Temp. K	Viscosity cp	Molar Volume cm^3/mol
Ethanol		338.0	0.544	61.39
n-Propanol	81.4	288.0	2.492	74.40
		297.0	1.9936	75.06
		298.0	1.9430	75.14
		308.0	1.537	75.91
		318.0	1.2319	76.71
		328.0	0.9993	77.57
		338.0	0.820	78.46
n-Butanol	103.6	297.0	-	91.88
		298.0	2.571	91.96
		308.0	2.000	92.84
		318.0	1.5786	93.74
n-Octanol	192.4	297.0	7.818	158.23

APPENDIX B

SAMPLE CALCULATIONS

Infinite Dilution Diffusion Coefficients

Liquid Metal Systems

Infinite dilution diffusion coefficients for liquid metal systems were calculated by using Equations (2-4) and (2-6). The numerical value of the term ($\partial \ln \gamma_A^\circ / \partial \ln x_A$) was calculated by following the procedure described elsewhere in this dissertation (page 32). The sample calculations are shown for the system Ag-Sn (A-B) at 1250 K.

From Table XI (Appendix A)

$$\Delta^\circ \bar{G}_A^{xs} (Ag\text{-}Sn) = -4160 \text{ cal/g atom}$$

$$\frac{\partial \ln \gamma_A^\circ}{\partial \ln x_A} (Ag\text{-}Sn) = 0.095$$

From Table X (Appendix A)

$$D_{BB} (Sn) = 10.74 \times 10^{-5} \text{ cm}^2/\text{s}$$

$$Z_B (Sn) = 8.8$$

Using Equation (2-4)

$$D_{AB}^\circ = 10.74 \times 10^{-5} (1+0.095)$$

$$= 11.76 \times 10^{-5} \text{ cm}^2/\text{s}$$

Using Equation (2-6)

$$D^{\circ}_{AB} = 10.74 \times 10^{-5} \left[1 - \frac{2(-4160)}{(1.987)(1250)(8.8)}\right]$$

$$= 14.83 \times 10^{-5} \text{ cm}^2/\text{s}$$

Organic Systems

Infinite dilution diffusion coefficients for organic systems were calculated by using Equation (2-10). Infinite dilution activity coefficients were calculated at the reference temperature by using the Wilson equation (22), expressed as

$$\ln \gamma^{\circ}_A = - \ln \Lambda_{AB} - \Lambda_{BA} + 1 \qquad \text{(B-1)}$$

The terms Λ_{AB} and Λ_{BA} are defined by the equations

$$\Lambda_{AB} = \frac{v_B}{v_A} \exp\left(- \frac{\lambda_{AB} - \lambda_{AA}}{RT}\right) \qquad \text{(B-2)}$$

and

$$\Lambda_{BA} = \frac{v_A}{v_B} \exp\left(- \frac{\lambda_{BA} - \lambda_{BB}}{RT}\right) \qquad \text{(B-3)}$$

where

v_A, v_B = molar volumes of components A and B, respectively, cm^3/mol

$\lambda_{AB} = \lambda_{BA}$ = interaction energy between A and B, J/mol

λ_{AA}, λ_{BB} = interaction energies for pure A and B, respectively, J/mol

T = absolute temperature, K

R = gas constant = 8.314 J/mol K

Sample calculations are shown for the system n-hexane-benzene (A-B) at 278 K. A reference temperature of 338 K was used for this system.

For Gothard et al. (65)

$$\lambda_{AB} - \lambda_{AA} = 393.0 \text{ J/mol}$$

$$\lambda_{BA} - \lambda_{BB} = 802.2 \text{ J/mol}$$

The densities of n-hexane and benzene at the reference temperature, 338 K, were obtained from the API Research Project 44 report (34, 41).

$$\rho_A = 0.6172 \text{ g/cm}^3$$

$$\rho_B = 0.8303 \text{ g/cm}^3$$

The molecular weights of n-hexane and benzene were obtained from Perry (38).

$$M_A = 86.17$$

$$M_B = 78.11$$

The molar volumes of n-hexane and benzene at the reference temperature were calculated from their densities.

$$v_A = \frac{M_A}{\rho_A} = \frac{86.17}{0.6172} = 139.61 \text{ cm}^3/\text{mol}$$

$$v_B = \frac{M_B}{\rho_B} = \frac{78.11}{0.8303} = 94.07 \text{ cm}^3/\text{mol}$$

The parameters Λ_{AB} and Λ_{BA} were calculatd by using Equations (B-2) and (B-3).

$$\Lambda_{AB} = \frac{94.07}{139.61} \exp\left(-\frac{393.0}{(8.314)\ (338)}\right)$$

$$= 0.5859$$

$$\Lambda_{BA} = \frac{139.61}{94.07} \exp\left(-\frac{802.2}{(8.314)\ (338)}\right)$$

$$= 1.1155$$

The infinite dilution activity coefficients were calculated by substituting these values into Equation (B-1).

$$\ln \gamma_A^{\circ} = -\ln (0.5859) - 1.1155 + 1$$

$$= 0.4191$$

From Table XIII (Appendix A)

$$\mu_B = 0.8235 \text{ cp at } 278 \text{ K}$$
$$= 0.368 \text{ cp at } 338 \text{ K}$$

From Table XIV (Appendix A)

$$D_{BB} = 4.07 \times 10^{-5} \text{ cm}^2/\text{s at } 338 \text{ K}$$

From Table XII (Appendix A)

$$Z^{\circ}_{AB} = 11.4$$

Using Equation (2-10)

$$D^{\circ}_{AB} = (4.07 \times 10^{-5}) \left(\frac{0.368}{0.8235}\right) \left(\frac{278}{338}\right) \left(1 - \frac{2(0.4191)}{11.4}\right)$$

$$= 1.39 \times 10^{-5} \text{ cm}^2$$

Self-Diffusion Coefficients for Organic Systems

In order to use the subroutine MARQ the initial estimates, and the upper and lower limits of the constants x, y, and r for the parameters T_c, $\ln D_c$, and A are required as input values. The initial estimates of the constants x, y, and r for T_c were obtained by plotting T_c versus the number of carbon atoms in the compound for the homologous series of n-alkanes and n-alcohols. The intercept at a carbon number of zero gave the initial estimate for x. The initial estimate of y was obtained as the slope of the best straight line passing through the first few points in the plot of T_c versus carbon number. The initial estimate of r was arbitrarily set as 0.90. The upper and lower limits of the constants x and y were arbitrarily set and adjusted while running the MARQ program so that they did not constitute a restraining condition during the

iterative procedure. However, the upper and lower limits of r were arbitrarily set as 0.9999 and 1 X 10^{-4}, respectively.

A plot of lnD versus T_r was made for each compound of the homologous series of n-alkanes and n-alcohols to obtain the values of $\ln D_c$ and A for each compound from the intercept and initial slope, respectively. The initial estimates, and the upper and lower limits of the constants x, y, and r were obtained for both parameters $\ln D_c$ and A by following the procedure used for T_c.

The group contributions given in Tables VIII and IX were used along with Equations (2-12), (2-15), and (2-18) to calculate the self-diffusion coefficients for n-alkanes and n-alcohols. The calculation procedure is illustrated for one compound of each homologous series.

n-Alkanes

n-Octane:

T = 273 K

n = 8

From Table VIII

For T_c:

x = 234.2

y = 56.884

r = 0.90857

For $\ln D_c$:

x = -8.9103

y = 0.06785

r = 0.80501

For A:

$$x = 1.1731$$

$$y = 0.18227$$

$$r = 0.90992$$

Using Equation (2-15)

$$T_c = 234.2 + 56.884 \frac{(1 - (0.90857)^8)}{(1 - 0.90857)}$$

$$= 567.4$$

$$\ln D_c = -8.9103 + 0.06785 \frac{(1 - (0.80501)^8)}{(1 - 0.80501)}$$

$$= -8.6237$$

$$A = 1.1731 + 0.18227 \frac{(1 - (0.90992)^8)}{(1 - 0.90992)}$$

$$= 2.2457$$

$$T_r = \frac{T}{T_c} = \frac{273.0}{567.4} = 0.4811$$

Using Equation (2-12)

$$\ln D = -8.6237 + 2.2457 \left(1 - \frac{1}{0.4811}\right)$$

$$= -11.0458$$

$D(n\text{-Octane}) = 1.60 \times 10^{-5}\ cm^2/s$

n-Alcohols

n-Octanol:

$T = 297\ K$

$n = 8$

From Table IX

For T_c:

$\Delta x = 219.6$

$\Delta y = -26.911$

$\Delta r = 0.03572$

For $\ln D_c$:

$\Delta x = 3.0712$

$\Delta y = -2.36605$

$\Delta r = -0.61933$

For A:

$\Delta x = 2.9005$

$\Delta y = -0.1841$

$\Delta r = 0.08998$

Using Equations (2-19) through (2-21)

For T_c:

$x_1 = 234.2 + 219.6 = 453.8$

$y_1 = 56.884 - 26.911 = 29.973$

$r_1 = 0.90857 + 0.03572 = 0.94429$

For $\ln D_c$:

$$x_1 = -8.9103 + 3.0712 = -5.8391$$

$$y_1 = 0.06785 - 2.36605 = -2.2982$$

$$r_1 = 0.80501 - 0.61933 = 0.18568$$

For A:

$$x_1 = 1.1731 + 2.9005 = 4.0736$$

$$y_1 = 0.18227 - 0.1841 = -0.00183$$

$$r_1 = 0.90992 + 0.08998 = 0.9999$$

Using Equation (2-18)

$$T_c = 453.8 + 29.973 \frac{(1 - (0.94429)^8)}{(1 - 0.94429)}$$

$$= 651.7$$

$$\ln D_c = -5.8391 - 2.2982 \frac{(1 - (0.18568)^8)}{(1 - 0.18568)}$$

$$= -8.6613$$

$$A = 4.0736 - 0.00183 \frac{(1 - (0.9999)^8)}{(1 - 0.9999)}$$

$$= 4.0590$$

$$T_r = \frac{T}{T_c} = \frac{297.0}{651.7} = 0.4557$$

Using Equation (2-12)

$$\ln D = -8.6613 + 4.0590 \left(1 - \frac{1}{0.4557}\right)$$

$$= -13.5095$$

$$D(\text{n-Octanol}) = 1.36 \times 10^{-6} \text{ cm}^2/\text{s}$$

VITA 2

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