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Binary molecular diffusivities in liquids: prediction and comparison with experimental data

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BINARY MOLECULAR DIFFUSIVITIES IN LIQUIDS: PREDICTION AND COMPARISON WITH EXPERIMENTAL DATA

by

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ABSTRACT

The Eyring rate theory equation has been modified successfully to enable predictions of binary molecular diffusivities for a wide variety of liquid-liquid systems. The activation free energy for binary diffusion has been evaluated in terms of the activation free energies for self diffusion of the solvent and solute. This was accomplished through the use of regular solution theory by relating the bond breaking energy of the jump step to the bond breaking energy in evaporation. Diffusivities estimated by this equation and the equations developed by Olander, by Gainer and Metzner, and by Wilke and Chang were compared with experimental data. All of the equations tested predicted adequately the diffusivities for most low viscosity as well as for some moderately high viscosity systems. The high viscosity system diffusivities are more accurately predicted by three modified absolute rate theory equations. An important result of this study was the observation that the jump step portion of the total activation energies generally constituted from 0 to 35 percent of the total energy for all of the modified absolute rate theory equations.

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I. INTRODUCTION

In almost all studies of mass transfer in liquids, accurate liquid molecular diffusion coefficients are needed for the liquid systems under consideration. At the present time, relationships are available with which one may estimate binary liquid diffusivities with reasonable accuracy for a variety of simple, low viscosity systems. However, there are several significant problems which tend to preclude the application of these relations for the prediction of diffusivities for certain classes of binary liquid systems. For example, estimations of the molecular diffusion coefficients for some high viscosity systems using existing approaches (except for one recently proposed mechanism) have resulted in order of magnitude errors. Large deviations between experimental and predicted diffusivities also have been observed for some systems exhibiting hydrogen bonding.

The objective of this work is to present a mechanism which will allow one to estimate binary molecular diffusivities for the simple, low viscosity systems and for liquid solutions with high viscosity components and/or components exhibiting hydrogen bonding. The proposed mechanism utilizes the Eyring rate theory as a basic starting point. The novel feature of this method is an application of regular solution theory in the calculation of the free energy of activation for binary diffusion.

The diffusivity prediction model developed in this work and other methods presented in the literature will be compared with experimental data. Since literature diffusion data for systems in the moderately high viscosity range are very limited, additional data were obtained experimentally during the course of the investigation. A radioactive tracer technique was used to obtain data in the very low solute concentration region, in contrast to the relatively high solute concentrations used in a previous study of high viscosity systems.

II. LITERATURE REVIEW

The many diverse methods of estimating binary molecular diffusivities will not be reviewed here since they are adequately described elsewhere (Reid and Sherwood, 1966). However, the diffusion mechanisms proposed by Olander (1963) and Gainer and Metzner (1965) will be described because some of the concepts which they introduced have been employed in the mechanism to be proposed later in this work.

The absolute rate theory equation for the prediction of the molecular diffusion coefficient is often expressed in the following form (Ree et al., 1958):

$$D_{AB} = \frac{kT}{\xi \eta_B} \frac{\lambda_1}{\lambda_2 \lambda_3} \exp\left[\frac{\Delta F_{\eta_B} - \Delta F_{D_{AB}}}{RT}\right] \tag{1}$$

Until 1963, the free energy of activation for viscous transfer ΔF_{η_B} and binary molecular diffusion $\Delta F_{D_{AB}}$ were usually considered to be equal, in part because there was no reliable way to evaluate the free energy of activation for binary molecular diffusion. In 1963, Olander proposed a method of estimating this free energy term.

In the development of his diffusion mechanism, Olander (1963) suggested that at low solute concentrations the mechanism of viscous transfer is determined almost entirely by the solvent molecule interactions. This viscous mechanism can be thought of as occurring via two processes. The first process is the formation of a hole or a vacant lattice site followed by the second process which is the movement of a neighboring molecule to fill the hole. This mechanism tells nothing of the relative importance of the two processes, but it does allow one to consider the total free energy of activation for viscous transfer in a pure substance as

$$\Delta F_{\eta_B} = \Delta F^{h}_{\eta_B} + \Delta F^{j}_{\eta_B} \qquad (2)$$

where the superscripts h and j refer to the hole formation and jump step contributions of the total process, respectively.

In the binary diffusion process for very dilute solutions where solute A can be considered to be almost completely surrounded by solvent molecules, B, the hole formation process can be considered as occurring in pure B. However, the movement (i.e., jump) of the solute molecule into the hole must ultimately take into account the interaction of the solvent and solute molecules. Thus,

$$\Delta F^{h}_{D_{AB}} = \Delta F^{h}_{D_{BB}} \qquad (3a)$$

and, consequently,

$$\Delta F_{D_{AB}} = \Delta F^{h}_{D_{BB}} + \Delta F^{j}_{D_{AB}} \qquad (3b)$$

Since the jump term is considered as passage up a potential energy barrier, ϵ_o', the following equation can be written by making use of the zero point energy difference:

$$\exp(-\Delta F^{j}_{D_{AB}}/RT) = \frac{Q_{\neq AB}}{Q_{AB}} \exp(-\epsilon'_{o_{AB}}/kT) \qquad (4)$$

There are no universally exact combination rules for the zero point energy difference between dissimilar species. However, Olander (1963) utilized a relation proposed by McLaughlin (1959) indicating that for both laminar viscous and self diffusion processes this zero point energy difference can be represented by a fraction (empirically determined) of the Lennard-Jones expression for the potential energy between the central molecule and its nearest neighbors. McLaughlin also indicated that the zero point energy difference depends primarily upon the force constant ϵ. Olander then assumed that, if a linear relation between ϵ and ϵ'_o is valid, the combination rules for the molecular constant ϵ could be applied to the zero point energy difference to give

$$\epsilon'_{o_{AB}} = \sqrt{\epsilon'_{o_{AA}} \, \epsilon'_{o_{BB}}} \qquad (5)$$

If it is then assumed that the product of the ratio of the partition functions for the activated and equilibrium states for binary diffusion times the inverse ratio of the partition functions for viscous transfer is approximately unity, then the following relation is obtained:

$$\Delta F^{j}_{\eta_B} - \Delta F^{j}_{D_{AB}} = \Delta F^{j}_{\eta_B} - \sqrt{\Delta F^{j}_{D_{AA}} \, \Delta F^{j}_{D_{BB}}} \qquad (6)$$

If one also assumes that the jump part of the free energy of activation constitutes a constant fraction, f', of the total free energy of activation, then the diffusion coefficient can be estimated by the following equation (Olander, 1963):

$$D_{AB} = \frac{kT}{\xi \, \eta_B} \left(\frac{N}{\overline{V}_B}\right)^{1/3} \exp\left[\frac{f'(\Delta F_{D_{BB}} - \sqrt{\Delta F_{D_{AA}} \, \Delta F_{D_{BB}}})}{RT}\right] \qquad (7)$$

It was assumed by Olander in the above development that the free energy of activation for viscous transfer and self diffusion are equal.

Olander (1963) empirically obtained a value of approximately one-half for the parameter f' and a value of about 5.6 for ξ from binary diffusion data.

Gainer and Metzner (1965) developed a somewhat similar method for estimating the activation energy for binary diffusion. They also started with the Eyring absolute rate theory equation in a form similar to Equation 1 but had the activation energy in the exponential term instead of the free energy of activation as used by Olander. However, they further extended their analysis and divided the contribution of the activation for the jump step into two parts by first assuming that the energy term was a measure of the solvent-solute bond energies. These two terms are assumed to account for ordinary dispersion forces and for hydrogen bonding forces. Thus,

$$E^j_{D_{AA}} = C_1 E^j_{D_{AA-H}} + C_2 E^j_{D_{AA-D}} \tag{8}$$

Consideration of the effects of these two forces as a function of the distance over which they act leads to the following expressions for the correction parameters C_1 and C_2 for the individual jump terms:

$$C_1 = R_A/R_{AB} \tag{9a}$$

and

$$C_2 = (R_A/R_{AB})^{1/12} \tag{9b}$$

where

$$R_A = (\bar{V}_A/N)^{1/3} \tag{9c}$$

$$R_B = (\bar{V}_B/N)^{1/3} \tag{9d}$$

$$R_{AB} = (R_A + R_B)/2 \tag{9e}$$

The ratio of the activation energy due to hydrogen bonding to the total activation energy is assumed by Gainer and Metzner (1965) to be related to the heat of vaporization by the following ratio:

$$\frac{E_{D_{AA-H}}}{E_{D_{AA}}} = \frac{\Delta H^{vap}_{A-H}}{\Delta H^{vap}_{A}} \tag{10}$$

where the ΔH^{vap}_{A-H} is the heat of vaporization due to hydrogen bonding and may be estimated as the heat of vaporization of the liquid of interest minus the heat of vaporization of the hydrocarbon homologue of that liquid at the same reduced temperature. Gainer and Metzner assumed that the activation energy for self diffusion was equal to that for the viscous process. Using this latter assumption, the parameter ξ was evaluated from self diffusion data, and an average of 6.0 was obtained.

Gainer and Metzner (1965) further assumed that the jump and hole formation portions of the total activation energy were of equal magnitude (i.e., $f' = 1/2$). Their final equation for the estimation of D_{AB} is given as follows:

$$D_{AB} = \frac{kT}{\xi_A \eta_B} \left(\frac{N}{\bar{V}_B}\right)^{1/3} \exp\left[\frac{E_{\eta_B} - E_{D_{AB}}}{RT}\right] \tag{11a}$$

where

$$E_{\eta_B} - E_{D_{AB}} = \frac{E_{\eta_B}}{2} - \frac{\xi_A}{\xi_B}\left[\sqrt{\frac{R_A}{R_{AB}}\,\frac{E_{\eta_{A-H}}}{2}\,\frac{R_B}{R_{AB}}\,\frac{E_{\eta_{B-H}}}{2}} + \sqrt{\left(\frac{R_A}{R_{AB}}\right)^{12}\frac{E_{\eta_{A-D}}}{2}\left(\frac{R_B}{R_{AB}}\right)^{12}\frac{E_{\eta_{B-D}}}{2}}\,\right] \tag{11b}$$

Gainer and Metzner (1965) recommended that E_{η_B} be calculated by the following equation:

$$E_{\eta_B} = RT \ln \left[\frac{\eta_B \bar{V}_B^{2/3} \quad \Delta E_B^{vap}}{1.09(10^{-3}) M^{1/2} T^{3/2}} \right] \qquad (12)$$

The above equation was developed assuming that the internal contributions to the total partition functions were the same for the equilibrium and activated states. This assumption was also made during the development of Equation 11. The procedure was used to estimate binary molecular diffusivities with reported average absolute deviations of about 20 percent or more for the intermolecular hydrogen bonded systems and highly viscous solvent systems studied in their work. The claim of superiority of the Gainer and Metzner equations over prior methods was based primarily on the comparison of predictions of their model with the high viscosity data obtained in their laboratories. These data appear to be based upon experiments in which somewhat high solute concentrations were used.

The primary assumption made in the developments of Olander (1963) and Gainer and Metzner (1965) is that the basic Eyring absolute rate theory adequately describes the mechanisms of viscous transfer and molecular diffusion. In addition to this assumption, the intermolecular distance terms (i.e., the λ's) were assumed to be equal and proportional to the cube root of the molar volume. The application of Eyring's theory by both Olander (1963) and Gainer and Metzner (1965) should primarily be applied to very dilute solute concentrations in binary systems. The energies of activation were assumed to be equal for viscous transfer and self diffusion. Both of these developments introduced the viscosity coefficient η into the equation for the diffusivity prediction. Consequently, it was assumed that the product of the ratio of the partition functions for the activated and equilibrium states for binary diffusion times the inverse ratio of the partition functions for viscous transfer was approximately unity. They also assumed that the combination rules for the force constants can be applied directly to the zero point energy difference to obtain the binary activation energy (or free energy) as a geometric average of the individual component activation energies.

The last two assumptions summarized above were eliminated in this investigation (1) by not introducing the viscosity coefficient into the Eyring prediction equation and (2) by considering that the contribution of the jump step to the total activation free energy of the diffusion process is proportional to the energy of vaporization. Once these assumptions were accepted, the relationship between $\Delta F_{D_{AB}}$ and the free energies of the individual species A and B were readily obtained through the use of regular solution theory.

III. THEORETICAL DEVELOPMENT

Eyring's absolute rate theory equation for the prediction of the molecular diffusion coefficient can also be represented in terms of the free energy of activation by the following relationship (Ree et al., 1964):

$$D_{AB} = \frac{kT}{\xi h} \left(\frac{\sqrt{2}\bar{V}_B}{N}\right)^{2/3} \exp\left[-\frac{\Delta F_{D_{AB}}}{RT}\right] \tag{13}$$

In this work, it is assumed that $\lambda_1 = \lambda_2 = \lambda_3 = \lambda = (\sqrt{2}\bar{V}_B/N)^{1/3}$.

The parameter ξ can be evaluated from a variation of Equation 13 and from a knowledge of viscosity and self diffusion data at any particular temperature if one assumes that the free energy of activation for self diffusion and viscous transfer are equal. Thus,

$$\xi_X = \frac{kT}{D_{XX} h} \left(\frac{\sqrt{2}\bar{V}_X}{N}\right)^{2/3} \exp\left[-\frac{\Delta F_{D_{XX}}}{RT}\right] \tag{14}$$

where

$$\Delta F_{D_{XX}} = \Delta F_{\eta_X} \tag{15}$$

and

$$\Delta F_{\eta_X} = RT \ln\left[\frac{\eta_X \bar{V}_X \sqrt{2}}{hN}\right] \tag{16}$$

The parameter ξ was re-evaluated by the author for a number of pure substances. Values of ξ, suggested for use in this model, are presented in another part of this work.

A. Evaluation of the Free Energy of Activation for Binary Diffusion.

As stated above, the free energy of activation for self diffusion and viscous transfer were assumed to be equal. However, for binary diffusion, this equality is invalid because of the difference in mechanism, as emphasized by Olander (1963). In order to estimate the free energy of activation for binary diffusion, $\Delta F_{D_{AB}}$ was related to the free energies of activation for pure solvent and pure solute: $\Delta F_{D_{XX}}$ and ΔF_{η_X}. As in the work of Olander, the total free energy of activation was assumed to equal the sum of two portions: that due to the hole formation step and the jump step. Thus,

$$\Delta F_{D_{AB}} = \Delta F^{h}_{D_{AB}} + \Delta F^{j}_{D_{AB}} \qquad (17)$$

If in this instance, it is further assumed that the hole formation contribution to the free energy of activation is the same in a dilute binary solution as it would be in a pure solvent, then

$$\Delta F_{D_{AB}} = \Delta F^{h}_{D_{BB}} + \Delta F^{j}_{D_{AB}} \qquad (18)$$

The problem of evaluating $\Delta F_{D_{AB}}$ now becomes one of estimating $\Delta F^{j}_{D_{AB}}$ in terms of $\Delta F^{j}_{D_{AA}}$ and $\Delta F^{j}_{D_{BB}}$ and also of estimating the portions of the total free energy, $\Delta F_{D_{AB}}$, that can be attributed to the hole formation and solute jump process.

The process of molecular motion for both diffusion and viscous flow requires additional space (a hole) in the liquid, as visualized in the absolute rate theory approach. Thus, a molecule that jumps from its surrounding cage into a hole can be considered as behaving in a manner very similar to a molecule that jumps from the bulk of a liquid near the vapor interface into the vapor layer above the liquid. (Although in the case of the jump step in diffusion or viscous transfer, the hole that must be available may not necessarily be the full size of the molecule that is jumping). This consideration suggests that the free energy of activation for diffusion due to the jump step may be taken as a fraction of the energy of vaporization so that

$$\Delta F^{j}_{D_{BB}} = k \Delta E^{vap}_{B} \tag{19}$$

Experimental evidence supporting the above relationship is only indirect. The jump step portion of the activation free energy of diffusion represents some fraction $f^{'}$ of the total activation free energy. Thus,

$$\Delta F^{j}_{D_{BB}} = f^{'} \Delta F_{D_{BB}} \tag{20}$$

By combining Equations 15, 17, and 19, the following relationship is obtained:

$$\Delta F_{\eta_B} = \left(\frac{k}{f^{'}}\right) \Delta E^{vap}_{B} = k^{'} \Delta E^{vap}_{B} \tag{21}$$

Experimental data by Glasstone <u>et</u> <u>al</u>. (1941) seem to suggest a relationship similar to Equation 21. The following relationship was found by Glasstone <u>et</u> <u>al</u>. to approximate the data of nearly 100 liquid substances:

$$\Delta F_{\eta_B} = \frac{1}{2.45} \Delta E^{vap}_{B} \tag{22}$$

The above relation applies for liquids as diverse as water and other associated liquids, for glycerol, and for nonpolar substances such as hydrocarbons. It does not apply, however, to liquid metals. The approximate nature of Equation 22 was discussed briefly by Bondi (1946). The similarity of the experimentally obtained relation (Equation 22) to Equation 21 suggests the possible validity of Equation 19.

It has been assumed that the above analysis for self diffusion and viscous transfer can be applied to a very dilute solution of A in B. The solution must approach infinite dilution in A so that any molecule of A can be considered to be surrounded only by B molecules. It follows, therefore, that the jump step portion of the activation free energy of diffusion can be approximated as a fraction Z of the energy of vaporization of solute A from almost pure B:

$$\Delta F^{j}_{D_{AB}} = Z\overline{\Delta E}^{vap}_{AB} \tag{23}$$

The above expression is used in the following application of regular solution theory.

Regular solution theory has several basic limitations. The theory assumes a nearly random distribution of solute molecules in the solvent medium. This assumption restricts the theory to systems exhibiting a zero excess entropy of mixing. In addition, regular solution theory accounts for only ordinary intermolecular dispersion forces. Hydrogen bonding or electrostatic interactions were not accounted for in the original treatment. In spite of its shortcomings, regular solution theory allows for a straightforward means of estimating $\Delta F_{D_{AB}}$.

From regular solution theory, it can be shown that for infinitely dilute binary solutions $\overline{\Delta E}^{vap}_{AB}$ can be given by (Hildebrand and Scott, 1964)

$$\overline{\Delta E}^{vap}_{AB} = \Delta E^{vap}_{A} - \bar{V}_{A}\left[\left(\frac{\Delta E^{vap}_{A}}{\bar{V}_{A}}\right)^{1/2} - \left(\frac{\Delta E^{vap}_{B}}{\bar{V}_{B}}\right)^{1/2}\right]^{2} \tag{24}$$

Upon assuming that the activation free energies of diffusion for the jump process are a fraction of the respective energies of vaporization for pure and binary systems (Equations 19 and 23), the following equation for $\Delta F^{j}_{D_{AB}}$ can be obtained:

$$\Delta F^{j}_{D_{AB}} = \Delta F^{j}_{D_{AA}} - \bar{V}_A \left[\left(\frac{\Delta F^{j}_{D_{AA}}}{\bar{V}_A}\right)^{1/2} - \left(\frac{\Delta F^{j}_{D_{BB}}}{\bar{V}_B}\right)^{1/2} \right]^2 \qquad (25)$$

In order to obtain Equation 25, it has been assumed that the proportionality constants k and Z for Equations 19 and 23 are the same. The validity of this assumption will be examined later.

Equation 23 may be substituted into Equation 3b to give

$$\Delta F_{D_{AB}} = \Delta F^{h}_{D_{BB}} + \Delta F^{j}_{D_{AA}} - \bar{V}_A \left[\left(\frac{\Delta F^{j}_{D_{AA}}}{\bar{V}_A}\right)^{1/2} - \left(\frac{\Delta F^{j}_{D_{BB}}}{\bar{V}_B}\right)^{1/2} \right]^2 \qquad (26)$$

If one now assumes that the portion of the free energy of activation due to the hole formation process constitutes a constant fraction, f, of the total free energy of activation, i.e.,

$$f = \Delta F^{h}_{D_{XX}} / \Delta F_{D_{XX}} \qquad (27)$$

where

$$f = 1 - f' \qquad (28)$$

then the binary molecular diffusion coefficient for dilute solutions may be expressed as

$$D_{AB} = \frac{kT}{\xi h} \left(\frac{\sqrt{2}\, \bar{V}_B}{N}\right)^{2/3} \exp\left(-\frac{\Delta F_{D_{AB}}}{RT}\right) \qquad (13)$$

where

$$\Delta F_{D_{AB}} = f\Delta F_{D_{BB}} - (1-f)\left\{\Delta F_{D_{BB}}\frac{\bar{V}_A}{\bar{V}_B} - 2\bar{V}_A\left[\left(\frac{\Delta F_{D_{AA}}}{\bar{V}_A}\right)\left(\frac{\Delta F_{D_{BB}}}{\bar{V}_B}\right)\right]^{1/2}\right\} \tag{29}$$

and where $\Delta F_{D_{AA}}$ and $\Delta F_{D_{BB}}$ are determined using Equations 15 and 16 along with a knowledge of the viscosity and molar volume of each component at the temperature in question. The recommended values for f and ξ will be given later. Thus, Equations 13 and 29 may be used for the estimation of the molecular diffusivity D_{AB}.

B. Summary of Assumptions.

The assumptions that have been introduced in the development of Equation 29 are summarized as follows:

1. Eyring's rate theory of unimolecular reactions is a valid representation of the processes of viscous and diffusional transport in a cell model of the liquid state.
2. Regular solution theory is valid for infinitely dilute solutions.
3. The activation free energy for diffusion can be divided into two parts--a hole formation and a jump term (Equation 17).
4. The activation free energy for self diffusion is equal to the activation free energy for viscous flow (Equation 15).
5. The activation free energy for the hole-forming process for the self diffusion process is a fraction, f, of the total free

energy for the self diffusion process (Equation 27).

6. The value of the fraction f for self diffusion of the pairs AA and BB is the same as that for binary diffusion of the AB system.
7. The activation free energies of the hole-forming process for both binary and solvent self diffusion are equal (Equation 3a).
8. The activation free energy for the diffusional jump steps can be considered as fractions of the total energy vaporization (Equations 19 and 23), and k is equal to Z.

It will be assumed later that f is a constant for all binary systems within a major category of systems but that the value of f may be different for each of the three major categories of systems.

The validity of the third, sixth, and seventh assumptions has been tested by using thermodynamic data. The development that led to Equation 29 can be followed in a similar manner using these assumptions to yield

$$\Delta F_{D_{AB}} = \Delta F_{D_{BB}} + k\left[\Delta E_A^{vap} - \Delta E_B^{vap} - \Delta\overline{H}_{AB}^{mix}\right] \qquad (30)$$

If the assumptions are valid, one would expect a plot of $\Delta F_{D_{AB}}$ versus $\Delta E_A^{vap} - \Delta E_B^{vap} - \Delta\overline{H}_{AB}^{mix}$ to be linear. The author was able to obtain thermodynamic solution data and diffusion activation free energy data for the solutes carbon tetrachloride, chloroform, ethanol, and methanol in the solvent benzene and for the solutes methanol, ethanol, n-propanol, and n-butanol in the solvent water. The data used for these calculations are given in Appendix A. In addition, the values of $\Delta F_{D_{BB}}$, were calculated using Equations 15 and 16, and included for the term $(\Delta E_A^{vap} - \Delta E_B^{vap} - \Delta\overline{H}_{AB}^{mix})$ equal to zero. These data are presented in Figures 1 and 2. One can tentatively conclude on the basis of this one comparison that the combined effect of the three assumptions may be valid. Studies with more systems and tests of the *non*-combined effect of assumptions would be necessary for final conclusions as to the validity of these assumptions.

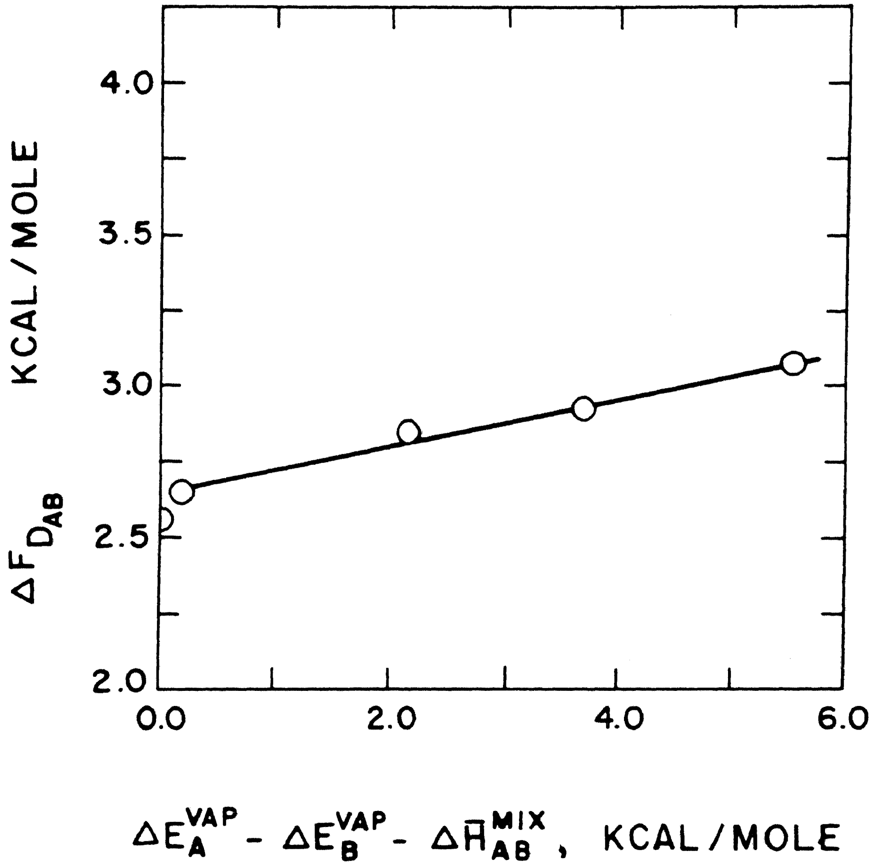

Figure 1. The binary activation free energy, $\Delta F_{D_{AB}}$, versus the term $\Delta E_A^{vap} - \Delta E_B^{vap} - \overline{\Delta H}_{AB}^{mix}$ for systems with water as the solvent.

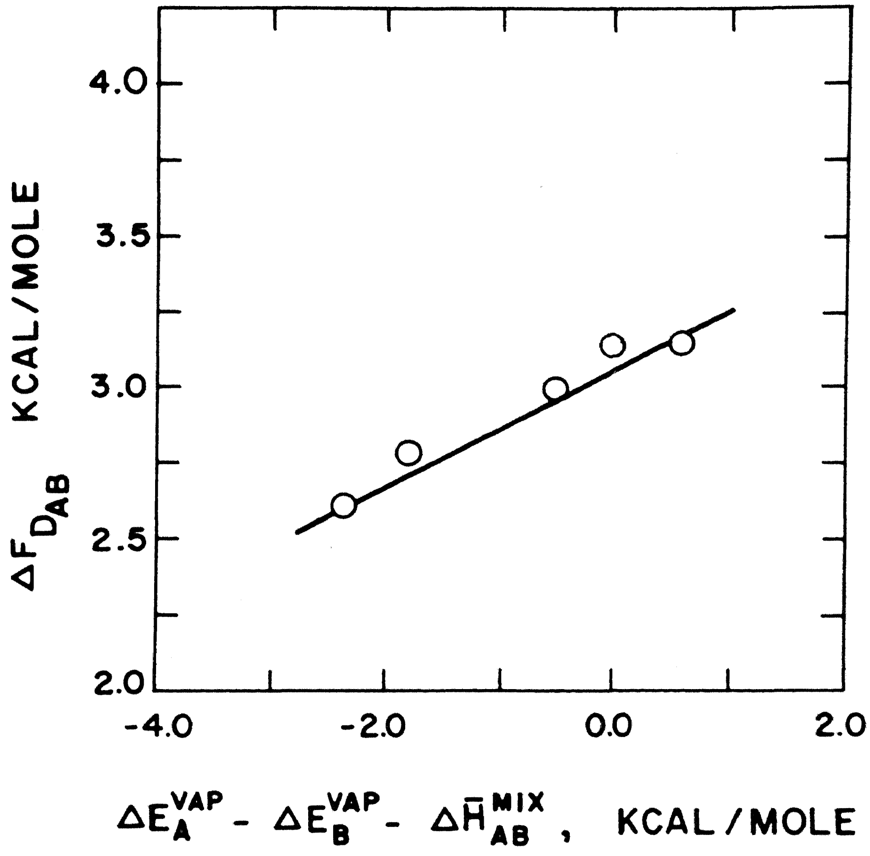

Figure 2. The binary activation free energy, $\Delta F_{D_{AB}}$, versus the term $\Delta E_A^{vap} - \Delta E_B^{vap} - \Delta \overline{H}_{AB}^{mix}$ for systems with benzene as the solvent.

IV. EXPERIMENTAL

In order to compare predicted binary molecular diffusivities with experimentally determined diffusivities for systems in the moderately high viscosity range, five binary systems were studied experimentally (Table VII). The solution viscosities for these systems ranged from 6.8 to 43.4 centipoise.

The conventional steady-state methods for determining diffusivities were not considered practical because of the very slow rates of mass transfer. In addition, previously used unsteady-state techniques require either relatively high initial solute concentrations (e.g., interferometric techniques) or a radiometric method with a strong beta or gamma source as the solute. Thus, an unsteady-state porous frit technique was devised, as described below, for use with solutes tagged with carbon-14. A detailed description of the technique and apparatus used to determine binary molecular diffusivities is given in Appendix B.

A. Equipment and Procedure.

The essential component of the apparatus is a porous ceramic plate about 2-7/8 inches square by 1/4 inch thick. The edges of the plate were sealed with an epoxy resin.

The clean, dry, porous plate was first soaked in a binary solution with a known concentration of solute. The solute consisted of a known mixture of radioactively tagged (C-14) solute and non-tagged pure solute. The initial concentration of the solute, ethylene glycol, in the solvents, propylene glycol and diethylene glycol, that were inside the porous plate was $4.50\ (10)^{-2}$ moles per liter. The initial concentration of the solute cyclohexanol in the solvents ethylene glycol, propylene glycol, and diethylene glycol was 2.41 $(10)^{-2}$ moles per liter. Following the pre-soak period, the porous plate was rigidly fastened inside a solvent bath which consisted of a 6x3-1/2x1-1/4 inch box. A stirring assembly was then lowered around the two faces of the plate. This assembly consisted of four horizontal blades which swept up and down very close to both surfaces of the plate. The blades could be reciprocated over a wide range of frequencies by means of a variable speed transmission. The stirring assembly was activated immediately before the solvent bath, holding the porous frit, was filled with 300 cc of pure solvent. The solvent bath was almost totally immersed in a constant temperature oil bath whose temperature was controlled at the desired temperature to within $\pm$ 0.01°C. The diffusivities were measured at temperatures of 25.0, 30.0, 40.0 and 50.0°C. The viscosity of these systems varies by less than 2.5 centipoise/°C at these temperatures.

The solute inside the porous plate was transported by molecular diffusion through the pores, to the surface of the plate, and then into the well-agitated solvent in the solvent bath box. The agitator frequency was adjusted to minimize the resistance to mass transfer in the solvent bath immediately adjacent to the porous plate and to assure a uniform solute concentration in the solvent bath (at any given time) during the unsteady state buildup of the bath solute concentration.

During the course of a run, one milliliter samples were removed from the solvent bath to determine the bath solute concentration as a function of time. About 12 samples were removed during each run and later analyzed.

The radioactivity of the solute in the samples was counted in a liquid scintillation counter. The total solute concentration was then determined from the solute activity. The effect of radioactive decay was considered to correct the measurements to the time each run was begun.

Certain calibration parameters for the porous frits were determined during standardization runs using a binary system for which the molecular diffusion coefficient was already known. The diffusion of radioactive sodium chloride in distilled water was used for this purpose [$D_{AB} = (1.61 \pm .01)10^{-5}$ cm^2 per sec. at 25^oC (Harned and Owen, 1958)]. The initial concentration of this solute was $1.10\ (10)^{-3}$ moles/liter. The activity of the Na-24 was determined using a standard Gieger-Mueller detector and a counter.

B. Analysis of the data.

The molecular diffusion coefficients were determined from the data for the bath solute concentration versus time. The molecular diffusion process inside the porous plate is described by the following relations during the "penetration-theory" portion of the diffusion process:

$$\frac{\partial C}{\partial t} = D_{AB} \frac{\partial^2 C}{\partial x^2} \tag{31a}$$

$$C(x, 0) = C_o \tag{31b}$$

$$C(\infty, t) = C_o \tag{31c}$$

$$C(0, t) = C_f(t) \tag{31d}$$

The solute balance, which describes the solute concentration in the solvent bath, is

$$V_f \frac{dC_f}{dt} = - 2D_{AB}A_T \frac{\partial C(0, t)}{\partial x} \tag{32a}$$

$$C_f(0) = C_f^o \tag{32b}$$

Equations 31 and 32 were solved simultaneously by using Laplace transforms to give the following expression for the solute concentration in the solvent bath, C_f, as a function of time (see Appendix B for details):

$$\frac{C_f - C_o}{C_f^o - C_o} = \exp (K^2 t). \left[1 - \text{erf} (Kt^{1/2})\right] \tag{33a}$$

where

$$K = 2A_T \sqrt{D_{AB}}/V_f \tag{33b}$$

and where the solvent bath volume, V_f, is assumed to be a constant during the entire run, even though V_f changes during the run. The average solvent bath volume is approximated by

$$V_f = 300 - N/2 \tag{34}$$

where N is the total number of one milliliter samples withdrawn from the sample bath.

The development of Equation 33 necessitated restricting sample times, t, to values less than $0.30L_{eff}^2/D_{AB}$, where L_{eff} is the effective length of the pores. Approximate values of L_{eff} were determined in a separate investigation (Wu, 1968) and varied from 0.38 to 0.58 cm for one-half of the plate thickness.

The molecular diffusion coefficients were determined from a knowledge of C_f versus t; however, the porous plate area parameter, A_T, first has to be determined using a system with a known diffusivity. Regardless of whether one is concerned with a diffusivity determination run or a calibration run, the term K was considered as a curve-fitting parameter. In order to consider any possible initial solute concentration in the bath, C_f^o also has to be regarded as a curve-fitting parameter.

An iterative, nonlinear, least-squares technique was used to determine the values of K and C_f^o. This technique minimized the weighted sum of the square of the deviation, S;

$$S = \sum_{i=1}^{N} W_i (C_{f_i} - C'_{f_i})^2 \tag{35}$$

where the weighting factor is

$$W_i = \sigma^{-2}(C_{f_i}) \tag{36}$$

The experimental measurement of the dependent variable is the counts per minute of the radioactive solute tracer in the solvent bath. This measurement is proportional to the total concentration of the solute in the bath, C_f. Thus, the standard deviation can be considered as

$$\sigma(C_f) = A\ C_f^{1/2} \tag{37}$$

assuming that all error is related to the normal randomness of the radioactive decay process. (The proportionality constant, A, disappears in the resulting least-squares "normal" equations.)

The porous plates were calibrated at the beginning of the study and recalibrated following their use in the determination of D_{AB}. The calibration of each plate consisted of about three determinations of A_T--at least one at the beginning and at least one at the end of the study; the average value of A_T was used in the parameter K to determine the molecular diffusivity. There were no consistent trends in the values of A_T. This indicated that foreign particles did not accumulate in the pores of the plates during the experiments. The cleaning procedures for the porous plates have been described in Appendix B.

The values of the binary molecular diffusivities that were determined experimentally are given in Table IV, along with values of D_{AB} that were estimated by using various models.

V. RESULTS AND DISCUSSION

The molecular diffusivity prediction model developed in this work as well as other methods presented in the literature (Wilke and Chang, 1955; Olander, 1963; Gainer and Metzner, 1965) are compared with the experimentally determined diffusivities given in the literature and obtained in this work. The comparisons that have been divided into three classes of experimental data will be preceded by a discussion of the estimation of the terms ξ and f.

A. Evaluation of the Parameter ξ.

The term ξ was introduced into the original rate theory as a lattice parameter to describe the geometric arrangement of the diffusing molecule with respect to its neighbors. Ree et al. (1958) determined the value of ξ to be six, based on the assumption that ξ equals the number of nearest neighbors in a plane normal to the direction of motion of the diffusing molecule for an assumed hexagonal close-pack structure.

Li and Chang (1955) experimentally determined ξ by assuming that the activation free energies for viscous transfer and self diffusion were equal. Thus, use of Equation 1 leads to

$$\xi_X = \frac{kT}{D_{XX}\eta_X}\left[\frac{N}{\bar{V}_X}\right]^{1/3} \tag{38a}$$

where $(\bar{V}_X/N)^{1/3}$ is assumed equal to $\lambda_2\lambda_3/\lambda_1$. This equation, along with self diffusion coefficients, viscosities, and molar volumes for pure components, was used by Li and Chang to obtain a value of 6.0 for ξ.

Ree et al. (1958) evaluated ξ in a similar manner by using dilute binary diffusivities and obtained an average value of 5.60. This value was subsequently used by Olander (1963).

Gainer and Metzner also evaluated ξ by using Equation 1. They obtained an average value of 6.0 for all solvents except the lower normal paraffin alcohols (i.e., methyl and ethyl alcohol) for which ξ was 8.0. They used self diffusion data and molar volumes that were possibly calculated by using Kopp's rule for the normal boiling temperature.

The parameter ξ was re-evaluated by the author to account for the hexagonal close-packing correction factor, $\sqrt{2}$, used in the evaluation of λ and also to use experimental values of the molar volumes at the <u>same</u> temperature as the self diffusion and viscosity measurements. The following equation, obtained from Equations 14, 15, and 16 was used to determine ξ:

$$\xi_X = \frac{kT}{D_{XX}\eta_X} \left(\frac{N}{\sqrt{2}\, V_X}\right)^{1/3} \tag{38b}$$

The results are indicated in Table I. As observed by earlier investigators, the average value of ξ found in this work for methanol and ethanol ($\xi = 7.5$) is considerably higher than that of most other solvents ($\xi = 5.6$). These average values have been used in the model developed in this work in the temperature range of about 0° to 30°C.

As may be noted in Table I, the values of the geometric parameter, ξ, for water were not included in the table or used in the calculation of the average ξ. These data were not included, because as indicated by Johnson and Babb (1956), serious disagreement exists among various investigators as

TABLE I

ξ AND THE VISCOUS ACTIVATION FREE ENERGY FOR VARIOUS PURE COMPOUNDS

Compound	Temp °C	ξ	$\Delta F_{D_{BB}}$ Kcal/Mole
Benzene	15	5.10	3.074
	25	5.34	3.099
	35	5.58	3.126
	45	6.06	3.156
Ethanol	15	7.27	3.197
	25	6.77	3.216
	35	6.59	3.230
	45	6.36	3.219
Methanol	15	7.06	2.574
	25	7.19	2.582
	35	7.29	2.591
n-Propanol	15	4.91	3.741
	25	5.24	3.747
	35	5.43	3.739
	45	5.54	3.730
i-Propanol	15	4.76	3.843
	25	4.63	3.830
	35	4.55	3.817
	45	4.55	3.791
n-Butanol	25	5.67	3.842
	35	5.28	3.930
	45	5.42	3.962
n-Pentane	25	5.28	2.659
n-Hexane	25	4.96	2.901

TABLE I (continued)

Compound	Temp ^{o}C	ξ	$\Delta F_{D_{BB}}$ Kcal/Mole
n-Heptane	25	4.94	3.120
n-Octane	25	5.54	3.358
n-Nonane	25	4.81	3.574
n-Decane	25	4.73	3.765

to the value of D_{XX} for water. If one used these widely varying data for the self diffusion coefficient, the values of ξ for water will range from 4.1 to 6.3. These values bracket the value of 5.6 used in this work.

The effect of temperature on the geometric parameter, ξ, was investigated to determine if any general relationship for systems of solvents could be obtained. Neutron and X-ray diffraction data (Eyring and Marchi, 1963) indicate that the number of nearest neighbors to a molecule increases in an orderly manner as the temperature is decreased. For some of the compounds studied in this work, ξ was found to increase as the temperature decreased; however, for other systems, ξ decreased as the temperature decreased. There appears to be no correlation of ξ with reduced temperature and reduced pressure.

The values of ξ in Table I were determined from self diffusion coefficients. Because the geometry with respect to the nearest neighbors for the pure solvents should vary when a solute molecule has a volume considerably different than a solvent molecule, the ξ value for binary systems might differ from those indicated in Table I. This possibility will be investigated at a later date.

B. Evaluation of the parameter f.

The parameter f is defined in this work as the fraction of the total diffusional activation free energy which can be attributed to the hole formation portion of the liquid phase transport process (see Equation 27). A similar term, f', was used by Olander (1963), except that it was based upon the jump step contribution ($f' = 1 - f$). Using a graphical analysis of a wide variety of diffusion data, Olander found f' equaled 0.50. Gainer and Metzner (1965) also used a value of f' equal to 0.50 in their development. Before determining the f value to be used in the model developed for this work, the value of f' determined by both Olander (1963) and Gainer (1964) was re-examined in this paper.

Olander (1963) graphically curve-fitted experimental data selected from the literature to the following relation:

$$Y = \frac{D_{AB}\eta_B}{T} \left(\frac{\xi}{k}\right)\left(\frac{\bar{V}_B}{N}\right)^{2/3} = \exp\,(f'\,\delta) \tag{39a}$$

where

$$\delta = \frac{\Delta F_{D_{BB}}}{RT} \left[1 - \frac{\Delta F_{D_{AA}}}{\Delta F_{D_{BB}}}\right]^{1/2} \tag{39b}$$

He obtained a value of f' equal to 0.50. However, by using the same data, the author obtained a value of 0.397 but employed a nonlinear, least squares, curve-fitting technique to obtain f' (i.e., $f \cong 0.60$). The data were also correlated with a slightly modified form of Equation 39a. The argument of the exponent was taken to equal ($f'\delta + b$), where b was merely an empirical constant that was included so as not to force the curve-fit through ($Y = 1.00$, $\delta = 0$). The value of f thus obtained was very close to 0.60 but still was not 0.50. The use of 0.60 rather than 0.50 leads to only a small difference in the estimation of D_{AB} using the Olander (1963) model; however, as will be shown later, the model developed in this article is much more sensitive to values of f. Olander (1963) discussed the possibility of f values being different from the tentative values of 0.50 recommended in his work.

As mentioned earlier, Gainer and Metzner (1965) used a value of f' equal to 0.5 in their model. They assumed this value on the basis of Olander's (1963) work. Gainer (1964) supported this choice with a study of *one* of about 14 systems used in his study. The value of D_{AB} predicted by his model was compared with the experimentally determined diffusivity for the methanol (A)-glycerol (B) system using three different values of f' (1/3, 1/2, 2/3). For this *one* system, the optimum value of f' obtained by Gainer appeared to about 0.50--similar to Olander's observation. In this work, the optimum value of f' using the original Gainer and Metzner (1965) model for *other* high-viscosity systems for which Gainer experimentally obtained molecular diffusivities was determined. Five systems were studied (hexanol-glycerol, hexanol-triethylene glycol, water-glycerol, water ethylene glycol, and methanol-glycerol). The value of f' which minimized the deviation between the experimental and the predicted D_{AB} for an individual system was determined, along with the value of f' which minimized the average absolute percentage deviation (AAPD) for *all* of the systems. The parameter, f', was varied from zero to one in increments of 0.025 in a direct search for the value of f' that minimized the deviation. The same type of search procedure is used later in this article for all models studied.

The above re-examination of Gainer's data, to test the assumption that f' equals one-half, resulted in some interesting observations not directly related to the determination of an optimum f'. The prediction D_{AB} using the Gainer and Metzner model is dependent upon good estimations of V_X, η_X, and ΔH_X^{vap}. According to Gainer and Metzner (1965), the values of the heats of vaporization were determined using the Bondi and Simkin (1957) article. Most of the values of the heats of vaporization used by Gainer and Metzner are not currently available (Gainer, 1969). Thus, one can only compare the viscous activation energies, E_{η_B}, that they obtained and tabulated (Gainer, 1964) with the E_{η_B} values that were calculated using Equation 12 and our values of ΔE_B^{vap} (calculated from ΔH_B^{vap}). In this study, either experimentally determined heats of vaporization were used or values of ΔH_B^{vap} were calculated using vapor pressure versus temperature data and the Clausius-Clapeyron equation. The values of E_{η_B} generally agree to within 10 percent. However, Gainer (1964) reports E_{η_B} of n-hexanol at 25°C to be 3910 cal / mole, compared with 1850 that was obtained in this work. Part of this large discrepancy may be due to Gainer's use of the Bondi and Simkin (1957) approach to evaluate ΔH_X^{vap} and part may be attributed to the values of the molar volume he used.

The molar volumes used in this work were those calculated from the density of the liquid components at the temperature of the diffusion experiment; whereas, the molar volumes used by Gainer <u>appear</u> to be calculated using Kopp's rule at the boiling point (although Gainer does not state this explicitly). In some cases, these values of the molar volume differ from one another by as much as 50 percent, e.g., for the solvent glycerol. Such differences can lead to final differences of 15 percent and more when estimating the molecular diffusivity.

The viscosity data used by Gainer and Metzner (1965) and those measured in this work or obtained in the literature agree within several percent except for the ethylene glycol and triethylene glycol data. The data used here for these two glycols were measured in this laboratory and the results agreed within about 5 percent with literature data; however, the viscosity data differed by about 20 percent from the values used by Gainer and Metzner. The value of the viscosity of n-hexanol used by Gainer and Metzner was not reported so no comparison was possible.

The predicted values of D_{AB} are sensitive to the physical property data one selects for use in the calculations and, as discussed above, there is some concern as to what these values are or should be. Thus in the author's re-estimation of optimum values of f, the study of the above-mentioned five systems was restricted first by using the exact physical property data of Gainer and Metzner and second by using our best estimations or measurements. The physical property data actually used in this study for each system are tabulated in Appendix A.

Using Gainer and Metzner's model and their physical property data, the value of f which minimized the AAPD for all five systems was determined as 0.550. The values of f which minimized the deviation for each system considered separately varied from 0.400 to 0.600. Thus, Gainer and Metzner's study of one system was fortunately very representative of most of their systems.

When Gainer and Metzner's model was used with what is believed to be more accurate physical property data, the value of f which minimized the AAPD for all five systems was 0.650. In this case, individual system f values ranged from 0.40 to 0.75. The effect of the use of the best estimates of physical property data on the predicted diffusivity was pronounced only with the glycerin (A) - hexanol (B) system. For this system, the experimental D_{AB} is 0.060×10^{-6} cm^2/sec, that predicted by Gainer's original model is 0.077 (10^{-6}) cm^2/sec. When an optimum f (viz., 0.650) and the best estimates or measurements of the physical property data is used, the D_{AB} predicted is 0.113×10^{-6} cm^2/sec.

In this work, the Gainer and Metzner model was also modified so that the viscous activation energy, E_{η_B}, is calculated from experimental viscosity versus temperature data using the following relation

$$E_{\eta_B} = R\frac{d(\ln \eta_B)}{d(T^{-1})} \tag{40}$$

instead of Equation 12. Using this method of determining E_{η_B} and the physical property data evaluated in this work, values of the parameter f vary from 0.725 to 0.900. The value of f for the methanol-glycerol system using this "modified" approach to the Gainer and Metzner model will be examined more carefully in the following sections.

There is also evidence in the literature to suggest that for many systems the fraction of the total energy of activation for molecular transport processes due to the hole formation step, f, is closer to 0.9 than to 0.5. Using the data of Jobling and Lawrence (1951) for the viscosity of normal liquids at constant volume, Bockris et al. (1964) concluded that the predominant term $\Delta H_{D_{AB}}$ is the enthalpy to form a hole, i.e., $\Delta H^h_{D_{AB}}$, and that $\Delta H^j_{D_{AB}}$ contributes very little (10 percent) to the total enthalpy of activation. The results of this analysis appear to be similar to an earlier analysis reported by Glasstone et al. (1941) who considered that the activation energy of viscosity for a constant volume process, E_{η_B}, equaled the activation energy of the jump step, $E^j_{\eta_B}$. Glasstone, et al. (1941) analyzed constant volume viscosity versus temperature data with a modified rate equation for viscous transport in order to compute $E^j_{\eta_B}$. They reported values of f ranging between 0.8 and 0.9 for most "normal" liquids.

Bockris et al. (1964) have indicated by using binary diffusion data how the ratio $(\Delta H^j_{D_{AB}}/\Delta H_{D_{AB}})$ should vary as a function of the isothermal compressibility coefficient of pressure. The ratio was reported to be equal to about 0.01 for normal alcohols, 0.04 for hydrocarbons, and 0.17 for glycols; that is f is approximately equal to 0.99, 0.96, and 0.83, respectively. They calculated $\Delta H^j_{D_{AB}}$ from the following expression:

$$\Delta H^j_{D_{AB}} = - R \frac{\partial \ln D_{AB}}{\partial (1/T)_V}$$

The assumption that the activation energy of diffusion (or viscous transport) at constant volume represents only the jump-step contribution has been disputed (Collins, 1957). The activation energy of diffusion measured at constant pressure is considered to be the sum of the jump and hole formation activation energies.

The calculation of f using the constant volume and constant pressure self diffusion energies $(E_{D_{BB}})_P$ and $(E_{D_{BB}})_V$ reported by McCall et al. (1959) has been re-examined in this work, and the parameter f has been calculated from the following expression:

$$f = \left[(E_{D_{BB}})_P - (E_{D_{BB}})_V\right] / (E_{D_{BB}})_P \tag{41}$$

The results are presented in Table II. With a few exceptions, notably water and methanol, f values tend to be concentrated in the range of values found by the above workers who used this general approach and also found in this work, by using the search for optimal f values in conjunction with the various diffusion models described earlier in this paper. For nonassociating solvents such as benzene and isopentane, f is generally greater than two-thirds. Olander (1963) suggests that for hydrogen bonded molecules f should be less than one-half--which is indicated in Table II.

It should be pointed out that the data in Table II for water imply that $\Delta H^j_{D_{BB}}$ is equal to the total activation enthalpy. This does not agree with the observations of Glasstone et al. (1941). They state that $\Delta H^j_{D_{BB}}$ is negative, but they do not reveal their source of data nor the magnitude of $\Delta H^j_{D_{BB}}$.

TABLE II

ACTIVATION ENERGY AT CONSTANT PRESSURE AND VOLUME, AND THE PARAMETER f FOR SELF DIFFUSION

Compound	$(E_{D_{BB}})_P$ Kcal/Mole	$(E_{D_{BB}})_V$ Kcal/Mole	f	Ref.
Benzene	2.780	0.780	0.72	a
Methanol	3.500	2.700	0.23	b
Water	4.950	4.950	0.00	c
Nitromethane	3.810	0.790	0.79	c
Acetone	2.030	1.000	0.51	c
Benzene	2.000	0.230	0.88	c
Cyclohexane	4.560	2.380	0.48	c
i-Pentane	1.730	0.190	0.89	c
Carbon Tetrachloride	3.300	1.070	0.68	d

a. Hiraoka _et_ _al_. (1958a)

b. Hiraoka _et_ _al_. (1958b)

c. McCall _et_ _al_. (1959)

d. Watts _et_ _al_. (1955)

The above discussion suggests that the value of f equal to one-half that was used by Olander (1963) and Gainer and Metzner (1965) should probably be somewhat larger--perhaps about 0.8. It is also recognized, however, that the value of f varies, and in cases widely, from system to system. The model developed in this work (D_M), the original Gainer and Metzner model (D_{GM}), the modified Gainer and Metzner model (D'_{GM}) and the Olander model (D_O) are dependent upon the value of f used. In the following sections, the best value of f to use for a given diffusivity prediction technique (D_{GM}, D'_{GM}, D_O, D_M) will be determined by the direct search optimization technique outlined above which minimizes the AAPD for all solute-solvent pairs within a given type of system (low viscosity, nonassociating; low viscosity, associating; high viscosity, associating).

The parameter f will be considered to be constant for its respective model within each of the three major types of systems, i.e., the hole formation step is assumed to require the same fraction of total activation energy for each binary solution within a major system category. In some special cases, a major type of system will also be broken into subsystems for which a single value of f will be used. (Such a generalization is an oversimplification in reality; and the best values of f for individual binary systems are expected to vary from the best f value for a given category of systems.)

In the following discussion, experimental binary diffusivities will be compared with six different diffusion coefficient prediction techniques: Wilke-Chang method (D_{WC}), original Olander model (D_O), original Gainer and Metzner model (D_{GM}), with f = 0.5, the Gainer and Metzner model with an optimum f and experimental values of E_{η_B}, and the model developed in this work (D_M) with an optimum value of f.

C. Predictions for nonassociating systems (low viscosity).

A comparison of the experimental values for the binary molecular diffusion coefficients of the 28 different solute-solvent systems that exhibit negligible hydrogen bonding between the binary pairs (Table III) and the predicted diffusivities of the various models will be made in this section.

The author's modification of the Gainer and Metzner model (optimum f = 0.850 and experimental E_{η_B}) predicts diffusion coefficients with an average absolute percent deviation (AAPD) of 16.9 percent. This may be compared with AAPD values of 17.3, 18.9, 21.0, 21.9 and 35.8 percent that result, respectively, from the predictions of the Olander equation (f = 0.5), the model proposed in this work (f = 0.675), the original Gainer and Metzner model (with an optimum f = 0.90), the Wilke-Chang equation, and the original Gainer and Metzner model (f = 0.5). The modified Gainer and Metzner model is clearly superior to the original Gainer and Metzner model. Likewise, the original Gainer and Metzner model is improved considerably by the optimization of f.

For those models for which AAPD was optimized, the best value of f was in the range of about 0.70 to 0.90--which appears to be in agreement with predictions based upon viscosity data discussed earlier. This range of f contrasts with the value of f equal to about one half that was found by Olander (1963) and used by Gainer and Metzner (1965).

TABLE III

EXPERIMENTAL AND PREDICTED DIFFUSIVITIES $(x10^5 Cm^2/SEC)$ FOR LOW VISCOSITY SYSTEMS

Solvent	Solute	Temp °C	η cp	D_{EXP}	(REF)	D_{WC}	$\Delta(WC)$ %	D_0	$\Delta(D_0)$ %	D_{GM}	$\Delta(GM)$ %	D_{GM}	$\Delta(GM)$ %	D'_{GM}	$\Delta'(GM)$ %	D_M	$\Delta(M)$ %
Benzene	Acetic acid	15	0.696	1.92	a	2.14	11.5	1.84	4.2	2.15	12.0	1.87	2.6	1.81	5.7	1.75	8.9
"	Carbon Tetrachloride	15	0.696	1.60	a	1.68	5.0	1.72	7.5	2.03	26.9	1.90	18.8	1.79	11.9	1.47	8.1
"	Chloroform	15	0.696	2.39	a	1.89	20.9	2.06	13.7	1.90	20.5	1.82	23.8	1.97	17.6	1.87	21.8
"	Hexane	15	0.696	2.15	a	1.39	35.3	2.11	1.9	2.89	34.4	2.15	0.0	1.86	13.5	2.13	0.9
"	Methanol	15	0.696	2.50	a	3.10	24.0	2.45	2.0	2.02	19.2	1.45	42.0	1.57	37.2	2.54	1.6
"	Ethanol	15	0.696	2.25	a	2.34	4.0	1.82	19.1	1.30	42.2	1.30	42.2	1.38	38.7	1.72	23.6
"	Methyl Ethyl Ketone	30	0.569	2.09	b	2.25	7.6	2.77	32.6	3.01	44.0	2.43	16.3	2.42	15.8	2.55	22.0
"	Cyclohexane	25	0.610	2.09	c	1.82	12.9	1.98	5.3	2.15	2.9	2.16	3.4	1.94	7.2	1.69	19.1
"	Acetone	25	0.610	4.12	c	2.42	41.3	2.86	30.6	3.96	3.9	2.44	40.8	2.87	30.3	2.69	34.7
Toluene	Ethanol	15	0.623	3.00	a	2.84	5.3	1.95	35.0	1.37	54.3	1.37	54.3	1.42	52.7	1.95	35.0
"	Chlorobenzene	15	0.623	1.90	a	1.91	0.5	1.91	0.5	1.81	4.7	1.88	1.1	1.91	0.5	1.67	12.1
"	Methyl Ethyl Ketone	30	0.523	2.21	b	2.66	20.4	2.91	31.7	3.02	36.6	2.48	12.2	2.46	11.3	2.69	21.7
"	n-Propanol	25	0.553	3.56	d	2.73	23.3	1.90	46.6	1.32	62.9	1.86	47.8	2.09	41.3	1.74	51.1
Hexane	Benzene	15	0.337	3.70	a	3.80	2.7	3.23	12.7	2.33	37.0	2.98	19.5	3.28	11.4	3.01	18.6
"	Methyl Ethyl Ketone	30	0.278	3.74	b	4.84	29.4	4.57	22.2	4.04	8.0	4.13	10.4	4.53	21.1	4.27	14.2
Methanol	Benzene	15	0.623	2.40	a	1.73	27.9	2.27	5.4	5.88	145.0	3.00	25.0	3.71	54.6	1.74	27.5
Chloroform	Benzene	15	0.596	2.51	a	2.53	0.8	2.19	12.6	2.01	19.9	2.09	16.7	2.03	19.1	1.92	23.5
Carbon Tetrachloride	Benzene	15	1.038	1.08	a	1.65	52.8	1.43	32.4	1.04	3.7	1.12	5.7	1.18	9.2	1.31	21.3
"	Cyclohexane	25	0.888	1.28	e	1.76	37.5	1.48	15.7	1.26	1.6	1.36	6.2	1.28	0.0	1.31	2.3
Chlorobenzene	Toluene	15	0.844	1.48	a	1.53	3.4	1.63	10.1	1.45	2.0	1.39	6.1	1.42	4.1	1.48	0.0
"	Bromobenzene	15	0.844	1.40	a	1.52	8.6	1.39	0.7	1.31	6.4	1.37	1.4	1.38	1.4	1.20	14.3
Ethanol	Benzene	15	1.327	1.67	a	0.84	49.7	1.21	27.6	3.19	91.0	1.31	21.6	1.60	4.2	0.93	44.3
"	Toluene	15	1.327	1.60	a	0.74	53.8	1.19	25.6	3.47	116.9	1.37	14.4	1.65	3.1	1.03	35.6
Bromobenzene	Chlorobenzene	15	1.196	1.10	a	1.30	18.2	1.17	6.4	1.05	4.5	1.00	9.1	1.03	6.4	1.07	2.7
Acetone	Benzene	25	0.308	2.75	c	3.50	28.7	3.91	42.2	7.09	157.8	4.85	76.4	4.93	79.3	3.22	17.1
n-Propanol	Toluene	25	1.950	1.35	d	0.50	63.0	0.96	28.9	1.22	9.6	0.78	42.2	1.32	2.2	1.04	23.0
Cyclohexane	Benzene	25	0.883	1.88	c	1.48	21.3	1.70	9.6	1.46	22.3	1.43	23.6	1.54	18.1	1.58	16.0
"	Carbon Tetrachloride	25	0.883	1.48	e	1.42	4.1	1.51	2.2	1.68	13.5	1.55	4.7	1.56	5.4	1.36	8.1
Average absolute percent deviation							21.9		17.3		35.8		21.0		18.8		18.9
Value of the parameter f used									0.50		0.50		0.900		0.850		0.675

a. Johnson and Babb (1956)
b. Amourdam and Laddha (1967)
c. McCall and Douglas (1967)
d. Shroff and Shemilt (1966)
e. Kulkarni *et al.* (1965)

Figure 3 indicates the dependence of the AAPD for each prediction model of the parameter f. In the case of the Olander model, the AAPD varies only slightly as the parameter f varies from zero to one. All other models, however, show a stronger dependence on f for these nonassociating, low viscosity systems. This shows, of course, that there is greater scatter in the optimum value of f for the individual solute-solvent systems for the Olander model. This appears to be so because the difference between ΔF_{η_B} and $\Delta F_{D_{AB}}$ is small, and thus, the exponential term is probably close to unity. This implies that a small error in the evaluation of that difference could yield a large error in the best value of the parameter f one obtains.

The values of f discussed above are for an assumed constant value for the entire set of nonassociating systems. The values of the optimum f for individual solute-solvent systems (not indicated in Table III) are consistently in the range of 0.6 to 1.0. For a few systems, they are, however, found to be nearer zero.

On the basis of this comparison, it would appear that the modified Gainer and Metzner equation best predicts diffusion coefficients for low viscosity, nonassociating systems. Except for the original Gainer and Metzner model, all prediction expressions are of comparable accuracy. In view of this, the relatively easy-to-use Wilke-Chang (1955) equation is recommended for these binary solutions.

D. Predictions for associating systems (low viscosity).

A comparison of the experimental values of the binary molecular

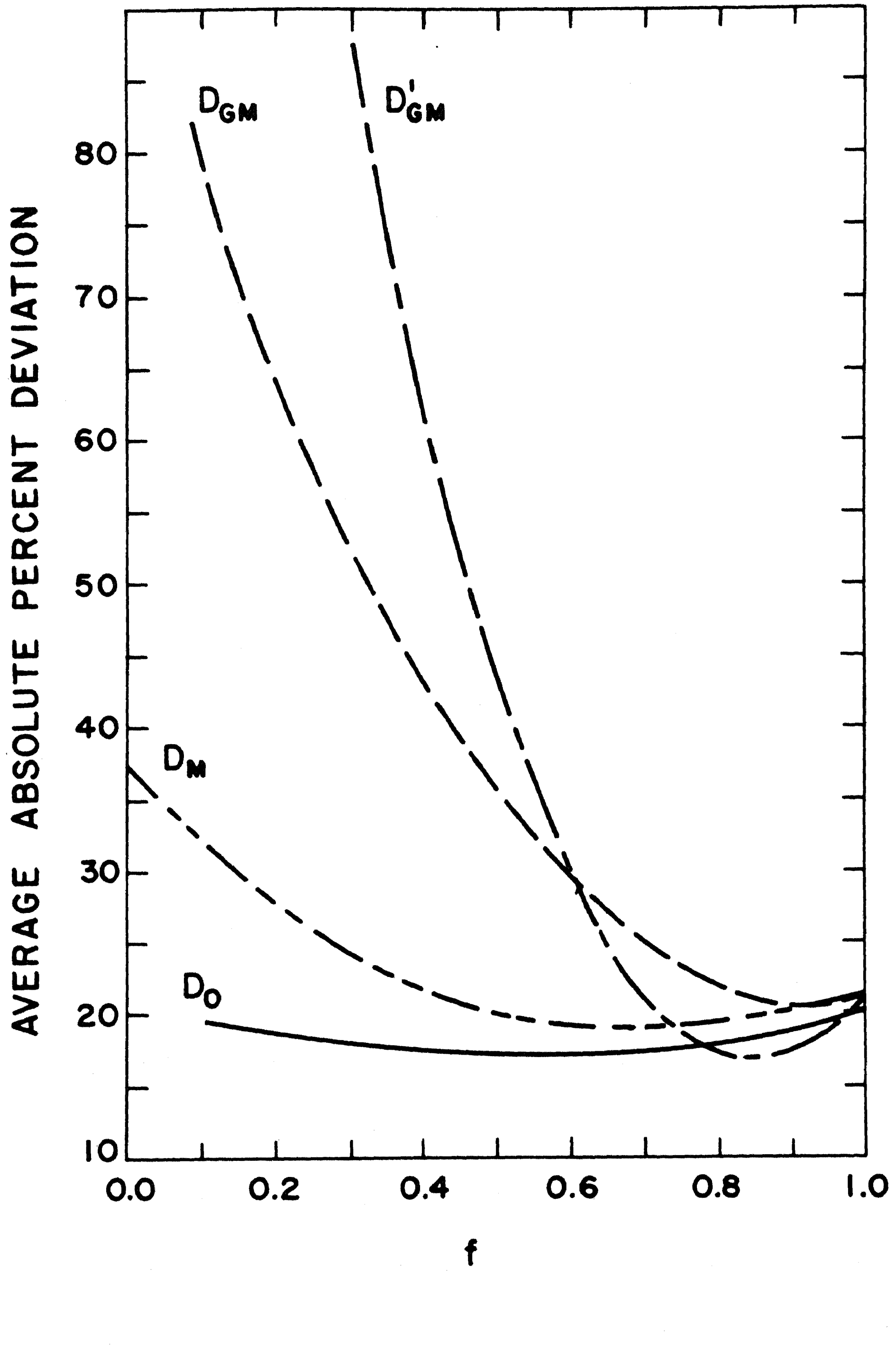

Figure 3. The average absolute percent deviation versus the fraction f for 28 low viscosity nonassociating systems.

diffusion coefficients for 19 different solute-solvent associating systems with with the predicted diffusivities for various models will be discussed in this section. These comparisons are shown in Tables IV, V and VI and in Figures 4, 5 and 6.

The Wilke-Chang equation clearly predicts the diffusivities for this class of systems far better than any of the other equations when all of the data are considered together (as in Table IV). Since the AAPD's are all greater than 40 percent for all the other equations and less than 20 percent for Wilke-Chang equation, this relatively easy-to-use equation is again recommended for this set of binary solutions.

A closer look at Table IV reveals that for all of the equations except the Wilke-Chang equation, the diffusivities for the systems where water is the solvent (aqueous systems) are predicted much less accurately than for systems where water is not the solvent. The reason for this condition is that the parameter f is quite different for these two subdivisions within this category of systems. On this basis, these subdivisions were studied separately, and the results are given in Tables V and VI and in Figures 5 and 6.

For the aqueous systems shown in Table V, the Wilke-Chang equation is still far superior to any of the other equations and is still recommended for calculating diffusivities for this subdivision. This result was not unexpected since a great deal of the data upon which the Wilke-Chang equation was based was of this particular type.

The optimum value of the parameter f for these aqueous solvent systems varies quite widely. Olander's model and the Gainer and Metzner modified

TABLE IV

EXPERIMENTAL AND PREDICTED DIFFUSIVITIES

($x10^5 cm^2/SEC$) FOR LOW VISCOSITY

ASSOCIATING SYSTEMS

Solvent	Solute	Temp °C	η cp	D_{EXP}*	D_{WC}	$\Delta(WC)$ %	D_0	$\Delta(D_0)$ %	D_{GM}	$\Delta(GM)$ %	D_{GM}	$\Delta(GM)$ %	D'_{GM}	$\Delta'(GM)$ %	D_M	$\Delta(M)$ %
Water	i-Butanol	15	1.104	0.77	0.82	6.5	1.07	39.0	2.30	198.7	1.93	150.6	1.86	141.6	1.84	139.0
"	n-Butanol	15	1.104	0.77	0.82	6.5	1.14	48.1	2.35	205.2	1.90	146.8	1.88	144.2	1.84	139.0
"	Ethanol	15	1.104	1.00	1.14	14.0	1.51	51.0	0.92	8.0	1.40	40.0	1.39	38.9	1.84	84.0
"	Methanol	15	1.104	1.26	1.51	19.8	1.96	55.6	1.15	9.6	1.43	13.5	1.39	10.6	1.84	46.0
"	i-Propanol	15	1.104	0.87	0.94	8.0	1.22	40.2	1.90	118.4	1.81	108.0	1.86	113.8	1.84	111.5
"	n-Propanol	15	1.104	0.87	0.94	8.0	1.26	44.8	1.88	116.1	1.78	104.6	1.87	114.9	1.84	111.5
"	Acetone	15	1.104	1.22	1.00	18.0	1.97	61.5	2.81	130.3	1.93	58.2	1.93	58.2	1.84	50.8
i-Butanol	Water	15	4.703	0.30	0.29	3.4	0.68	126.7	0.74	146.7	0.26	13.3	0.31	3.3	0.25	16.7
Ethanol	Water	15	1.327	1.02	0.97	4.9	1.65	61.8	2.40	135.3	1.07	4.9	1.14	11.8	0.76	25.5
Methanol	Water	15	0.623	1.75	1.99	13.7	2.98	70.3	3.83	118.9	2.57	46.8	2.77	58.3	1.87	6.9
i-Propanol	Water	15	2.859	0.38	0.43	13.2	0.97	155.3	1.07	181.6	0.45	18.4	0.54	42.1	0.44	15.8
n-Propanol	Water	15	2.522	0.61	0.49	19.7	1.06	73.8	1.21	98.4	0.52	14.8	0.59	3.3	0.50	18.0
Methanol	Acetic Acid	15	0.623	1.54	2.12	37.7	2.17	40.9	4.70	205.2	2.62	70.1	2.71	76.0	1.87	21.4
Chloroform	Ethanol	15	0.569	2.20	3.38	53.6	2.07	5.9	1.47	33.2	1.57	28.6	1.62	26.4	2.08	5.5
"	Ether	15	0.569	2.07	2.36	14.0	2.75	32.9	3.21	55.1	2.18	5.3	2.23	7.7	2.08	0.5
"	Acetone	15	0.569	2.35	2.95	25.5	2.77	17.9	4.01	70.6	2.18	7.2	2.25	4.3	2.08	11.5
Ether	Chloroform	15	0.247	4.40	5.17	17.5	4.45	1.1	4.06	7.7	4.82	9.5	4.78	8.6	4.61	4.8
Ethanol	Chloroform	15	1.327	1.63	0.91	44.2	1.30	20.2	3.36	106.1	1.08	33.7	1.15	29.7	0.76	53.4
Acetone	Chloroform	15	0.355	3.92	3.36	14.3	3.63	7.4	6.46	64.8	3.76	4.1	4.07	3.8	3.79	3.3
Average absolute percent deviation						18.0		50.2		105.8		46.2		49.8		45.5
Value of the parameter f used.								0.500		0.500		1.00		0.975		1.00

*Johnson and Babb (1956)

TABLE V

EXPERIMENTAL AND PREDICTED DIFFUSIVITIES ($\times 10^5$ Cm^2/SEC) FOR LOW VISCOSITY ASSOCIATING AQUEOUS SYSTEMS

Solvent	Solute	Temp °C	η cp	D_{EXP}	(D_{WC})	$\Delta(WC)$ %	D_0	$\Delta(D_0)$ %	D_{GM}	$\Delta(GM)$ %	D_{GM}	$\Delta(GM)$ %	D'_{GM}	$\Delta'(GM)$ %	D_M	$\Delta(M)$ %
Water	i-Butanol	15	1.104	0.77	0.82	6.5	1.07	39.0	2.30	205.2	0.99	28.6	0.78	1.4	0.76	1.3
"	n-Butanol	15	1.104	0.77	0.82	6.5	1.14	48.1	2.35	198.7	1.00	29.9	0.99	28.6	0.42	45.5
"	Ethanol	15	1.104	1.00	1.14	14.0	1.51	51.0	0.92	8.0	0.64	36.0	0.49	51.0	1.16	16.0
"	Methanol	15	1.104	1.26	1.51	19.8	1.96	55.6	1.15	9.6	0.68	46.0	0.54	57.2	0.80	36.5
"	i-Propanol	15	1.104	0.87	0.94	8.0	1.22	40.2	1.90	118.4	0.91	4.6	0.69	20.7	1.18	35.6
"	n-Propanol	15	1.104	0.87	0.94	8.0	1.26	44.8	1.89	116.1	0.90	3.4	0.88	1.1	1.07	23.0
"	Acetone	15	1.104	1.22	1.00	18.0	1.97	61.5	2.81	130.3	1.04	14.8	1.75	43.4	0.16	86.7
Average absolute percentage deviation						11.5		48.6		112.3		21.9		29.1		35.0
The parameter f used								0.50		0.50		1.10		0.375		2.20

TABLE VI

EXPERIMENTAL AND PREDICTED DIFFUSIVITIES ($\times 10^5$ Cm^2/SEC) FOR LOW VISCOSITY ASSOCIATING NONAQUEOUS SYSTEMS

Solvent	Solute	Temp °C	η cp	D_{EXP}	(D_{WC})	$\Delta(WC)$ %	D_0	$\Delta(D_0)$ %	D_{GM}	$\Delta(GM)$ %	D_{GM}	$\Delta(GM)$ %	D'_{GM}	$\Delta'(GM)$ %	D_M	$\Delta(M)$ %
i-Butanol	Water	15	4.703	0.30	0.29	13.4	0.68	126.7	0.74	146.7	0.26	13.3	0.26	13.3	0.30	0.0
Ethanol	Water	15	1.327	1.20	0.97	4.9	1.65	61.8	2.40	135.3	1.07	4.9	1.06	11.7	0.84	30.0
Methanol	Water	15	0.623	1.75	1.99	13.7	2.98	70.3	3.83	118.9	2.57	46.8	2.62	49.7	1.94	10.9
i-Propanol	Water	15	2.859	0.38	0.43	13.2	0.97	155.3	1.07	181.6	0.45	18.4	0.46	21.1	0.51	34.2
n-Propanol	Water	15	2.522	0.61	0.49	19.7	1.06	73.8	1.21	98.4	0.52	14.8	0.53	13.1	0.58	4.9
Methanol	Acetic Acid	15	0.623	1.54	2.12	37.7	2.17	40.9	4.70	205.2	2.62	70.1	2.62	70.1	1.78	15.6
Chloroform	Ethanol	15	0.569	2.20	3.38	53.6	2.07	5.9	1.47	33.2	1.57	28.6	1.64	25.5	2.05	6.8
"	Ether	15	0.569	2.07	2.36	14.0	2.75	32.9	3.21	55.1	2.18	5.3	2.18	5.3	2.17	4.8
"	Acetone	15	0.569	2.35	2.95	25.5	2.77	17.0	4.01	70.6	2.18	7.2	2.18	7.2	2.15	8.5
Ether	Chloroform	15	0.247	4.40	5.17	17.5	4.45	1.1	4.06	7.7	4.82	9.5	4.83	9.8	4.50	2.3
Ethanol	Chloroform	15	1.327	1.63	0.91	44.2	1.30	20.2	3.36	106.1	1.08	33.7	1.06	35.0	0.79	51.5
Acetone	Chloroform	15	0.355	3.92	3.36	14.3	3.63	7.4	6.46	64.8	3.76	4.1	3.97	1.3	3.67	6.4
Average absolute percent deviation						21.8		51.2		102.0		21.4		22.0		14.7
The parameter f used								0.50		0.50		1.00		1.00		0.95

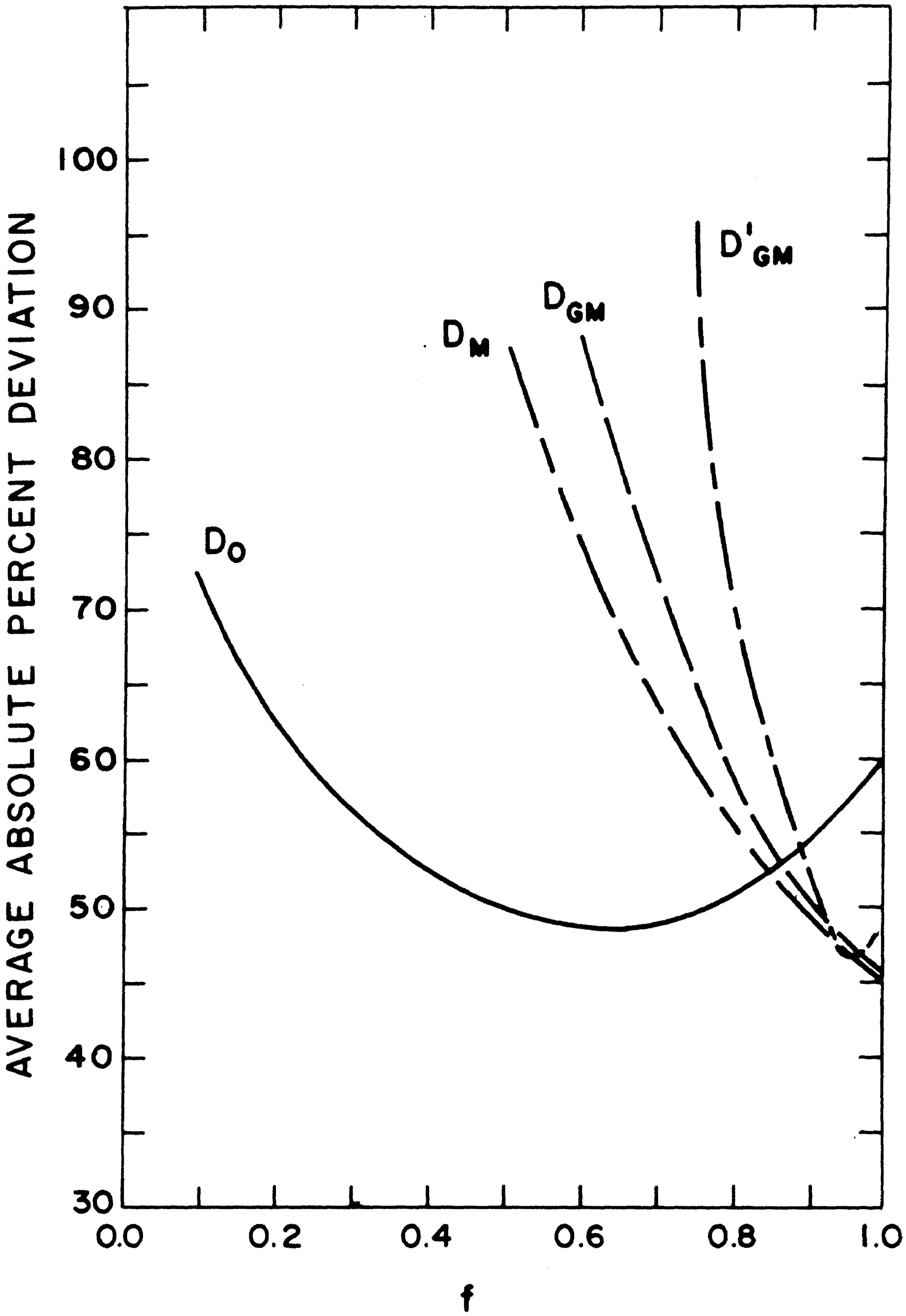

Figure 4. The average absolute percent deviation versus the fraction f for 19 low viscosity associating systems.

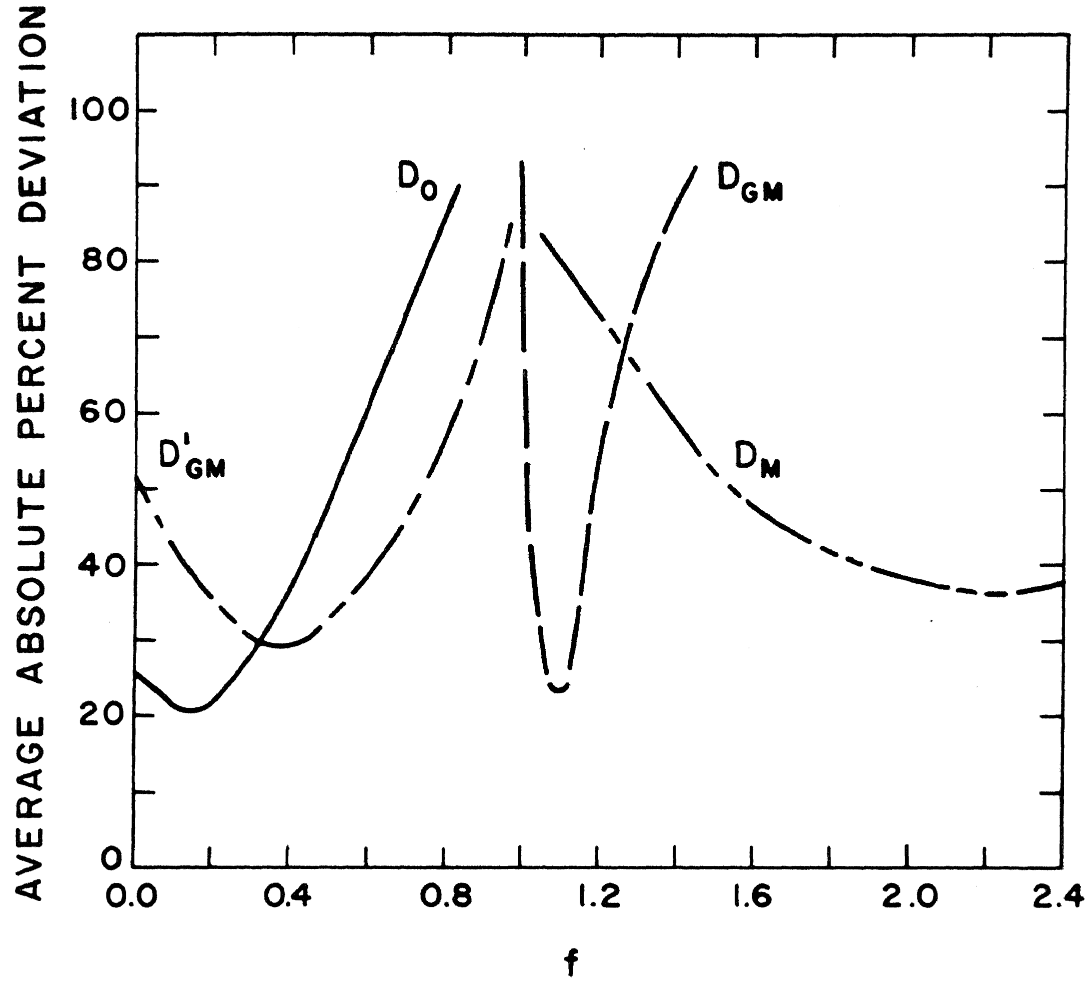

Figure 5. The average absolute percent deviation versus the fraction f for 7 low viscosity associating aqueous systems.

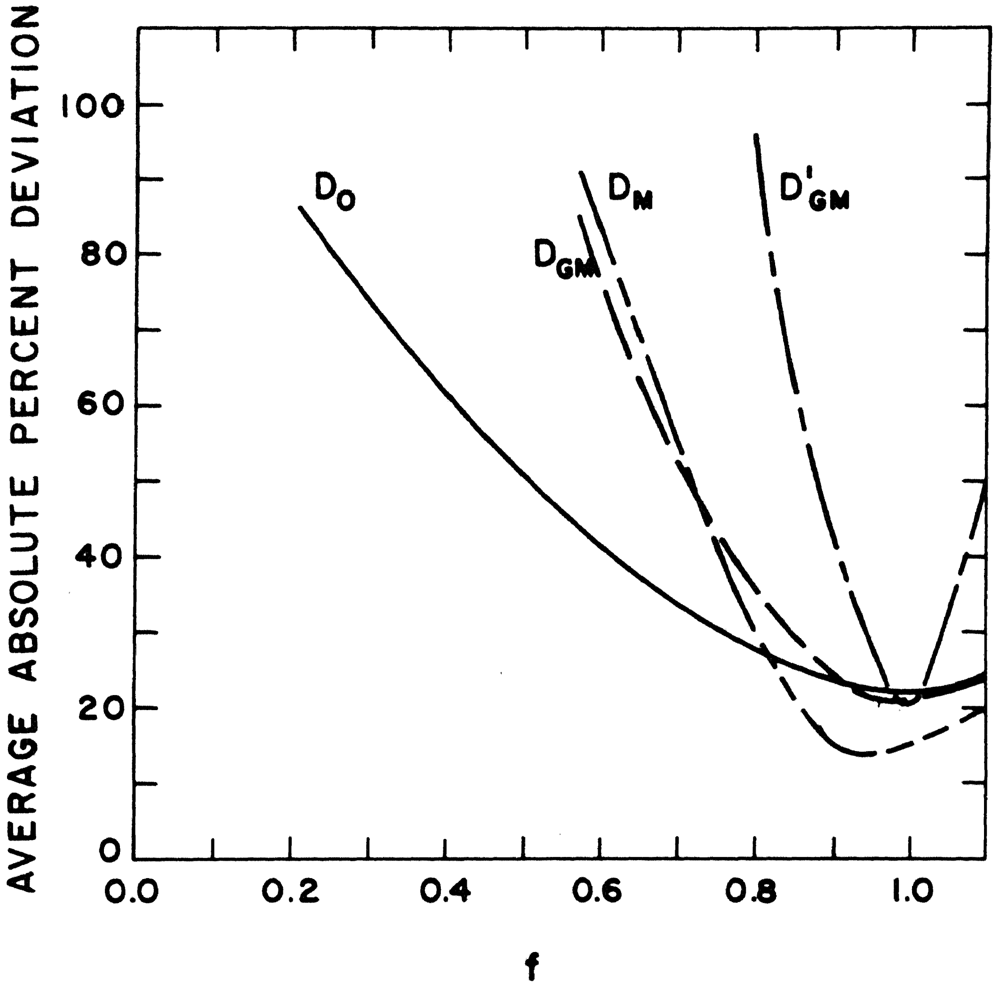

Figure 6. The average absolute percent deviation versus the fraction f for 12 low viscosity associating nonaqueous systems.

model both give values of f that are less than 0.5. This fact agrees with Olander's statement that $\Delta F^{j}_{D_{AB}}$ should be larger than normal for hydrogen-bonded substances. On the other hand, Gainer and Metzner's original model and the model developed in this work give values of f that are greater than 1.0. Eyring, in Glasstone et al. (1941), indicates that the activation energy for the jump step is negative for water. This agrees with an f value of more than 1.0. Thus the proper value for the parameter f is still open to question when water is the solvent.

For those systems where water is not the solvent shown in Table VI and Figure 6, but where association between binary pairs exists, the model developed in this work predicts the diffusivities significantly better than any of the other models tested. The AAPD for the model developed in this work is 14.7 as compared to 21.8 for the Wilke-Chang equation, 22.0 for the modified Gainer and Metzner model, 21.4 and 102.0 for the original Gainer and Metzner model with an optimum f and f equal to 0.5, respectively, and 51.2 for Olander's model.

For those models for which the AAPD is optimized, the best value of f for the nonaqueous solvent systems ranges from 0.950 to 1.0. This range agrees very well with the value of f (0.99) estimated by Bockris et al. (1964) for normal alcohols.

This comparison shows that the model developed in this work gives the best prediction for the diffusivities of nonaqueous solvent, low viscosity, associating systems. When the proper optimum value of f is used, all of the models give average deviations of less than 25 percent. Because the model developed in this work gives significantly lower deviations, the model is recommended for calculating diffusivities for this subclass of systems. When the necessary data are not available, the Wilke-Chang equation serves as an excellent substitute.

E. Predictions for high viscosity systems.

The results of a comparison of the experimental values of the binary molecular diffusion coefficients for 19 high viscosity, solute-solvent systems with the predicted diffusivities of the various models are summarized in Table VII and in Figure 7 when all the data are analyzed together.

The diffusivities for the first five systems shown in Table VII (i.e., those where ethylene glycol and cyclohexanol are the solutes) were measured in this work. The diffusivities of these systems at other temperatures were also measured in this work, but were not included in Table VII. They were not used here so that the results would not be unduly weighted by these few moderately high viscosity glycol systems. The effect of temperature on the diffusivities for these systems will be investigated in a separate study. The diffusivities for the remainder of the systems shown in Table VII are from the work of Gainer and Metzner (1965).

None of the equations tested adequately predict the entire set of data. The best model is the modified Gainer and Metzner model (with an optimum f of 0.850), which has an average deviation of 39.9 percent. Table VI reveals, however, that some of the equations tested do adequately predict some of the

TABLE VII

EXPERIMENTAL AND PREDICTED DIFFUSIVITIES ($\times 10^6 cm^2/SEC$) FOR HIGH VISCOSITY SYSTEMS

Solvent	Solute	Temp °C	η poise	D_{EXP}	(D_{WC})	$\Delta(WC)$ %	D_0	$\Delta(D_0)$ %	D_{GM}	$\Delta(GM)$ %	D_{GM}	$\Delta(GM)$ %	D'_{GM}	$\Delta(GM)$ %	D_M	$\Delta(M)$ %
Propylene Glycol	Ethylene Glycol	30	0.326	0.53	0.483	8.9	0.621	17.2	0.545	2.8	0.513	3.2	0.639	20.6	0.505	4.7
Diethylene Glycol	Ethylene Glycol	30	0.216	0.65	0.861	32.5	0.826	27.1	0.795	22.3	0.739	13.7	0.717	10.3	0.710	9.2
Ethylene Glycol	Cyclohexanol	30	0.135	0.64	0.681	6.4	0.803	25.5	1.27	98.4	1.23	92.2	0.859	34.2	0.882	37.8
Propylene Glycol	Cyclohexanol	30	0.326	0.31	0.313	1.0	0.398	28.4	0.476	53.5	0.464	49.7	0.388	25.2	0.386	24.5
Diethylene Glycol	Cyclohexanol	30	0.216	0.50	0.559	11.8	0.531	6.2	0.548	9.6	0.560	11.9	0.403	19.4	0.498	0.4
Glycerin	Hexanol	25	9.5	0.060	0.011	81.7	0.138	130.0	0.273	355.0	0.131	118.3	0.122	103.3	0.124	106.7
Triethylene Glycol	Hexanol	0	1.60	0.51	0.077	84.9	0.324	36.5	0.360	29.4	0.234	54.1	0.207	47.1	0.0175	65.7
Glycerin	Water	20	14.8	0.133	0.0105	92.1	0.162	21.8	0.190	42.9	0.089	33.1	0.099	25.6	0.041	69.2
Glycerin	Methanol	21	13.6	0.064	0.0179	72.0	0.540	140.6	0.052	18.8	0.032	50.0	0.065	1.6	0.044	31.3
Ethylene Glycol	Water	20	0.206	1.80	0.618	65.7	2.64	46.7	2.65	47.2	1.91	6.1	1.32	26.7	1.46	18.9
Glycerin	Hexanol	0	121.0	0.0137	0.0008	94.2	0.0182	32.5	0.0386	181.8	0.0157	14.6	0.0149	8.8	0.0157	14.6
Ethylene Glycol	n-Amyl Alcohol	30	0.135	2.08	0.716	65.6	1.51	27.4	2.34	12.5	1.95	6.2	1.48	28.8	1.66	20.2
Ethylene Glycol	n-Hexane	30	0.135	8.20	0.670	91.8	2.85	65.2	12.03	46.7	6.66	18.8	3.60	56.1	4.01	51.1
"Chrysene"	n-Hexanol	23.4	24.5	0.193	0.00692	96.4	0.0302	84.4	0.0504	73.9	0.0265	86.3	0.0478	75.2	0.0122	93.7
"Chrysene"	n-Amyl Alcohol	23.4	24.5	0.160	0.00763	95.2	0.0350	78.1	0.0621	61.2	0.0310	80.6	0.0536	66.5	0.0131	91.8
"Chrysene"	n-Decane	22.0	24.5	0.077	0.00530	93.1	0.0467	39.4	0.0392	49.1	0.0219	71.6	0.0537	30.2	0.0177	77.0
"Hendecane"	n-Hexanol	22.0	40.0	0.103	0.00557	94.6	0.0211	79.5	0.0584	43.3	0.0247	76.0	0.0492	52.2	0.0078	92.4
"Hendecane"	n-Octanol	22.0	40.0	0.0635	0.00476	92.5	0.0163	74.3	0.0368	42.0	0.0175	72.4	0.0353	44.3	0.0067	89.5
"Hendecane	n-Decane	22.0	40.0	0.150	0.00428	97.1	0.0339	77.4	0.0354	76.4	0.0170	88.7	0.0456	69.6	0.0090	94.0
Average absolute percent deviation						66.5		54.6		66.7		49.9		39.9		52.3
The parameter f used								0.50		0.50		0.625		0.850		0.825

"Chrysene" is 1, 2, 3, 4, 5, 6, 7, 8, 13, 14, 15, 16 dodecahydrochrysene

"Hendecane" is 1, 1-di-(alpha-decalyl)-hendecane

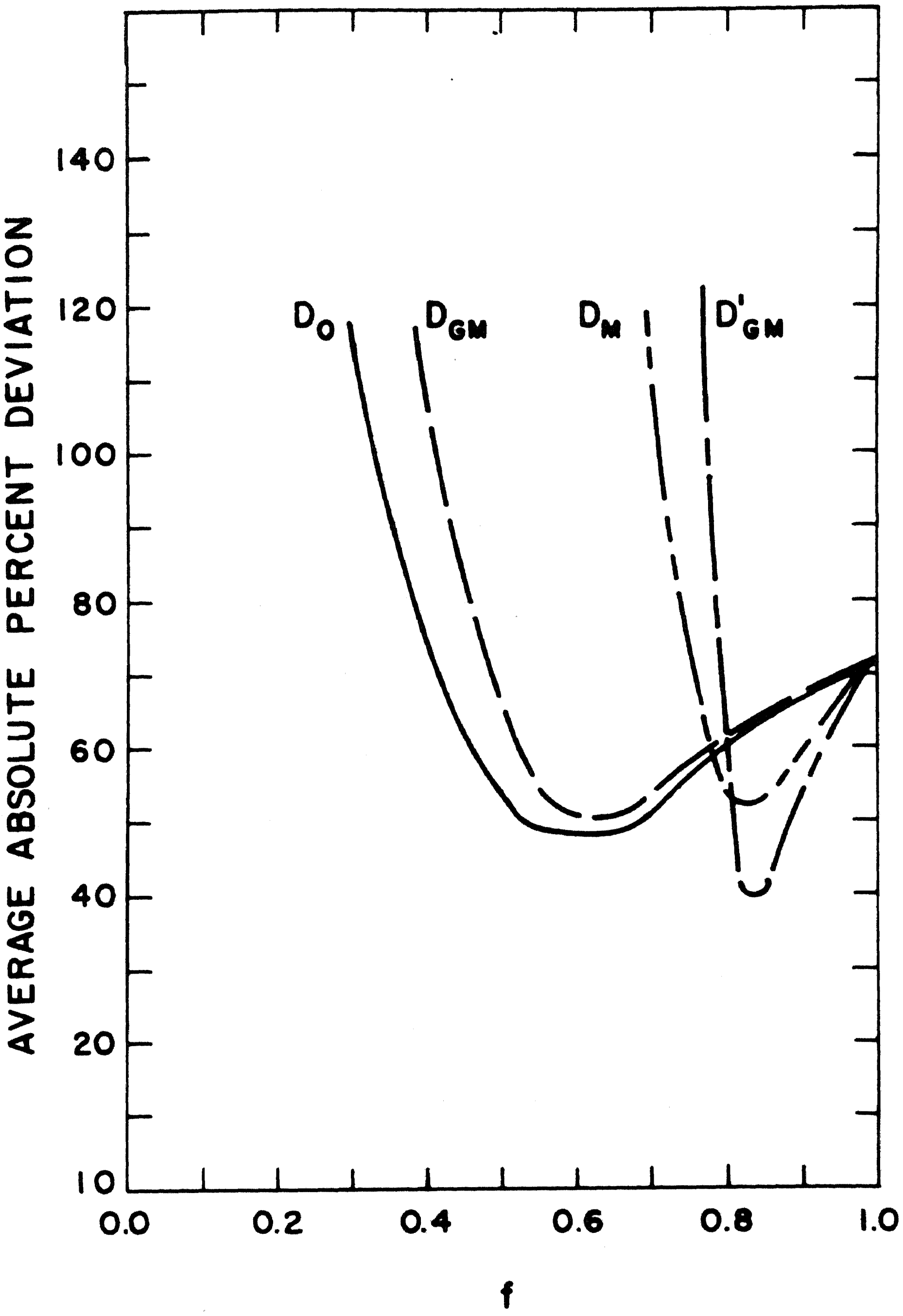

Figure 7. The average absolute percent deviation versus the fraction f for 19 high viscosity systems.

individual systems and that logical subgroups of systems do exist. The most logical subgroups of systems seem to be the extremely high viscosity systems and the more moderate high viscosity systems. Because of this, the systems whose solvents are labeled "hendecane" and "chrysene" were studied as one subgroup and the remainder as another subgroup.

The first subgroup, shown in Table VIII, contains (see Figure 8) the more moderate high viscosity systems. These systems have at least one material that exhibits hydrogen bonding, and for most of the binary pairs both the solute and solvent exhibit hydrogen bonding. The results show that the original Gainer and Metzner model, the modified Gainer and Metzner model, and the model developed by the author all predict the data to about the same degree of accuracy; namely the average percent deviation is around 35. Olander's model gives a slightly higher deviation when the parameter f is taken to be one half, but when the optimized value of 0.650 is used, the average deviation is 31.0 percent.

The optimum f values range from 0.65 to 0.85. This range is also in agreement with the range predicted by Eyring in Glasstone et al. (1941). Bockris et al. (1964) shows, as discussed earlier, that for glycols the value of f should be around 0.83. The modified Gainer and Metzner model and the model developed in this work have optimum values of f of 0.850 and 0.825, respectively. Thus, these two models substantiate Bockris' results almost exactly.

The second subgroup, shown in Table IX and Figure 9, consists of

TABLE VIII

EXPERIMENTAL AND PREDICTED DIFFUSIVITIES ($\times 10^6$ cm²/SEC) FOR MODERATELY HIGH VISCOSITY SYSTEMS

Solvent	Solute	Temp °C	η poise	D_{EXP}	D_{WC}	$\Delta(WC)$ %	D_0	$\Delta(D_0)$ %	D_{GM}	$\Delta(GM)$ %	D_{GM}	$\Delta(GM)$ %	D'_{GM}	$\Delta'(GM)$ %	D_M	$\Delta(M)$ %
Propylene Glycol	Ethylene Glycol	30	0.326	0.53	0.483	8.9	0.621	17.2	0.545	2.8	0.507	4.3	0.639	20.6	0.505	4.7
Diethylene Glycol	Ethylene Glycol	30	0.216	0.65	0.461	32.5	0.826	27.1	0.795	22.3	0.729	12.2	0.717	10.3	0.710	9.2
Ethylene Glycol	Cyclohexanol	30	0.135	0.64	0.681	6.4	0.803	25.5	1.21	98.4	1.23	92.2	0.859	34.2	0.882	37.8
Propylene Glycol	"	30	0.326	0.31	0.313	1.0	0.398	28.4	0.476	53.5	0.461	48.7	0.388	25.2	0.386	24.5
Diethylene Glycol	"	30	0.216	0.50	0.559	11.8	0.513	6.2	0.548	9.6	0.562	12.9	0.403	19.4	0.498	0.4
Glycerin	Hexanol	25	9.5	0.06	0.011	81.7	0.138	130.0	0.273	355.0	0.113	83.3	0.122	103.3	0.124	106.7
Triethylene Glycol	Hexanol	0	1.60	0.51	0.077	51.0	0.324	36.5	0.360	29.4	0.215	57.8	0.207	47.1	0.175	65.7
Glycerin	Water	20	14.8	0.133	0.0105	92.1	0.162	21.8	0.190	42.9	0.076	42.9	0.099	25.6	0.041	69.2
Glycerin	Methanol	21	13.6	0.064	0.0179	72.0	0.154	140.6	0.052	18.8	0.029	54.7	0.065	1.6	0.044	31.3
Ethylene Glycol	Water	20	0.206	1.80	0.618	65.7	2.64	46.7	2.65	47.2	1.78	1.1	1.32	26.7	1.46	18.9
Glycerin	Hexanol	0	121.0	.0137	.008	94.2	0.182	32.5	.0386	181.8	0.131	4.4	.0149	8.8	.0157	14.6
Ethylene Glycol	n-Amyl Alcohol	30	0.135	2.08	0.716	65.6	1.51	27.4	2.34	12.5	1.88	9.6	1.48	28.8	1.66	20.2
Ethylene Glycol	Hexane	30	0.135	8.20	0.670	91.8	2.85	65.2	12.03	46.7	5.92	27.8	3.60	56.1	4.01	51.1
Average absolute percent deviation						51.9		46.5		70.8		35.1		31.4		34.9
Value of f used								0.50		0.50		0.65		0.85		0.825

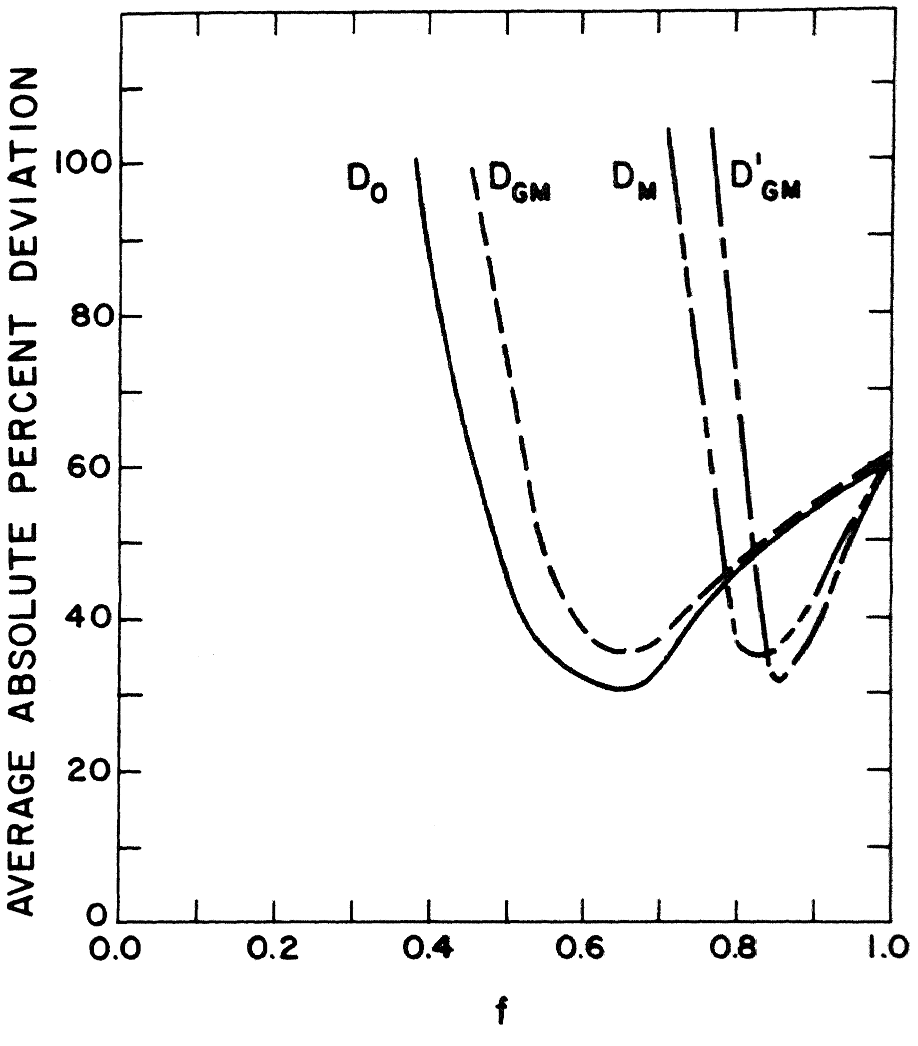

Figure 8. The average absolute percent deviation versus the fraction f for 13 moderately high viscosity systems.

TABLE IX

EXPERIMENTAL AND PREDICTED DIFFUSIVITIES ($x\ 10^6 cm^2/SEC$) FOR EXTREMELY HIGH VISCOSITY SYSTEMS

Solvent	Solute	Temp ^oC	η poise	D_{EXP}	D_{WC}	$\Delta(WC)$ %	D_0	$\Delta(D_C)$ %	D_{GM}	$\Delta(GM)$ %	D_{GM}	$\Delta(GM)$ %	D'_{GM}	$\Delta'(GM)$ %	D_M	$\Delta(M)$ %
"Chrysene"	Hexanol	23.4	24.5	0.193	0.00674	96.4	0.030	84.4	0.050	73.9	0.034	56.5	0.073	62.2	0.095	50.8
"	n-Amyl Alcohol	23.4	24.5	0.160	0.00744	95.2	0.035	78.1	0.062	61.2	0.108	32.5	0.083	48.1	0.116	27.5
"	Decane	22.0	24.5	0.077	0.00516	93.1	0.047	39.4	0.039	49.1	0.062	19.5	0.083	7.2	0.264	242.8
"Hendecane"	Hexanol	22.0	40.0	0.103	0.00557	94.6	0.021	79.5	0.058	43.3	0.116	12.6	0.085	17.5	0.098	4.9
"	Octyl Alochol	22.0	40.0	0.0635	0.00476	92.5	0.016	74.3	0.037	42.0	0.067	5.5	0.058	8.7	0.065	2.4
"	Decane	22.0	40.0	0.150	0.00428	97.1	0.034	77.4	0.035	76.4	0.064	57.3	0.078	48.0	0.143	4.7
Average absolute percent deviation						94.8		72.2		57.6		30.6		32.0		55.5
Value of the parameter f used								0.50		0.50		0.40		0.825		0.525

"Chrysene" is 1, 2, 3, 4, 5, 6, 7, 8, 13, 14, 15, 16 dodecahydrochrysene

"Hendecane" is 1, 1-di-(alpha-decalyl)-hendecane

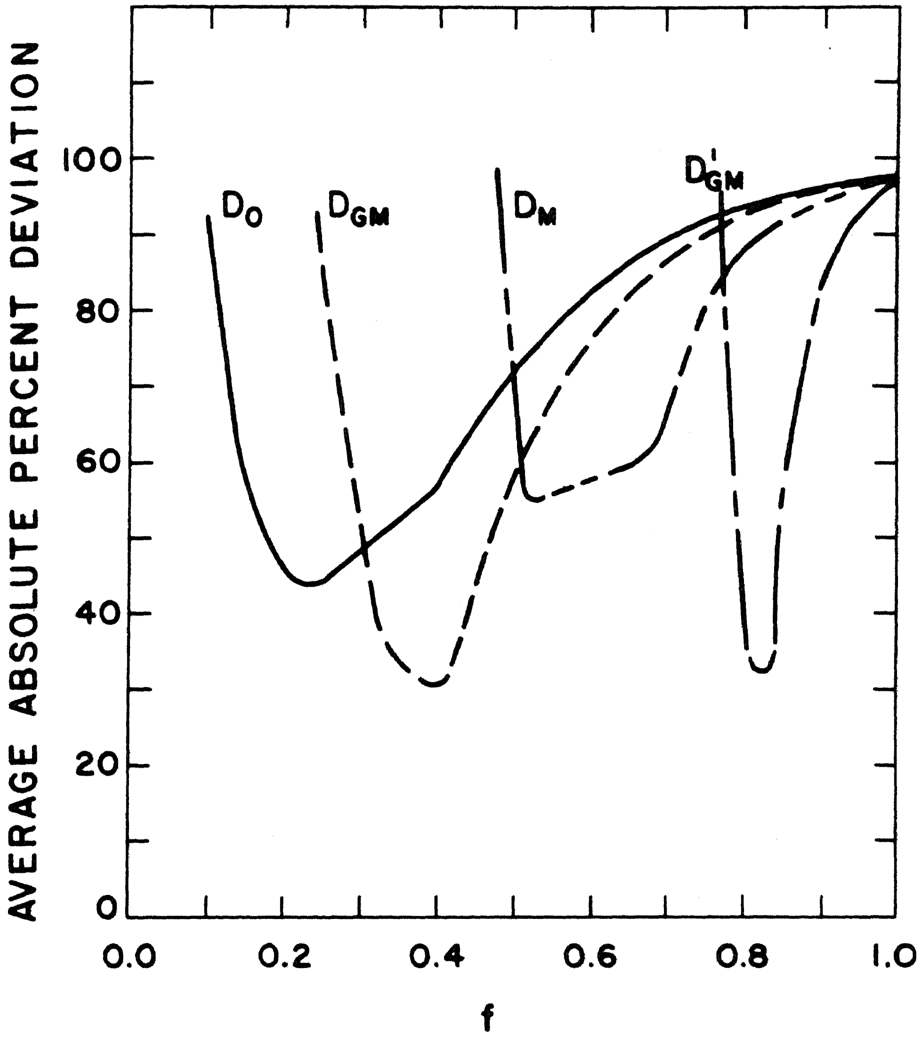

Figure 9. The average absolute percent deviation versus the fraction f for 6 extremely high viscosity systems.

systems whose solvents are "hendecane" and "chrysene". The modified and original Gainer and Metzner models, with optimized f values, give average deviations of about 30 percent. None of the other models tested adequately predicted the diffusivities for this subgroup. The optimum f values for this subgroup vary from 0.225 to 0.825. There appears to be no systematic correlation for these f values.

The average absolute percent deviations in Table VI range from 39.9 to 67.2 percent when all of the 19 high-viscosity systems are considered together. One significant fact that can be obtained from this table is that the diffusion coefficients measured in this laboratory (i.e., the systems whose solutes are ethylene glycol and cyclohexanol) are predicted generally with greater precision than those taken from Gainer and Metzner's work. The apparent reason for this is that the diffusivities reported by Gainer and Metzner were not measured at very low solute concentrations as was done in this work. The highest solute concentration used in this work was approximately 0.025 moles per liter. In contrast, the concentrations used in the work of Gainer and Metzner were not explicitly stated, but an analysis of their data indicates interfacial concentrations ranging from a high of eight moles per liter to a low of 0.1 moles per liter.

One would expect their data to be very concentration dependent (or concentration average values) since the diffusion coefficients of associating systems, especially high viscosity systems, are known to vary greatly with concentration. This is expected to happen even at fairly low concentrations.

On the basis of this, the average absolute percent deviations versus f were recalculated using only the experimental results of this project.

The results of this recalculation are shown in Table X and in Figure 10. The average deviation is lowest for the Wilke-Chang equation--the value being 12.1 percent. This is comparable with the 14.8, 17.9, 20.8, and 37.3 percent deviation for the authors' model, the modified Gainer and Metzner model, Olander's model, and the original Gainer and Metzner model, respectively. It is interesting to note that none of the equations tested gives an average value of the absolute percent deviation greater than 25 except the original Gainer and Metzner model. Thus, one might speculate that all of the equations tested predict adequately the diffusion coefficients for all types of systems at concentrations approaching infinite dilution. This could apply even to the ability of the Wilke-Chang equation to predict the diffusion coefficients of moderately high viscosity systems.

The optimum f values are between 0.775 and 0.925--as expected from the results of Eyring in Glasstone *et al.* (1941) and Bockris (1964)--for all of the models except Olander's.

On the basis of the author's study, the Wilke-Chang equation can adequately predict the diffusivities for moderately high viscosity systems--to about 30 centipoise or more--but it is definitely not adequate for high viscosity systems. All of the other equations tested also predict quite adequately the diffusivities for the moderately high viscosity systems. It is also important to note that the predictions are much more accurate for these other equations when an optimized f value is used than when a value of one-half

TABLE X

EXPERIMENTAL AND PREDICTED DIFFUSIVITIES (x $10^6 Cm^2/SEC$) FOR HIGH VISCOSITY SYSTEMS MEASURED IN THIS WORK

Solvent	Solute	Temp ^oC	η poise	D_{EXP}	D_{WC}	$\Delta(WC)$ %	D_0	$\Delta(D_0)$ %	D_{GM}	$\Delta(GM)$ %	D_{GM}	$\Delta(GM)$ %	D'_{GM}	$\Delta'(GM)$ %	D_M	$\Delta(M)$ %
Propylene Glycol	Ethylene Glycol	30	0.326	0.53	0.483	8.7	0.621	17.1	0.545	2.8	0.461	13.0	0.524	1.7	0.536	1.1
Diethylene Glycol	Ethylene Glycol	30	0.216	0.65	0.461	32.4	0.826	27.0	0.795	22.3	0.649	0.2	0.653	0.5	0.757	16.4
Ethylene Glycol	Cyclohexanol	30	0.135	0.64	0.681	6.4	0.803	25.4	1.21	98.2	1.17	83.0	0.987	54.2	0.832	30.0
Propylene Glycol	Cyclohexanol	30	0.326	0.31	0.313	1.1	0.398	28.4	0.476	53.5	0.443	42.8	0.409	31.8	0.380	22.5
Diethylene Glycol	Cyclohexanol	30	0.216	0.50	0.559	11.7	0.513	6.3	0.548	9.7	0.580	16.1	0.490	20.4	0.480	4.0
Average absolute percent deviation						12.1		20.8		37.3		31.0		17.9		14.8
Value of the parameter f used								0.50		0.50		0.85		.925		.775

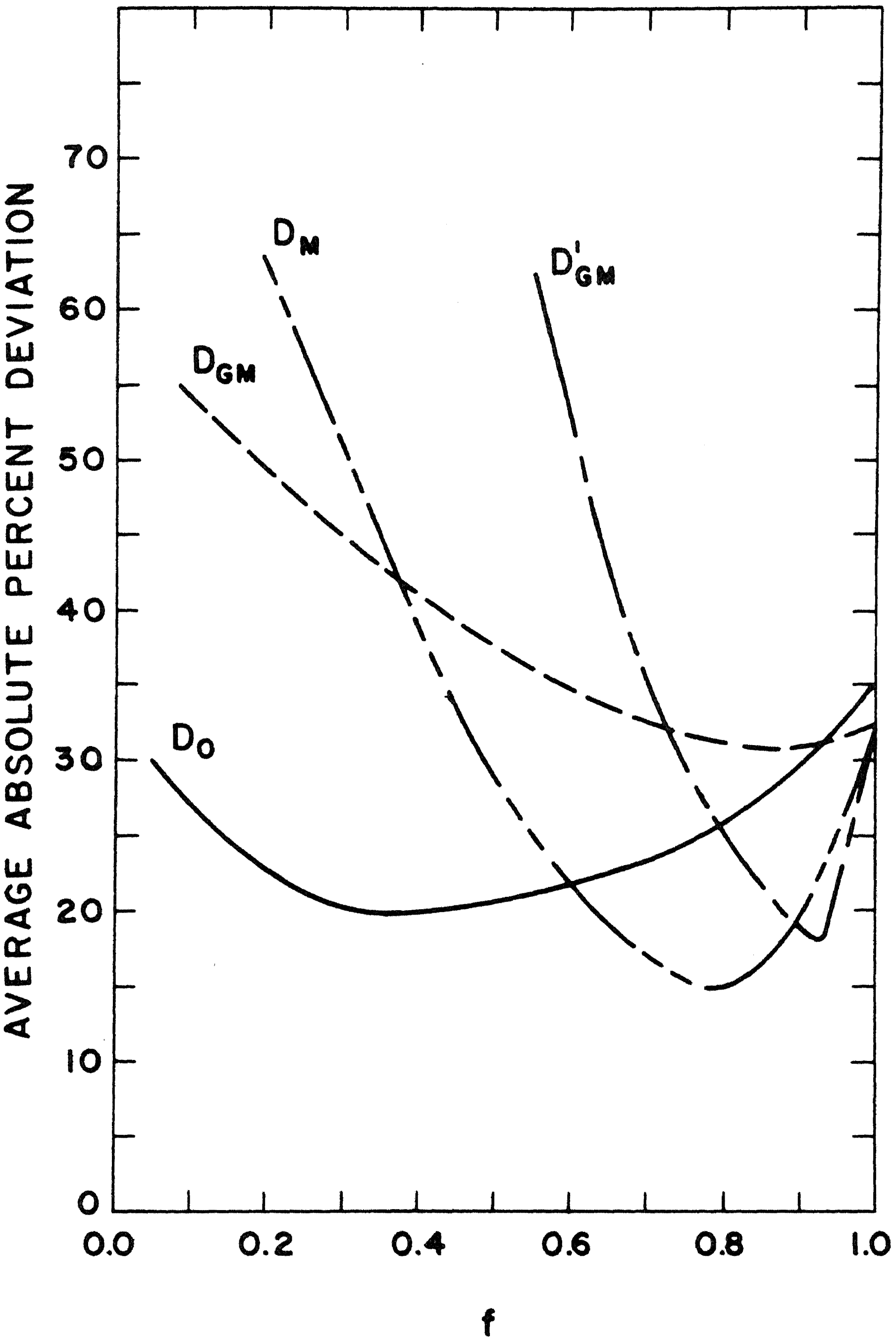

Figure 10. The average absolute percent deviation versus the fraction f for 5 high viscosity systems measured in this work.

is used for the f parameter.

For the higher viscosity systems, the equation developed in this work, the original and modified Gainer and Metzner model, and the Olander model, all can be used to predict the diffusion coefficients. Again, an optimized value of f will give more accurate results. Since the data reported by Gainer and Metzner are probably concentration dependent, the value of the parameter f shown in Table VIII should be used for these calculations. It is obvious here that more high-viscosity diffusivities at low solute concentrations are needed.

VI. CONCLUSIONS

The Eyring rate theory equation has been successfully modified to enable one to predict binary molecular diffusion coefficients for a variety of liquid-liquid systems. The activation free energy, $\Delta F_{D_{AB}}$, has been evaluated in terms of the self-diffusion, activation-free energies of the solute and solvent. This was accomplished through the use of regular solution theory by relating the bond-breaking energy of the jump step to the bond-breaking energy in evaporation. The assumptions used in this development have been tested (with the meager data available in the literature), and these preliminary results showed the assumptions to be valid.

Comparisons of the ability of the equation developed in this work with the equations developed by Olander, by Gainer and Metzner, and by Wilke and Chang to accurately predict the diffusion coefficients were made for three general types of systems. Generally, the results showed the Wilke-Chang equation to be adequate for most low viscosity systems as well as for the moderately high viscosity systems studied in this project. Likewise, all of the other equations tested adequately predicted the diffusion coefficients for these same systems. This is especially true if the optimized value of the parameter f is used instead of the value of one-half suggested by Olander and by Gainer and Metzner.

The diffusivities for the high viscosity systems are more accurately predicted by the three modified forms of the Eyring absolute rate theory equation than by the Wilke-Chang equation. Since these three equations give similarily adequate results, the availability of data for the system of interest is a very important consideration. The equation developed in this work and the equation developed by Olander require less data than the Gainer and Metzner model and are thus preferred. As for the low viscosity systems, the three modified forms of the Eyring absolute rate theory equation give superior results when an optimized value of the parameter f is used. This is even more evident for the high viscosity systems, since the AAPD's are more dependent upon f for these systems.

The parameter f generally is in the range of 0.65 to 1.0 for most of the systems and for most of the equations studied. This range agrees with the estimation by Eyring that the jump step portion of the total activation energy should constitute about 10 to 20 percent of the total activation energy.

More specifically, the value of the parameter f is between 0.95 and 1.00 for all of the equations tested for the low viscosity associating systems--excepting those containing water as the solvent. This agrees almost exactly with the estimation by Bockris et al. (1964) that f is about 0.99 for normal alcohols. On the other hand, the value of the parameter f for aqueous systems varies considerably depending upon the model being tested.

Olander's equation shows very little dependence of the average absolute percent deviation on the parameter f. For normal liquids, this means that the choice of f equal to one-half by Olander was a good one. In general, however, the optimized value of f gives better agreement between calculated and experimental diffusivities than the value of one-half. This is especially true for the low viscosity associating systems and for some high viscosity systems.

The diffusion coefficients reported by Gainer and Metzner may be subject to severe error due to a possible concentration dependence. Thus, the values of f used for future predictions should only be based on the data obtained in this laboratory until more accurate high viscosity diffusion data are available.

VII. APPENDICES

APPENDIX A

PHYSICAL PROPERTIES AND PARAMETERS USED FOR CALCULATIONS

A. Selection of Data.

In this section the methods used to select the various physical properties and parameters used in calculating the binary diffusivities will be presented. They are as follows:

1. k, the Boltzman constant $1.3805(10)^{-16}$ erg/°K.
2. h, the Planck constant $6.6242(10)^{-27}$ erg/sec.
3. N, the Avogadro number $6.023(10)^{23}$ molecules/mole.
4. R, the universal gas constant $1.987(10)^{-3}$ Kcal/mole.
5. T, the temperature at which the diffusivity was required in °K.
6. $\bar{V}_X$, the molar volume of component X at the temperature of interest (except for use with the Wilke-Chang equation) was used in units of cm^3/mole. This is readily obtainable from the density and the molecular weight of the component. The density is usually obtainable from one of the following references:
    a. The Handbook of Chemistry and Physics, (1965).
    b. Perry (1963)
    c. The International Critical Tables (1926).
    d. Timmermans (1959).
    e. Tables of the A.P.I. Research Project 44 (1968).

If not available from these references, the density can be measured [Daniels et al. (1962)]. For all the systems reported in this work, the density data were available in the above references except for the solvents ethylene glycol, diethylene glycol and propylene glycol. The densities for these were measured by Moore (1967). The densities of the systems "Hendecane" and "Chrysene" were also not available in the above references; they were measured by Lowitz et al. (1959).

When used in the Wilke-Chang equation, the solute molar volume in cm^3/mole is required at the boiling point. This was calculated using Kopp's rule and the "Atomic Volumes" given in Treybal (1963).

7. η_B, the viscosity of the solvent (or solution of solute A in solvent B at infinite dilution) was used in units of poise. The viscosity is usually available from one of the references discussed above.

8. ξ, the geometric parameter in the diffusion coefficient was set equal to 5.6 for all solvents for Olander's equation. It was 5.6 for D_M for all solvents except methanol and ethanol for which it was equal to 7.5. ξ was 6.0 for Gainer and Metzner's equation for all solvents except methanol and ethanol for which the value of 8.0 was used.

9. ϕ, the molecular association constant in the Wilke-Chang equation was equal to 2.6 for water, 1.9 for methanol, 1.5 for ethanol and 1.0 for all other solvents.

10. $\Delta F_{D_{XX}}$, for use in Olander's equation was calculated by the following

equation:

$$\Delta F_{\eta_X} = RT \ln(\eta_X \bar{V}_X / hN) \qquad \text{(A-1)}$$

and the assumption that $\Delta F_{D_{XX}}$ equals ΔF_{η_X}. The selection of the terms in this equation has been described previously. When used in Equation 29, $\Delta F_{D_{XX}}$ is calculated using the following equation

$$\Delta F_{\eta_X} = RT \ln(\sqrt{2}\eta_X \bar{V}_X / hN) \qquad \text{(A-2)}$$

and the assumption that $\Delta F_{D_{XX}}$ equals ΔF_{η_X}.

11. E_{η_X}, for use in the modified Gainer and Metzner equation was calculated from viscosity data versus temperature with the following equation:

$$E_{\eta_X} = RT \frac{d\ln\eta_X}{d(1/T)} \qquad \text{(A-3)}$$

When used in the original Gainer and Metzner equation, E_{η_X} was calculated with the following equation:

$$E_{\eta_X} = RT \ln((\eta_X \bar{V}_X \Delta E_X^{vap})/(1.09(10)^{-3} M^{\frac{1}{2}} T^{3/2})) \qquad \text{(A-4)}$$

The data necessary for use in both of the above equations have already been discussed, except the energy of vaporization term which will be discussed later.

12. α, the volumetric coefficient of thermal expansion, is calculated from the following equation:

$$\alpha_X = \frac{1}{\bar{V}_X} \frac{d\bar{V}_X}{dT} \qquad \text{(A-5)}$$

and molecular volume data as a function of temperature.

13. $E_{D_{XX}}$, when used for all forms of the Gainer and Metzner equation, $E_{D_{XX}}$ is assumed equal to E_{η_X}. All of the necessary data used in these equations have been discussed previously.

14. The term ΔH_X^{vap} is usually given in one of the references discussed earlier. These data are usually at the normal boiling point. When it was not available at the desired temperature, it was corrected by the following equation (see Perry, 1963)

$$\frac{\Delta H_{T_1}^{vap}}{\Delta H_{T_2}^{vap}} = \left(\frac{T_c - T_2}{T_c - T_1}\right)0.38 \qquad \text{(A-6)}$$

When no value of the ΔH_X^{vap} was available, it was calculated from the Claperyon-Clausis equation [see Moore (1955)] and the vapor pressure data given in Jordan (1954). In just two cases (viz. for "Hendecane" and "Chrysene"), the enthalpy of vaporization at the normal boiling was estimated by Trouton's rule (see Perry, 1963)

$$\Delta H_X^{vap} = (21)T_{boiling} \qquad \text{(A-7)}$$

15. $E_{\eta_{X-D}}$ (used in the Gainer and Metzner equation) was calculated from the ratio

$$\frac{E_{\eta_{X-D}}}{E_{\eta_X}} = \frac{\Delta H_{X-D}^{vap}}{\Delta H_X^{vap}} \qquad \text{(A-8)}$$

The evaluation of ΔH_X^{vap} is discussed above. The term ΔH_{X-D}^{vap} is the enthalpy of vaporization of the hydrocarbon homologue of X at the same reduced temperature.

16. $E_{\eta_{X-H}}$ is calculated from the equation

$$E_{\eta_{X-H}} = E_{\eta_X} - E_{\eta_{X-D}} \qquad \text{(A-9)}$$

17. ΔE_X^{vap} is simply obtained from the ΔH_X^{vap} by the equation

$$\Delta E_X^{vap} = \Delta H_X^{vap} - RT \qquad \text{(A-10)}$$

B. Data

The following tables contain the data collected from the literature and the parameters used in order to perform the necessary calculations throughout the thesis.

Table A-I shows the molecular weight, the solvent association parameter used in the Wilke-Chang correlation, and the parameter ξ used in the various forms of the absolute rate theory equations.

Table A-II gives the density data used to calculate the diffusion coefficients and the volumetric coefficient of expansion at constant pressure.

Table A-III gives the viscosity data used in the calculations.

Table A-IV gives the value of the molar volume obtained from Kopp's rule, the heat of vaporization, and the ratio of the heat of vaporization due to dispersion force bonds to the total heat of vaporization

Table A-V gives the viscosity, self diffusion, and volumetric coefficient of thermal expansion at constant pressure data used in the calculation of the parameter ξ.

Table A-VI gives the binary diffusion and heat of mixing at infinite dilution data used to test the validity of assumptions as shown in Figures 1 and 2.

TABLE A-I

MOLECULAR WEIGHT AND PARAMETERS USED FOR DIFFUSIVITY PREDICTIONS

Solvent	Temp °C	Solvent Assoc. Parameter for D_{WC}	Molecular Weight	ξ		
				D_{GM}	D_O	D_M
Benzene	15.0	1.0	78.11	6.0	5.6	5.6
Benzene	25.0	1.0	78.11	6.0	5.6	5.6
Benzene	30.0	1.0	78.11	6.0	5.6	5.6
Toluene	15.0	1.0	92.13	6.0	5.6	5.6
Toluene	25.0	1.0	92.13	6.0	5.6	5.6
Toluene	30.0	1.0	92.13	6.0	5.6	5.6
Hexane	15.0	1.0	86.17	6.0	5.6	5.6
Hexane	30.0	1.0	86.17	6.0	5.6	5.6
Methanol	15.0	1.9	32.04	8.0	5.6	7.5
Methanol	30.0	1.9	32.04	8.0	5.6	7.5
n-Propanol	15.0	1.0	60.09	6.0	5.6	5.6
n-Propanol	25.0	1.0	60.09	6.0	5.6	5.6
i-Propanol	15.0	1.0	60.09	6.0	5.6	5.6
n-Butanol	15.0	1.0	74.12	6.0	5.6	5.6
i-Butanol	15.0	1.0	74.12	6.0	5.6	5.6
Acetic Acid	15.0	1.0	60.05	6.0	5.6	5.6
Chloroform	15.0	1.0	119.39	6.0	5.6	5.6
Carbon Tetrachloride	15.0	1.0	153.84	6.0	5.6	5.6
Carbon Tetrachloride	25.0	1.0	153.84	6.0	5.6	5.6
Chlorobenzene	15.0	1.0	112.56	6.0	5.6	5.6
Bromobenzene	15.0	1.0	157.02	6.0	5.6	5.6
Ethanol	15.0	1.5	46.07	8.0	5.6	7.5
Ether	15.0	1.0	74.12	6.0	5.6	5.6
Acetone	15.0	1.0	58.08	6.0	5.6	5.6
Acetone	25.0	1.0	58.08	6.0	5.6	5.6
Water	15.0	2.6	18.00	6.0	5.6	5.6
Water	21.0	2.6	18.00	6.0	5.6	5.6
Methyl Ethyl Ketone	30.0	1.0	72.10	6.0	5.6	5.6
Cyclohexane	25.0	1.0	84.16	6.0	5.6	5.6
Ethylene Glycol	30.0	1.0	62.10	6.0	5.6	5.6
Ethylene Glycol	20.0	1.0	62.10	6.0	5.6	5.6

TABLE A-I (continued)

Solvent	Temp °C	Solvent Assoc. Parameter for D_{WC}	Molecular Weight	ξ		
				D_{GM}	D_O	D_M
Propylene Glycol	30.0	1.0	76.10	6.0	5.6	5.6
Diethylene Glycol	30.0	1.0	106.10	6.0	5.6	5.6
Triethylene Glycol	0.0	1.0	150.20	6.0	5.6	5.6
Cyclohexanol	30.0	1.0	100.20	6.0	5.6	5.6
Glycerin	0.0	1.0	92.10	6.0	5.6	5.6
Glycerin	20.0	1.0	92.10	6.0	5.6	5.6
Glycerin	21.0	1.0	92.10	6.0	5.6	5.6
Glycerin	25.0	1.0	92.10	6.0	5.6	5.6
Hexanol	0.0	1.0	102.20	6.0	5.6	5.6
Hexanol	25.0	1.0	102.20	6.0	5.6	5.6
Hexanol	22.0	1.0	102.20	6.0	5.6	5.6
Hexanol	23.4	1.0	102.20	6.0	5.6	5.6
n-Amyl Alcohol	23.4	1.0	88.20	6.0	5.6	5.6
n-Amyl Alcohol	30.0	1.0	88.20	6.0	5.6	5.6
"Chrysene"	22.0	1.0	240.40	6.0	5.6	5.6
n-Decane	22.0	1.0	142.30	6.0	5.6	5.6
"Hendecane"	22.0	1.0	418.80	6.0	5.6	5.6
n-Octanol	22.0	1.0	130.20	6.0	5.6	5.6

"Chrysene" is 1, 2, 3, 4, 5, 6, 7, 8, 13, 14, 15, 16 - dodecahydrochrysene
"Hendecane" is 1, 1-di-(alpha-decalyl)-hendecane

TABLE A-II

DENSITY DATA USED FOR DIFFUSIVITY PREDICTIONS

Solvent	Temp °C	Density at T°C Gr./Cm^3	Density at T+15°C# Gr./Cm^3	Ref-Page
Benzene	15.0	0.88420	0.86844	T-144
Benzene	25.0	0.87365	0.85760	T-144
Benzene	30.0	0.86844	0.85220*	T-144
Toluene	15.0	0.87160	0.85770	T-152
Toluene	25.0	0.86258*	0.84830	T-152
Toluene	30.0	0.85770	0.84360*	T-152
Hexane	15.0	0.66380	0.65055	T- 44
Hexane	30.0	0.65055	0.63508**	T- 44
Methanol	15.0	0.79609	0.78208	T-304
Methanol	30.0	0.79030*	0.77610*	T-304
n-Propanol	15.0	0.80749	0.79600	T-315
n-Propanol	25.0	0.79980	0.78500	T-315
i-Propanol	15.0	0.78916	0.77690	T-317
n-Butanol	15.0	0.81337	0.80206	T-319
i-Butanol	15.0	0.80576	0.79437	T-321
Acetic Acid	15.0	1.05310*	1.03802	T-382
Chloroform	15.0	1.49845	1.47060	T-220
Carbon Tetrachloride	15.0	1.60370	1.57480	T-226
Carbon Tetrachloride	25.0	1.58430	1.55570	T-226
Chlorobenzene	15.0	1.11172	1.09550	T-284
Bromobenzene	15.0	1.50170	1.48150	T-288
Ethanol	15.0	0.79367	0.78096	T-310
Ether	15.0	0.71925	0.70205	T-344
Acetone	15.0	0.79597	0.77931	T-355
Acetone	25.0	0.78458	0.76820	T-355
Water	15.0	0.99913	0.99568	P-3.70
Water	21.0	0.99723	0.99406	P-3.70
Methyl Ethyl Ketone	30.0	0.79452	0.77970**	T-361
Cyclohexane	25.0	0.77385	0.75985*	T-195
Ethylene Glycol	30.0	1.10620	1.09580*	M
Ethylene Glycol	20.0	1.11320**	1.10280*	M

TABLE A-II (continued)

Solvent	Temp ^{o}C	Density at T^{o}C Gr./Cm^{3}	Density at T+15^{o}C$^{\#}$ Gr./Cm^{3}	Ref-Page
Propylene Glycol	30.0	1.02920	1.01770*	M
Diethylene Glycol	30.0	1.10920	1.09850*	M
Triethylene Glycol	0.0	1.13880**	1.12730**	M
Cyclohexanol	30.0	0.94155	0.92994	T-491
Glycerin	0.0	1.27370**	1.26440	T-336
Glycerin	20.0	1.26130**	1.25190*	T-336
Glycerin	21.0	1.26080*	1.25130*	T-336
Glycerin	25.0	1.25830*	1.24900	T-336
Hexanol	0.0	0.83285	0.82239	T-330
Hexanol	25.0	0.81560*	0.81524**	T-330
Hexanol	22.0	0.81750*	0.80710*	T-330
Hexanol	23.4	0.81660*	0.80610*	T-330
n-Amyl Alcohol	23.4	0.81240*	0.80170*	T-326
n-Amyl Alcohol	30.0	0.80760	0.79700**	T-326
"Chrysene"	22.0	0.04800**	1.03850**	L
n-Decane	22.0	0.72850*	0.71710*	A-288
"Hendecane"	22.0	0.93020**	0.92090**	L
n-Octanol	22.0	0.82730*	0.81710**	T-332

* Interpolated from data given in specified reference

** Extrapolated from data given in specified reference

T Timmermans (1959a)

P Perry (1963)

M Moore (1967)

A American Petroleum Institute Research Project 44 (1968)

L Lowitz et al. (1959)

\# The densities at T and T+15^{o}C were used in Equation A-5 to calculate α.

TABLE A-III

VISCOSITY DATA USED FOR DIFFUSIVITY PREDICTIONS

Solvent	Temp °C	Viscosity at T °C cp	Viscosity at T+15 °C# cp	Ref-Page
Benzene	15.0	0.696	0.569	T-146
Benzene	25.0	0.610	0.504*	T-146
Benzene	30.0	0.569	0.475*	T-146
Toluene	15.0	0.623	0.523	T-152
Toluene	25.0	0.553*	0.467*	T-152
Toluene	30.0	0.523	0.440*	T-152
Hexane	15.0	0.337	0.278	T- 44
Hexane	30.0	0.278	0.229**	T- 44
Methanol	15.0	0.623	0.510	T-305
Methanol	30.0	0.567*	0.476*	T-305
n-Propanol	15.0	2.522	1.722	T-315
n-Propanol	25.0	1.950*	1.325**	T-315
i-Propanol	15.0	2.859	1.765	T-317
n-Butanol	15.0	3.379	2.271	T-320
i-Butanol	15.0	4.703	2.876	T-322
Acetic Acid	15.0	1.314	1.040	T-382
Chloroform	15.0	0.569	0.514	T-220
Carbon Tetrachloride	15.0	1.038	0.845	T-227
Carbon Tetrachloride	25.0	0.888	0.739	T-227
Chlorobenzene	15.0	0.844	0.711	T-285
Bromobenzene	15.0	1.196	0.985	T-288
Ethanol	15.0	1.327*	1.065*	T-311
Ether	15.0	0.247	0.227**	T-344
Acetone	15.0	0.355	0.295	T-355
Acetone	25.0	0.308	0.271**	T-355
Water	15.0	1.104	1.011	P-3.201
Water	21.0	1.005	0.722	P-3.201
Methyl Ethyl Ketone	30.0	0.365	0.312**	T-361
Cyclohexane	25.0	0.883*	0.683*	T-195
Ethylene Glycol	30.0	13.56	7.98 *	M
Ethylene Glycol	20.0	20.62 **	11.30 *	M

TABLE A-III (continued)

Solvent	Temp °C	Viscosity at T°C cp	Viscosity at T+15°C# cp	
Propylene Glycol	30.0	32.63	15.50 *	M
Diethylene Glycol	30.0	21.61	12. *	M
Triethylene Glycol	0.0	160. **	56. *	M
Cyclohexanol	30.0	41.07	17.19	T-491
Glycerin	0.0	12100. +	2267.	T-337
Glycerin	21.0	1360. *	349. **	T-337
Glycerin	20.0	1480. *	382. **	T-337
Glycerin	25.0	950. *	245. **	T-337
Hexanol	0.0	0.880**	0.620	T-330
Hexanol	25.0	0.437*	0.287**	T-330
Hexanol	22.0	0.498*	0.310*	T-330
Hexanol	23.4	0.476*	0.297**	T-330
n-Amyl Alcohol	23.4	3.610*	2.310**	T-326
n-Amyl Alcohol	30.0	2.987**	1.880**	T-326
"Chrysene"	22.0	2450. +	570. **	L
n-Decane	22.0	0.906*	0.703*	T-116
"Hendecane"	22.0	4000. +	810. **	L
n-Octanol	22.0	8.22 *	4.76 **	T-332

* Interpolated from data given in specified reference
** Extrapolated from data given in specified reference
\+ Gainer and Metzner (1965)
T Timmermans (1959)
M Moore (1967)
A American Petroleum Institute Research Project 44 (1968)
L Lowitz et al. (1959)
\# The viscosity at T and T+15°C were used in Equation A-3 to calculate E_{η_B}.

TABLE A-IV

MOLAR VOLUME AND ΔH_X^{vap} USED FOR DIFFUSIVITY PREDICTIONS

Solvent	Temp ^oC	$\bar{V}_A$ at B.P. Kopp's Rule Cm^3/Mole	ΔH_X^{vap} Cal/Mole	Ref-Page	$\frac{\Delta H_{X-D}^{vap}}{\Delta H_X^{vap}}$
Benzene	15.0	96.0	8100	T-149	1.000
Benzene	25.0	96.0	8100	T-149	1.000
Benzene	30.0	96.0	8100	T-149	1.000
Toluene	15.0	118.2	8840	T-153	1.000
Toluene	25.0	118.2	8840	T-153	1.000
Toluene	30.0	118.2	8840	T-153	1.000
Hexane	15.0	140.6	7540*	T- 47	1.000
Hexane	30.0	140.6	7540*	T- 47	1.000
Methanol	15.0	37.0	8950*	T-306	0.395
Methanol	30.0	37.0	8950*	T-306	0.395
n-Propanol	15.0	81.4	10400*	T-316	0.555
n-Propanol	25.0	81.4	10400*	T-316	0.555
i-Propanol	15.0	81.4	10240*	T-318	0.540
n-Butanol	15.0	103.6	10530*	T-320	0.611
i-Butanol	15.0	103.6	10460*	T-322	0.598
Acetic Acid	15.0	68.4	6030*	P-3.112	0.910
Chloroform	15.0	84.8	8360*	T-221	1.000
Carbon Tetrachloride	15.0	103.2	7830*	T-228	1.000
Carbon Tetrachloride	25.0	103.2	7830*	T-228	1.000
Chlorobenzene	15.0	114.4	8900*	P-3.113	1.000
Bromobenzene	15.0	119.3	9200*	P-3.113	1.000
Ethanol	15.0	59.2	10000*	T-312	0.463
Ether	15.0	107.2	6620*	T-345	0.900
Acetone	15.0	74.0	7610*	T-356	0.384
Acetone	25.0	74.0	7610*	T-356	0.384
Water	15.0	75.6	10250	P-3.191	0.202
Water	21.0	75.6	10250	P-3.191	0.100
Methyl Ethyl Ketone	30.0	96.2	6500*	T-361	0.960
Cyclohexane	25.0	118.2	7050	T-197	1.000

TABLE A-IV (continued)

Solvent	Temp ^{o}C	$\bar{V}_A$ at B.P. Kopp's Rule Cm^3/Mole	ΔH_X^{vap} Cal/Mole	Ref-Page	$\frac{\Delta H_{X-D}^{vap}}{\Delta H_X^{vap}}$
Ethylene Glycol	30.0	66.6	19100+	J- 72	0.331
Ethylene Glycol	20.0	66.6	19300+	J- 72	0.331
Propylene Glycol	30.0	88.8	15500+	J- 73	0.454
Diethylene Glycol	30.0	118.4	12250+	J- 73	0.568
Triethylene Glycol	0.0	170.2	17400+	J- 73	0.914
Cyclohexanol	30.0	136.9	12700+	J- 73	0.666
Glycerin	0.0	96.2	23400+	J- 80	0.365
Glycerin	20.0	96.2	24000+	J- 80	0.365
Clycerin	21.0	96.2	23800+	J- 80	0.365
Glycerin	25.0	96.2	23800+	J- 80	0.365
Hexanol	0.0	148.0	12700+	J- 67	0.750
Hexanol	25.0	148.0	12420+	J- 67	0.754
Hexanol	22.0	148.0	12420+	J- 67	0.754
Hexanol	23.4	148.0	12730+	J- 67	0.754
n-Amyl Alcohol	23.4	125.8	12730*	P-3.113	0.668
n-Amyl Alcohol	30.0	125.8	12580*	P-3.113	0.668
"Chrysene"	22.0	340.2	8620	TR	1.000
n-Decane	22.0	229.4	12280	A-436	1.000
"Hendecane"	22.0	658.6	8960	TR	1.000
n-Octanol	22.0	192.4	16220	P-3.113	0.696

* Corrected for temperature by Equation A-6

\+ Estimated from vapor pressure data and Claperyon-Clausis equation, Moore (1955)

T Timmermans (1959a)

P Perry (1963)

J Jordan (1954)

A American Petroleum Institute Research Project 44 (1968)

TR Estimated by Troutons Rule, Perry (1963).

TABLE A-V

DENSITY, VISCOSITY, SELF DIFFUSION COEFFICIENT AND α USED FOR CALCULATING THE PARAMETER ξ

Compound	Temp ^{o}C	Density Gr./Cm^3	Viscosity cp	Ref-Page	$D_{BB}(10)^5$ Cm^2/sec	Ref	$\alpha(10)^{3\#}$ $^{o}C^{-1}$	Ref-Page
Benzene	15	0.88420	0.696	T-146	1.88	JB	1.206	I-29
Benzene	25	0.87365	0.610*	T-146	2.15	JB	1.225	I-29
Benzene	35	0.86277*	0.525*	T-146	2.40	JB	1.245	I-29
Benzene	45	0.85220*	0.475*	T-146	2.67	JB	1.268	I-29
Ethanol	15	0.79367	1.360*	T-311	0.80	JB	1.062	I-27
Ethanol	25	0.78503	1.120	T-311	1.05	JB	1.088	I-27
Ethanol	35	0.77641**	0.949*	T-311	1.31	JB	1.116	I-27
Ethanol	45	0.76706**	0.780*	T-311	1.70	JB	1.152	I-27
Methanol	15	0.79609	0.623	T-305	1.93	JB	1.178	I-27
Methanol	25	0.78660	0.551**	T-305	2.27	JB	1.202	I-27
Methanol	35	0.77711*	0.479**	T-305	2.65	JB	1.228	I-27
n-Propanol	15	0.80749**	2.522	T-315	0.504	JB	0.987	I-28
n-Propanol	25	0.79980*	1.950*	T-315	0.646	JB	0.983	I-28
n-Propanol	35	0.79207*	1.710**	T-315	0.814	JB	1.014	I-28
n-Propanol	45	0.78545*	1.380**	T-315	1.017	JB	1.046	I-28
i-Propanol	15	0.78916	2.859	T-317	0.474	JB	1.035	I-28
i-Propanol	25	0.78095	2.420*	T-317	0.649	JB	1.053	I-28

TABLE A-V (continued)

Compound	Temp ^{o}C	Density Gr./Cm^3	Viscosity cp	Ref-Page	$D_{BB}(10)^5$ Cm^2/sec	Ref	$\alpha(10)^{3\#}$ $^{o}C^{-1}$	Ref-Page
i-Propanol	35	0.77275**	1.900**	T-317	0.867	JB	1.071	I-28
i-Propanol	45	0.76445**	1.480**	T-317	1.145	JB	1.090	I-28
n-Pentane	25	0.62133	0.22	DM	5.45	DM	1.466	I-29
n-Hexane	25	0.65502	0.29	DM	4.21	DM	1.250	I-29
n-Octane	25	0.69882	0.51	DM	2.00	DM	1.147	I-29
n-Nonane	25	0.71328	0.67	DM	1.70	DM	1.022	I-30
n-Decane	25	0.72043	0.85	DM	1.31	DM	0.968	I-30

* Interpolated from data given in specified reference
** Extrapolated from data given in specified reference
\# Calculated from data given in reference

T Timmermans (1959a)
JB Johnson and Babb (1956)
I International Critical Tables (1926)
DM Douglass and McCall (1959)

TABLE A-VI

BINARY DIFFUSION AND HEAT OF MIXING AT INFINITE DILUTION DATA

Solvent	Solute	Temp °C	$D_{AB}(10)^5$ Cm^2/Sec	Ref	$\Delta \bar{H}_{AB}^{mix}$ Kcal/Mole	Ref
Benzene	Carbon Tetrachloride	10.0	1.466	JB	0.100 (at 20°C)*	T
Benzene	Carbon Tetrachloride	25.3	1.912	JB		
Benzene	Carbon Tetrachloride	40.0	2.432	JB		
Benzene	Ethanol	15.0	2.37#	JB	3.690 (at 20°C)**	M
Benzene	Ethanol	27.0	3.22#	JB		
Benzene	Chloroform	15.0	2.39	JB	-0.290 (at 15°C)**	T
Benzene	Methanol	11.0	3.14#	JB	3.64 (at 20°C)**	M
Benzene	Methanol	27.1	3.08#	JB		
Water	n-Butanol	1.0	0.44#	JB	-2.85 (at 15°C)	Ba
Water	n-Butanol	25.0	0.97#	JB		
Water	n-Propanol	11.0	0.79#	JB	-2.85 (at 15°C)	Ba
Water	n-Propanol	15.0	0.87	JB		
Water	Methanol	15.0	1.26	JB	-1.756 (at 25°C)	Bb
Water	Ethanol	10.0	0.85#	JB	-2.75 (at 15°C)	Bb
Water	Ethanol	15.0	1.00	JB		
Water	Ethanol	25.0	1.24	JB		

* Interpolated from data given in specified reference

TABLE A-VI (continued)

** Extrapolated from data given in specified reference

Extrapolated linearly to zero concentration from data given in specified reference

M Mrazek and Van Ness (1961)
JB Johnson and Babb (1956)
T Timmermans (1959b)
Ba Bertrand *et al.* (1966)
Bb Bertrand *et. al.* (1968)

APPENDIX B

EXPERIMENTAL PROCEDURES AND RESULTS

Wall et al. (1952 and 1958) devised a method for measuring molecular diffusivities for binary systems of low viscosity, high molecular weight aqueous polymer solutions. The conventional steady-state methods available at that time were impractical due to the slow rate of mass transfer of these high molecular weight polymers.

The original method employed a porous disc of unglazed porcelain. This disc was first soaked in an aqueous solution of the polymer for a time sufficient to enable a uniform concentration of the polymer in the solvent to develop throughout the disc. The disc was then transferred to a well agitated pure solvent bath. At various time intervals the water agitation was stopped, and the apparent weight of the disc was measured. These data allowed the molecular diffusivity to be calculated. This method should be applicable to the high viscosity systems of interest here where the mass transfer rate is also expected to be small.

Marcinkowsky, Nelson and Kraus (1965) devised an experimental technique very similar to the method described above except that the disc was filled with a radioactive tracer of strong gamma emission (viz., Na-22). They flushed fresh solvent past the disc so that the solute concentration outside the disc was nearly zero. By placing their detector close to the disc but outside the apparatus, they were able to measure the radioactivity of the tracer left in the porous disc versus time and, subsequently, determine the molecular diffusivity. This radioactive tracer method could be used for organic solvents only by measuring the activity of the solute in the bath, because the low beta energy of C-14 could not be detected by the technique used above.

These methods have been modified for use in this work as described in the following sections.

A. Description of Apparatus

The apparatus used in this investigation is shown in Figures B-1 through B-6. The basic components include (1) a porous plate immersed in a solvent bath which is stirred vigorously with a mechanical stirrer, (2) a constant temperature bath, and (3) a counting apparatus. The details of the apparatus are as follows.

1. The Porous Disc. The porous plates are about 2-7/8 inches square and about 1/4 inch thick. The plates were obtained from Fisher Scientific Company and were ground on a carborundum (No. 203) grinding sheet with water. They were cleaned with 12 molar HCl and distilled water and then with acetone, and again with distilled water. The edges of the porous plates were sealed with an epoxy resin (with a thickening filler to prevent capillary action) and cured. They were then mounted in aluminum frames for support.

2. Solvent Bath. The solvent baths are aluminum boxes about 6x3 1/2x 1 1/4 inches with small clips in the bottom. These clips held the porous plates in place.

3. Stirring Apparatus. The stirring assemblies are mounted on rods

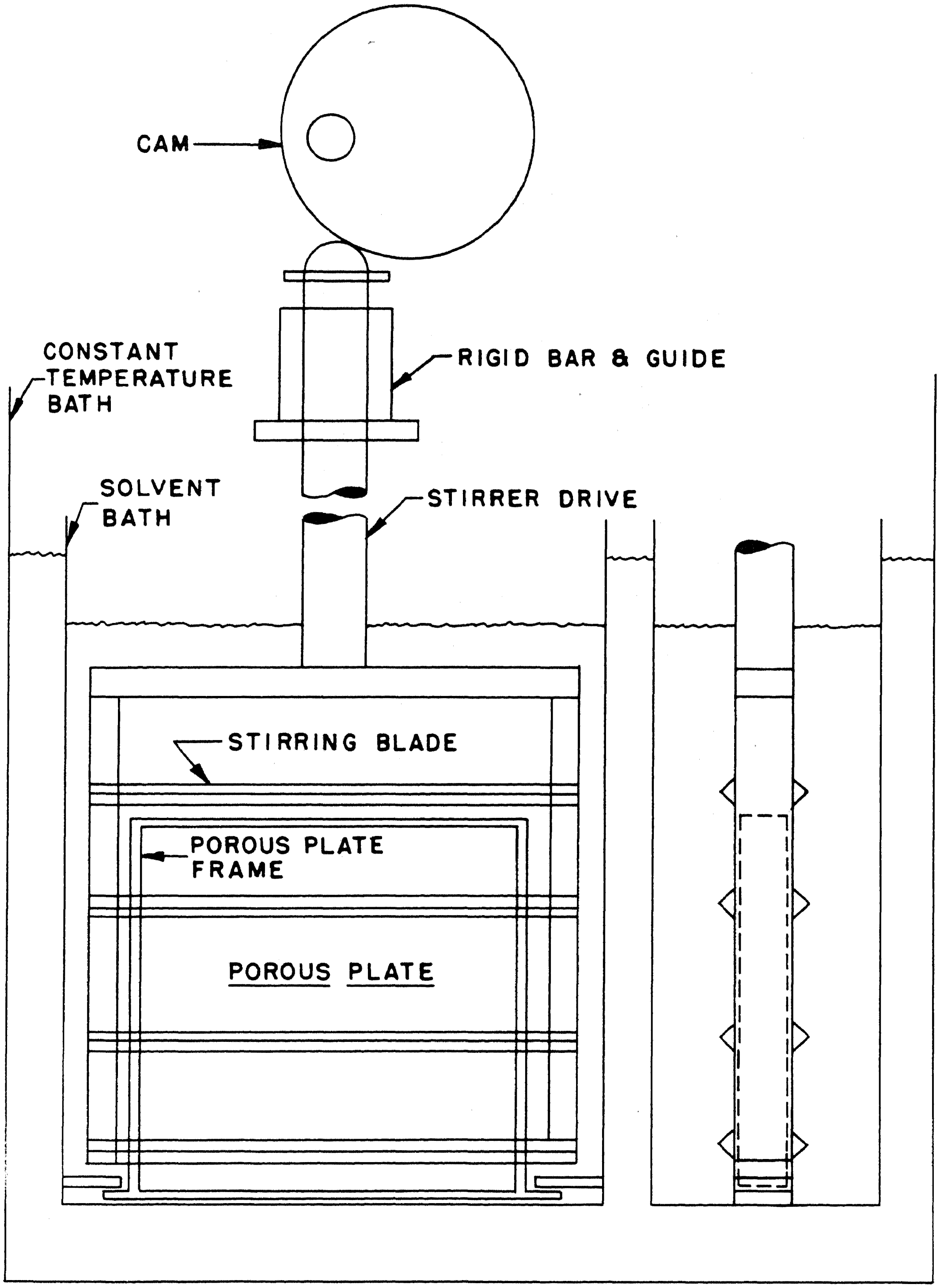

Figure B-1. Schematic diagram of porous plate and associated equipment.

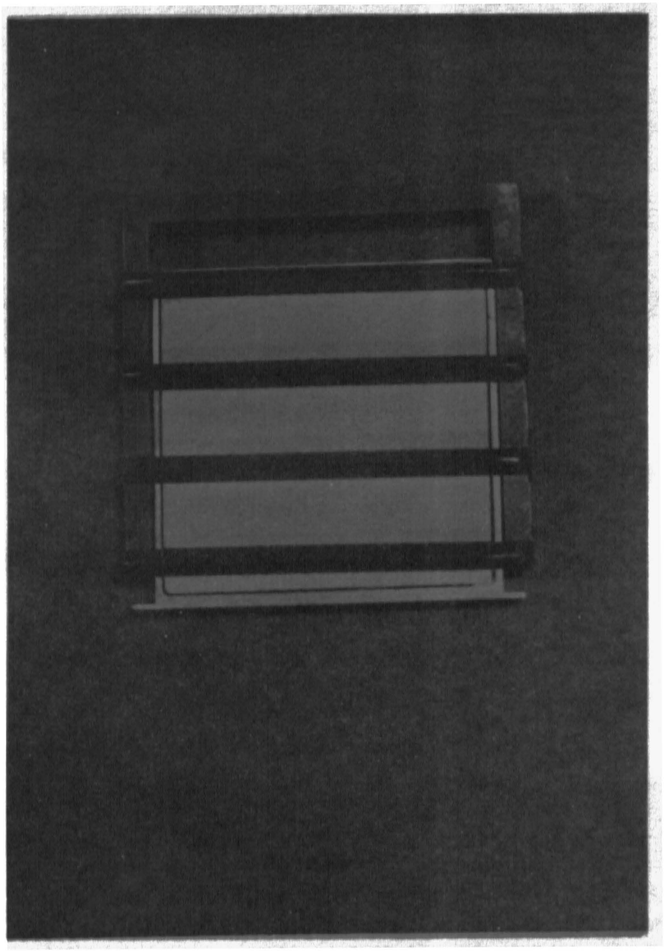

Figure B-2. Porous plate fitted with stirring blades used to measure diffusivities.

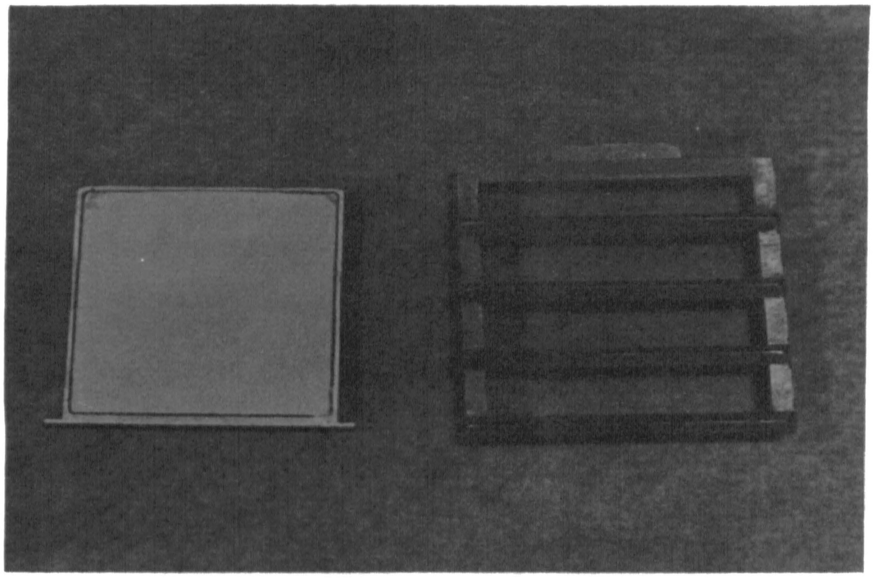

Figure B-3. Porous plate beside stirring blade used to measure diffusivities.

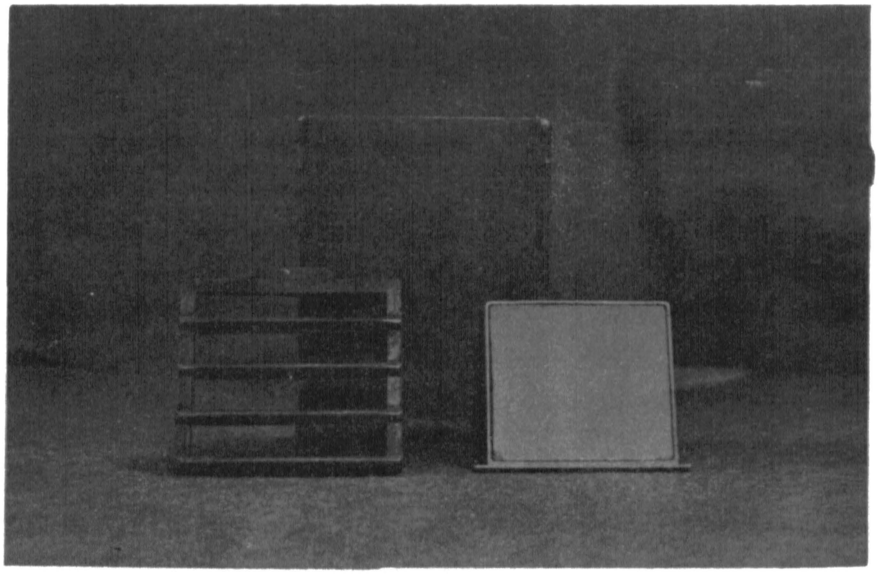

Figure B-4. Porous plate, stirring blade and solvent bath used to measure diffusivities.

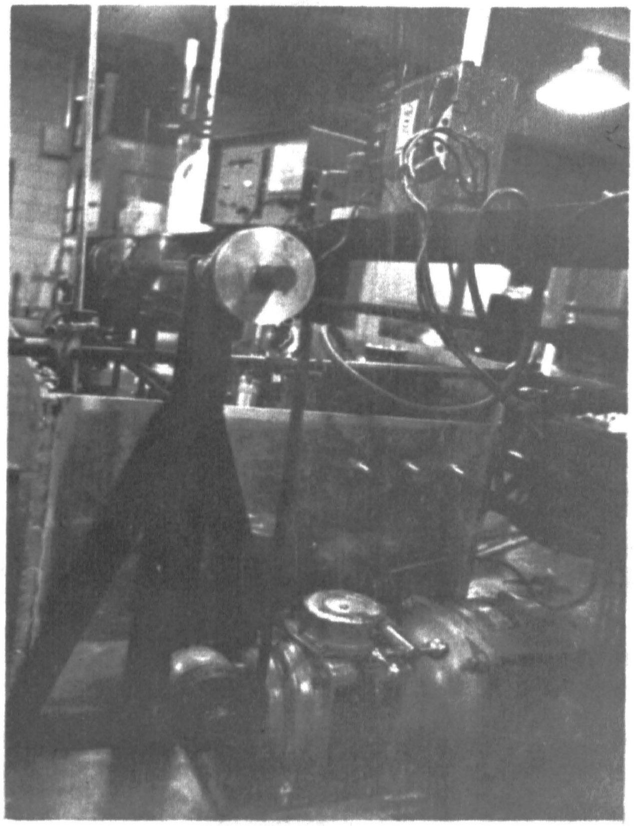

Figure B-5. End view of constant temperature bath showing cams and variable speed motor.

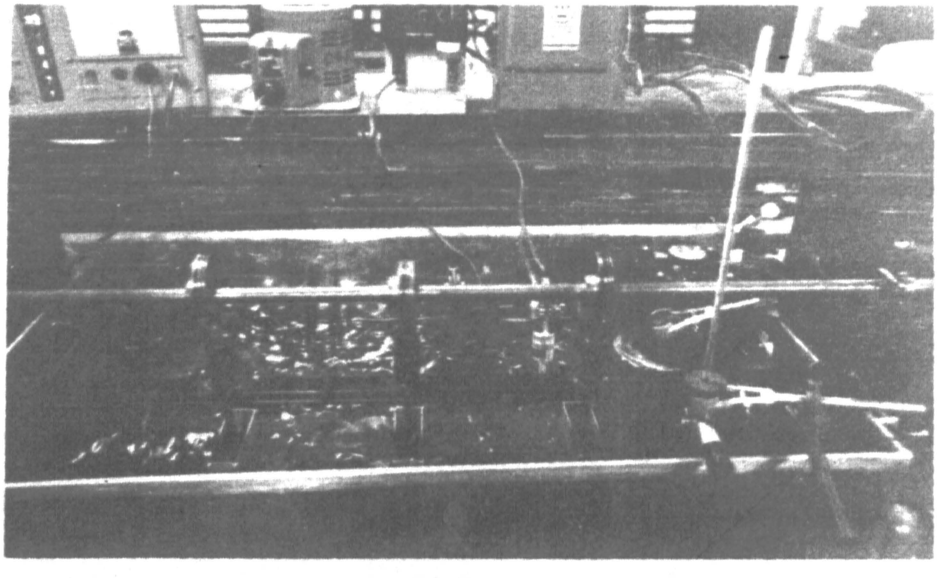

Figure B-6. Front view of constant temperature bath.

which are allowed to move vertically and are connected to eccentrically mounted cams. The cams are mounted on a shaft which is driven by a variable speed transmission motor. The stirring blades are mounted on a frame which has four horizontal stirring blades on each side of a porous plate. The blades themselves are equilaterally triangular in shape, and as they move up and down they wipe the solvent away from the surface of the porous plates. The blades serve to reduce the resistance to mass transfer in the solvent bath immediately adjacent to the porous plates, and they also keep the solute concentration in the bath uniform during the unsteady-state buildup of the solute concentration.

4. Constant Temperature Bath. The constant temperature bath is made of sheet aluminum and contains approximately thirty gallons of transformer oil. The oil is agitated by a centrifugal pump. The temperature in the bath is coarsely controlled by a cooling coil (through which tap water is passed) and a heating element that is controlled by a variable voltage rheostat. The fine temperature control heater is made of about 30 feet of 30 gauge nichrome wire wrapped on a plexiglass frame. This fine-control heater is connected to a relay which is in turn connected to a mercury, thermometer-type thermoregulator. The bath temperature can be controlled to within $\pm 0.01^{\circ}C$ over the desired temperature range. The temperature of the experiments ranged from about 25° to $50^{\circ}C$.

5. Counting Apparatus. The tracer materials used were C-14 tagged. No good-quality, inexpensive method is available for continuously counting the C-14 tracer in the solvent bath. Perhaps the best method of doing this would

be by a liquid scintillation method. However, the scintillation materials, if added to the solvent, would alter the physical properties of the solvent and give rise to erroneous molecular diffusivities (i. e., a diffusivity through a multicomponent system). Because of these difficulties, small samples of the liquid in the solvent bath (i. e., outside of the porous plate) were removed at various time intervals.

The radioactivity of the solute in the liquid was counted using a liquid scintillation technique. Liquid scintillation counting is a method of assay in which self-absorption and window absorption of nuclear radiation are eliminated by dissolving or suspending the sample in a scontillation liquid as described by Overman and Clark (1960). The samples to be counted were dissolved in a solution of toluene (the primary solvent which absorbs most of the energy of the beta particle and transfers the energy to the primary scintillator), 5-diphenyloxazole (the primary scintillator), 1, 4-bis-2-(4 methyl-5-phenyl-oxazolyl)-benzene (the secondary scintillator), and ethyl alcohol (a diluent which aids in the dissolution of the sample to be counted). These solutions are described in detail later.

The samples were counted in the Soils Laboratory in the Agriculture Department on the Columbia campus of the University of Missouri on a Packard model 3310 liquid scintillation spectrometer. The results of each count were automatically typed out on a Monroe digital printer.

For the standardization runs, the aqueous sodium chloride samples were evaporated to dryness and counted using a standard Gieger-Mueller detector and scaler. Due to the poor condition of the scalers used, each sample was counted in two different units and the results averaged.

B. Experimental Procedure.

The porous plates were first soaked in a solution of solute plus solvent until a constant concentration of solute was obtained throughout the porous plate. This soaking period varied from ten hours for a standardization run to three days for the highly viscous solvents. The time necessary to obtain a constant concentration of solute throughout the porous plate was decreased by heating the soaking solution to $50^{o}$to 70^{o}C.

After the porous plates were removed from the soaking solution and blotted to remove excess solution from the surfaces, they were mounted in the solvent baths. The solvent baths were then mounted in the constant temperature bath. The stirring plates were set in motion and approximately 300 milliliters of pure solvent were added to the bath. The initial time was recorded as the average of the initial pouring time and the final pouring time, usually ± 0.1 minutes.

During the course of the run, one milliliter samples were removed from the solvent baths and set aside for later counting. The number of samples removed during a run generally was twelve. This caused the volume of the solvent bath to decrease from 300 milliliters to about 288 milliliters.

Preliminary experiments showed that there was very little change in the rate of increase in solute concentration as the stirring speed was changed from 100 to 200 cycles per minute. Thus, this latter speed was used.

After each run, the cells were soaked in a very dilute solution (about 0.5 molar) of nitric acid for several hours, in several batches of distilled water for about five to eight hours each, and then dried at 110°C for twelve hours.

The standardization runs were performed at the beginning of this work and at the end to see if there was any significant change in the characteristics of the porous diffusion plates as a result of either rubbing of the stirring blades on the porous plates, adsorption of foreign material in the pores, or any other causes.

C. Measurements of Solvent Viscosities

Moore, (1967) determined the solvent viscosities of the glycols used in this work. The results obtained from his work are listed in Appendix A as well as in an unpublished report. The viscosities were measured using a series of modified Canon-Fenske capillary viscometers. The densities were also measured by Moore (1967) using a standard pycnometer. The temperature was controlled during the viscosity and density measurements to ± 0.02°C.

The thermometers used for both the diffusion coefficient measurements and the viscosity and density measurements were calibrated by Moore (1967) by using a National Bureau of Standards thermometer.

D. Description of Materials

1. Solvents. The solvents used include ethylene glycol, diethylene glycol, and propylene glycol and were donated for use in this project by the Dow Chemical Company. Each was further purified by vacuum distillation.

2. Solutes. The solutes ethylene glycol and cyclohexanol were C-14 tagged. Both were purchased from the New England Nuclear Corporation in

standard form.

The sodium chloride was obtained from the University of Missouri - Rolla, Department of Chemistry. For each standardization run 0.0195 gram of salt was irradiated in the University of Missouri - Rolla Nuclear Reactor Facility. The time the samples were irradiated varied from ten minutes to one hour depending upon core position, power and time elapsed before using.

3. Solutions for Measuring Diffusivities. The ethylene glycol came as a solution of 3.65 milligrams of ethylene glycol in methanol. To this was added about four milliliters of non-tagged ethylene glycol. The methanol was distilled off by applying an aspirator vacuum (approximately 20 millimeters of mercury) for forty minutes with stirring and heating up to about 35°C. One milliliter of this solution was then added to each of three battery jars containing 150 milliliters each of ethylene glycol, propylene glycol, and diethylene glycol. These solutions were then used to soak the porous plates in before each run when ethylene glycol was the solute. The concentration of ethylene glycol was $4.5(10)^{-2}$ moles per liter in the solvents propylene glycol and diethylene glycol. The concentration of C-14 tagged ethylene glycol in the non-active ethylene glycol was $3.6(10)^{-5}$ moles per liter.

The cyclohexanol comes in standard form as a solution in benzene. (In this case 5.40 mg/.094 ml of benzene). To this was added exactly 4 milliliters of nonradioactive cyclohexanol. The benzene was then removed under an aspirator vacuum. One milliliter of this solution was then added to each of three battery jars, each of which contained 200 milliliters of the appropriate solvent. The porous plates were then soaked in these solutions when cyclohexanol was the solute. This gave a concentration of 2.41×10^{-2} moles per liter of cyclohexanol in each of the three solvents. The fourth aliquots of both the ethylene glycol and cyclohexanol were kept for future work.

4. Scintillation Liquid. The scintillation liquid was made of toluene (spectro quality) purchased from Arthur Thomas Co. as the primary solvent with ethanol obtained from the University of Missouri - Rolla, Department of Chemistry as a diluent. The primary scintillator was PPO, and the secondary scintillator was Dimethyl-POPOP (both these were purchased from Packard Instrument Co.). Slightly different amounts of ethanol were used to dissolve each of the different solvents used as mentioned above. The scintillation liquid was made up of the following amounts as shown in Table B-I for the solvents shown, each in one liter of toluene.

5. Standardization Solutions. The solutions used for standardizing the cells were of sodium chloride in water. They were made up of 0.0195± .0003 grams of NaCl, which had been irradiated in the University of Missouri - Rolla Reactor Facility for about one hour, which was dissolved in 300 milliliters of distilled water. The porous plates were soaked overnight in this solution before the run was begun. These solutions had a concentration of 0.00111 moles of NaCl/liter.

E. Analysis of Data

1. Equations Describing Diffusion. The following is a development of the equations necessary for the analysis of data for diffusion of a solute out of

TABLE B-I

AMOUNTS OF ETHANOL, PPO, AND DIMETHYL-POPOP IN ONE LITER OF TOLUENE FOR SCINTILLATION COUNTING

Solvent	Milliliters of Ethanol	Grams of PPO	Grams of Dimethyl POPOP
Ethylene Glycol	250	4.40	0.1150
Propylene Glycol	160	3.71	0.1060
Diethylene Glycol	140	3.64	0.1040

a porous plate which is suspended in an initially pure solvent. Diffusion in only one direction out of the plate need be considered since the edges of the porous plates were sealed with an epoxy glue. The experimental conditions to be imposed such that the following equations are valid are:

1. For dilute solutions the diffusivity is not a function of concentration; thus all solutions will be less than 10^{-2} molar.
2. The diffusivity is a function of temperature, thus it will be controlled to ± 0.01°C.
3. The pores in the porous plate are small enough that any natural convection effects within the plate may be disregarded.
4. The bulk flow terms in the diffusion equations are negligible.
5. The solvent is stirred sufficiently fast so that there is no resistance to diffusion outside the porous plate.

Referring to Figure B-7, the equation for diffusion can be written

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

The subscripts AB are omitted from D in this section for simplicity.

With the boundary conditions:

1. For short time periods, i.e., $t \leqslant 0.3\ L_{eff}^{2}/D$

$$C(\infty, t) = C_o \tag{B-2}$$

2. The initial concentration in the porous plate is C_o

$$C(x, 0) = C_o \tag{B-3}$$

3. There is no resistance to diffusion outside the porous plate at x equal

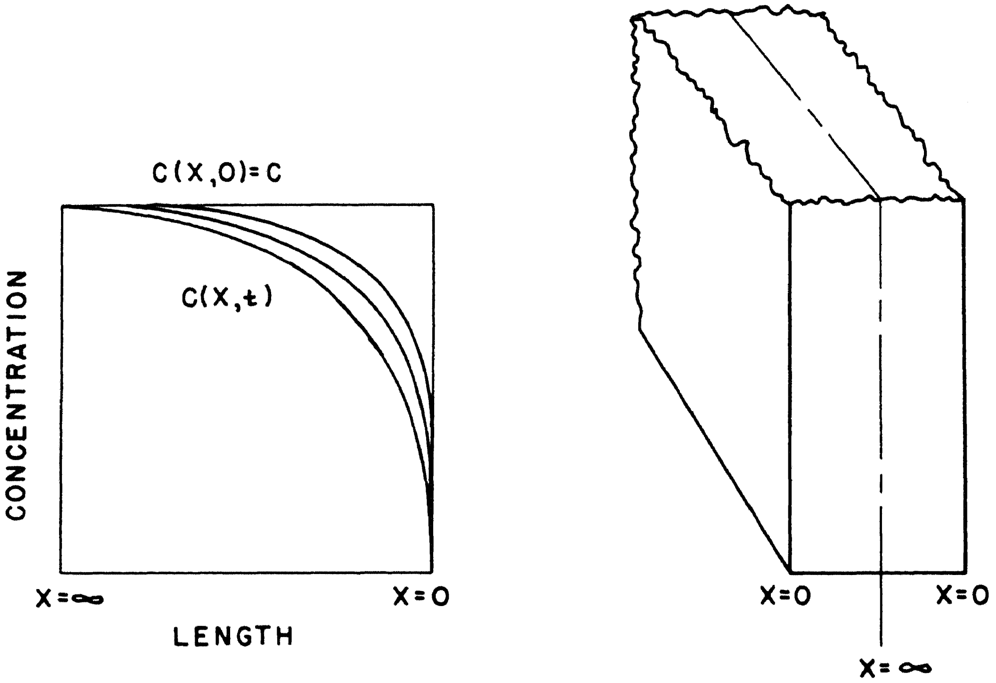

Figure B-7. Boundaries of porous plate and concentration profiles at times indicated.

zero

$$C(0, t) = C_f(t) \tag{B-4}$$

The equations describing the conditions in the solvent bath are

1. The amount of solute diffusing out of the porous plate may be accounted for by a material balance at the surfaces (i.e., x = 0) as:

$$V_f \frac{dC_f(t)}{dt} \equiv -2DA_T \frac{\partial C(0, t)}{\partial x} \tag{B-5}$$

2. If initially the concentration in the solvent bath is C_f^o, then

$$C_f(0) = C_f^o \tag{B-6}$$

Taking the Laplace transforms of equations B-1, B-2, B-4 and B-5 gives

$$s\bar{C}(x, s) - C_o = D\frac{d^2\bar{C}(x, s)}{dx^2} \tag{B-7}$$

$$\bar{C}(\infty, s) = C_o/s \tag{B-8}$$

$$\bar{C}(0, s) = \bar{C}_f(s) \tag{B-9}$$

$$V_f(s\bar{C}_f(s) - C_f^o) = -2DA_T\frac{d\bar{C}(0, s)}{dx} \tag{B-10}$$

The Laplace transform of equation B-1 was taken without justification that the Laplace transform of the second derivative of C(x, t) with respect to x is equal to the second derivative of the Laplace transform of C(x, t) with respect to x. This cannot be justified since the function C(x, t) is unknown. Justification of the final function will be made with respect to the boundary conditions to show that they are satisfied. The total solution of Equation B-7 becomes

$$\overline{C}(x, s) = A_1' \exp(-\sqrt{s/D}\,x) + A_2' \exp(\sqrt{s/D}\,x) + C_o/s \qquad \text{(B-11)}$$

From Equation B-8, $A_2' = 0$. Thus the total solution reduces to

$$\overline{C(x, s)} = A_1' \exp(-\sqrt{s/D}\,x) + C_o/s \qquad \text{(B-12)}$$

The derivative of Equation B-12 with respect to x is

$$d\overline{C}(x, s)/dx = -\sqrt{s/D}\; A_1' \exp(-\sqrt{s/D}\,x) \qquad \text{(B-13)}$$

By introducing Equation B-12 into Equation B-9 and the result along with Equation B-13 into Equation B-10, the resulting equation can be solved for A_1' to give

$$A_1' = (C_f^o - C_o)/ \left[(2A_T D\sqrt{s/D}\,/V_f) + s\right] \qquad \text{(B-14)}$$

Introducing Equation B-14 into Equation B-13 and the result into B-10 gives

$$V_f\,(s\overline{C}_f(s) - C_f^o) = V_f K\sqrt{s}\,(C_f^o - C_o)/(K\sqrt{s} + s) \qquad \text{(B-15)}$$

where

$$K = 2A_T\sqrt{D}/V_f \qquad \text{(B-16)}$$

Rearranging gives

$$\overline{C}_f(s) = C_f^o/s + (C_f^o - C_o)/\,s(1 + K^{-1}\sqrt{s}) \qquad \text{(B-17)}$$

The inverse Laplace transform is given in the Handbook of Chemistry and Physics (1965) as

$$C_f(t) = C_o + (C_f^o - C_o)\exp(K^2 t)\,\mathrm{erfc}(K\sqrt{t}) \qquad \text{(B-18)}$$

or

$$C_f(t) = C_o + (C_f^o - C_o)\exp(K^2 t)(1. - \mathrm{erf}(K\sqrt{t})) \qquad \text{(B-19)}$$

Equation B-19 at t=0 gives the value of C_f as C_f^o. Thus, this satisfies the boundary conditions. This equation is good for short diffusion times, and when rearranged takes the form

$$\frac{C_o - C_f}{C_o - C_f^o} = \exp(K^2 t)(1 - \mathrm{erf}(Kt^{\frac{1}{2}}) \qquad \text{(B-20)}$$

Holander and Barker (1963) have shown that a much more simple equation can be obtained when the concentration outside of the porous plate is assumed to be the same as the initial concentration outside the porous plate. The boundary conditions for Equation B-1 are now

1. For short time periods,

$$c(\infty, t) = C_o \qquad \text{(B-2)}$$

2. The initial concentration in the porous plate is C_o

$$C(x, 0) = C_o \qquad \text{(B-3)}$$

3. If there is no resistance to diffusion outside the porous plates (at x = 0)

$$C(0, t) = C_f^o \qquad \text{(B-21)}$$

Taking the Laplace transform of Equations B-1, B-2, and B-21 gives

$$s\bar{C}(x, s) - C_o = D\frac{d^2\bar{C}(x, s)}{dx^2} \qquad \text{(B-7)}$$

$$\bar{C}(\infty, s) = C_o/s \qquad \text{(B-8)}$$

and

$$\bar{C}(0, s) = C_f^o/s \qquad \text{(B-22)}$$

The total solution of Equation B-7 is again

$$\bar{C}(x, s) = A_1' \exp(-\sqrt{s/D}\, x) + A_2' \exp(\sqrt{s/D}\, x) + C_o/s \qquad \text{(B-11)}$$

From equation B-8, A_2' is zero and

$$\bar{C}(x, s) = A_1' \exp(-\sqrt{s/D}\, x) + C_o/s \qquad \text{(B-12)}$$

From Equation B-22

$$A_1' = (C_f^o - C_o)/s \tag{B-23}$$

Thus, $\overline{C}(x, s)$ is

$$\overline{C}(x, s) = s^{-1}(C_f^o - C_o) \exp(-\sqrt{s/D}\, x) + C_o/s \tag{B-24}$$

The inverse Laplace transform of B-24 is given in the Handbook of Chemistry and Physics (1965) as

$$c(x,t) = C_o + (C_f^o - C_o)\left[1. - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right] \tag{B-25}$$

The material balance

$$\frac{dC_f(t)}{dt} = -2DA_T \frac{C(0,t)}{x} \tag{B-26}$$

can now be solved by introducing Equation B-26 to give

$$C_f = C_f^o + \frac{4A_T C_o \sqrt{D/\pi}}{V_f} \sqrt{t} \tag{B-27}$$

Equation B-27 at t = 0 gives the value of C_f as C_f^o. Thus, this satisfies the boundary conditions. This equation and Equation B-20 are only valid when the product Dt/L_{eff}^2 is equal to or less than 0.3. This is due to the choice of the boundary condition that C(x, t) does not change at $x = \infty$ (i.e. the center of the diffusion cell, where x really is equal to L_{eff}).

Equation B-27 can be considered a linear approximation to Equation B-20 and can be used without prior knowledge of the parameters to be obtained during the least squares analysis. It will be used only to obtain an estimate of C_f^o and D (or A_T, whichever is unknown). These estimates will then be used to enter the nonlinear least squares analysis of Equation B-20 for C_f^o and D (or A_T, whichever is unknown). The details of the least squares analysis and the program used is given later.

2. Conversion of Activity Data to Concentration Data. The activity data obtained for a standardization or diffusivity measurement were corrected only by subtracting the measured background. It was not necessary to correct for counting efficiency for the samples taken for the standardization runs because the geometry for each count was the same. Correction for self absorption of sodium chloride was negligible due to the very dilute solutions that were sampled. The decay of Na-24 is sufficiently fast (half life of 15.0 hours) that it was necessary to allow for decay time. The radioactive decay was accounted for by multiplying the measured activity less the background by

$$\exp \frac{0.693\ t}{t_{\frac{1}{2}}}$$

where t is the time elapsed from the beginning of the run to the time the sample was counted. The half life used for the decay correction ($t_{\frac{1}{2}} = 15.0$ hours) was measured since it was possible, upon irradiation of the sodium chloride sample, to obtain radioactive species other than Na-24.

The counting efficiency in liquid scintillation spectrometers varies with the concentration of diluent, and with the concentration of the primary and secondary scintillators. To avoid the necessity of correcting for slight variations in the concentration of these materials, enough of the solution was prepared to add to all the samples for each run.

The initial concentration inside the porous plate is known for the sample that is taken from the soaking cell. The concentrations of all samples removed from the solvent bath were obtained readily since the activity is directly proportional to the concentrations.

3. Method of Least Squares Analysis. Equation B-27 may be used with the concentration data directly for very short time periods to obtain an initial estimate of the diffusivity (or the area of mass transfer in the case of a standardization run). To perform this technique, the concentration versus the square root of time is fit by least squares to a straight line. The slope of this line is

$$\frac{4A_T C_o \sqrt{D}}{\sqrt{\pi} V_f}$$

and the intercept at time equals zero is assumed to equal C_f^o.

The average value of V_f was used in this and all subsequent analyses. This average value was calculated as follows

$$V_f = 300.0 - N/2 \tag{B-28}$$

For these experiments, 300 milliliters of solvent were added during each run and N is the number of data points used in the analysis. The use of an average value of V_f will lead to slightly erroneous results. However, the error introduced by this should be less than 3 or 4% since the true volume is in the worst case 292 ± 8 milliliters.

The number of data points to be used was determined in the following manner. Equations B-20 and B-27 are valid as long as the time for which the diffusion was allowed to occur did not exceed

$$t \leq 0.3 L_{eff}^2 / D \tag{B-29}$$

The effective value of L was approximated by Wu (1968) by using a nonlinear, three variable, least square fitting technique with the following equation:

$$\frac{C_f - C_o}{C_o - C_f^o} = \frac{1}{1 + \alpha} - \sum_{n=1}^{\infty} \frac{\exp(-Db_n^2 t/L_{eff}^2)}{(1 + \alpha + \alpha^2 b_n^2)} \tag{B-30}$$

In this equation, b_n is the nth root of the equation

$$\tan b_n = \alpha b_n \tag{B-31}$$

and α is the volume of the liquid surrounding the plate divided by the volume of the porous plate that is occupied by the liquid.

In his work, Wu assumed C_f^o, L_{eff}, and α were all unknown for the standardization runs. An average value of L_{eff} was found by him to be 0.544 and was used to determine the number of terms to be used in the analysis of a standardization run in this work. For the diffusivity determination runs, the values of L_{eff} as calculated by Wu varied considerably from run to run. Thus, the value that he obtained for each individual run was used. These values are listed with the results for each run in Tables B-IV through B-IX.

The values of the diffusivity obtained by Wu (1968) were used as the initial values to estimate t in Equation B-29.

Equation B-20 may be written in the following form

$$C_{f_i} = C_o + (C_f^o - C_o) \exp\left[\frac{4DA_T^2 \pi t_i}{V_f^2}\right]\left[1. - \operatorname{erf} \frac{2A_T\sqrt{Dt_i}}{V_f}\right] \tag{B-32}$$

where C_{f_i} is the actual experimentally measured value of the concentration at the time t_i.

For the following analysis, the two parameters that will be determined by least squares technique are C_f^o and A_T. Since Equation B-32 is not linear in the parameters, a nonlinear least squares analysis was used. This analysis requires an iterative technique.

The initial values of A_T will be denoted by A_T^o, and the initial value of C_f^o will be denoted by C_f^{oo}. If A_T^o and C_f^{oo} are substituted into Equation B-32, the result will be an approximate value of C_{f_i}, C'_{f_i}, which is given by

$$C'_{f_i} = C_o + (C_f^{oo} - C_o) \exp\left[\frac{4DA_T^{o\,2}\, t_i}{V_f^2}\right]\left[1. - \operatorname{erf} \frac{2A_T^o\sqrt{Dt}}{V_f}\right] \qquad \text{(B-33)}$$

The residuals or differences for each data point, i, of the actual value of C_{f_i} from the approximate value, C'_{f_i}, are then

$$r_i = C_{f_i}(t_i, C_f^o, A_T) - C_{f_i} \qquad \text{(B-34)}$$

where C'_{f_i} is given by Equation B-33. Letting δA_T be a small correction to the initial value of A_T, A_T^o, such that

$$A_T = A_T^o + \delta A_T \qquad \text{(B-35)}$$

and similarly for C_f^o, such that

$$C_f^o = C_f^{oo} + \delta C_f^o \qquad \text{(B-36)}$$

then Equation B-34 for the residual terms becomes

$$C_{f_i} + r_i = C'_{f_i}(t_i, C_f^{oo} + \delta C_f^o, A_T^o + \delta A_T) \qquad \text{(B-37)}$$

By considering the right hand side of Equation B-33 as a function of A_T and C_f^o, the following Taylor series expansion can be applied to Equation B-37 to give

$$C_{f_i} + r_i = C'_{f_i}(t_i, C_f^{oo}, A_T^o) + \left(\frac{\partial C_{f_i}}{\partial C_f^o}\right)_o \delta C_f^o + \left(\frac{\partial C_{f_i}}{\partial A_T}\right)_o \delta A_T \qquad \text{(B-38)}$$

The subscript o means a quantity is evaluated at t_i, A_T^o and C_f^{oo}. All the second and higher order terms in the Taylor series expansion have been neglected.

Each data point may be described by Equation B-38. The resulting equations are linear in the correction terms δC_f^o and δA_T and may be handled in a manner similar to any other linear equation containing two unknown variables.

Once the correction terms are evaluated by applying the linear least squares technique to Equation B-32. The new values of A_T and C_f^o, namely

$$A_T = A_T^o + \delta A_T \tag{B-39}$$

and

$$C_f^o = C_f^{oo} + \delta C_f^o \tag{B-40}$$

may be substituted back into Equation B-38 for A_T^o and C_f^{oo} and the process repeated. The process may be repeated as many times as is necessary to allow the correction terms δA_T and δC_f^o to approach zero.

Since all the data were obtained by counting a radioactive sample for a specified time, the probable error for each sample or data point is different. Thus each data point should carry a different weight during the least square fitting technique. This is simply accomplished by multiplying the residual (as determined by Equation B-34) by an appropriate weighting factor.

The probable error for a total count of a radioactive sample is equal to the square root of that count. Since the concentrations were obtained by merely multiplying the total count by a constant for any one run, the probable error of the concentration terms is also approximately equal to the square root of the concentration. (This is true for all the diffusivity determination runs since all of the samples were counted for the same length of time and for most of the standardization runs).

The relation between the probable error and the proper weighting factor is shown by Scarborough (1962) to be:

$$\text{weighting factor} = 1/(\text{probable error})^2$$

Thus a weighting factor of this type was used. Since the probable error is equal to the square root of the count, the weighting factor becomes,

$$\text{weighting factor} = 1/\text{count}$$

Radioactive decay is a statistical process. For this reason some total counts that are measured for a short period of time may be excessively lower (and others excessively higher) than the true or mean count rate for that period. The weighting factor as given above could conceivably be wrong for counts that are measured for a short time period. To avoid this possibility, the counts were all measured for a sufficient length of time (viz. from several minutes for high activity samples up to one hour for low activity samples). Most samples were counted for five minutes.

The actual program used to determine the area of mass transfer for a standardization run with the input data and the results are given below.

F. Experimental Results

The results shown in this section will include the results obtained from the standardization runs as well as the results of the experimentally measured diffusion coefficients.

```
$ID     YGW0645 R.MITCHELL    DIFFUSIVITY
$ID     YGW0645 R.MITCHELL    DIFFUSIVITY
$TCP            TIME=3,PAGES=45
$IBJOB          GO
$IBFTC MAIN     LIST,DECK
      DIMENSION  DATA(20,3),A(5),DA(2),LIST(4),D2SQ(20)
      EXTERNAL STNI
      EXTERNAL STDZ
      DO 11 KKK=1,19
      READ(5,101)     NTOT,NRUN,NSOU,NSOV,TEMP
C.....NTOT IS THE NUMBER OF DATA POINTS.
C.....NRUN IS THE NUMBER OF THE RUN.
C.....NSOU IS THE NUMBER OF THE SOLUTE.
C.....NSOV IS THE NUMBER OF THE SOLVENT.
C.....TEMP IS THE TEMPERATURE OF THE RUN IS DEG C.
      READ(5,100)(DATA(I,2),DATA(I,1),I=1,NTOT)
C.....DATA(I,2) IS THE TIME THE SAMPLE WAS REMOVED FROM THE BATH IN SECONDS.
C.....DATA(I,1) IS THE MOLAR CONCENTRATION OF THE SAMPLE.
      READ (5,101) LIST(1)
C.....LIST(1) IS THE NUMBER OF DATA POINTS USED IN THE ANALYSIS.
      READ(5,100)(A(I),I=1,5)
C.....A(1) IS THE INITIAL CONCENTRATION IN THE BATH.
C.....A(2) IS THE DIFFUSIVITY.
C.....A(3) IS THE INITIAL CONCENTRATION IN THE POROUS PLATE.
C.....A(4) IS THE AREA OF MASS TRANSFER.
C.....A(5) IS THE AVERAGE VOLUME IN THE SOLVENT BATH.
      READ(5,100) XKZ
C.....XKZ IS THE COUNT OF THE LAST DATA POINT READ IN.
      DO 15 I=1,NTOT
      DATA(I,3)=DATA(NTOT,1)/XKZ
C.....DATA(I,3) IS THE RATIO OF THE CONCENTRATION TO THE COUNT.
      IF(5514.3-DATA(I,2))14,14,13
   13 LIST(1)=I
   14 CONTINUE
      D2SQ(I)=SQRT(DATA(I,2))
C.....D2SQ IS THE SQUARE ROOT OF THE TIMEAT WHICH THE SAMPLE WAS REMOVED
C     FROM THE BATH.
   15 DATA(I,1)=1.11*DATA(I,1)
      XXX=LIST(1)
      A(5)=300.0-(XXX/2.)
      A(3)=1.11*A(3)
      WRITE(6,109) NRUN,NSOU,NSOV,TEMP
      WRITE(6,110)(DATA(I,1),DATA(I,2),D2SQ(I),I=1,NTOT)
      WRITE(6,105) DATA(1,3)
      LIST(2)=2
C.....LIST(2) IS THE NUMBER OF VARIABLES BEING FITTED.
      LIST(3)=2
C.....LIST(3) IS THE NUMBER OF ITERATIONS ALLOWED OR PERFORMED.
      LIST(4)=0
C.....LIST(4) IS THE ERROR SIGNAL.
      CALL FITALL(STNI,DATA,A,DA,Q,LIST)
      WRITE(6,111)
      WRITE(6,120) LIST(1)
      WRITE(6,112) A(1)
      WRITE(6,113) A(2)
      WRITE(6,114) A(3)
      WRITE(6,115) A(4)
      WRITE(6,116) A(5)
      WRITE(6,117)
```

```
      LIST(2)=2
      LIST(3)=10
      LIST(4)=0
      WRITE(6,120) LIST(1)
      CALL FITALL(STDZ,DATA,A,DA,Q,LIST)
      WRITE(6,118) A(1)
      WRITE(6,119) A(2)
      WRITE(6,123)XL
      WRITE(6,122)  LIST(3)
      SUM=0.0
      NJA=LIST(1)
      DO 10  J=1,NJA
      R=A(1)+(2.*A(3)*A(2)*SQRT(DATA(J,2)/(A(4)*3.14159))/A(5))*A(4)*2.-
     2DATA(J,1)
   10 SUM=SUM+(ABS(R)/DATA(J,1))
      XJA=LIST(1)
      SUM=100.*SUM/XJA
C....SUM IS THE AVERAGE ABSOLUTE DEVIATION OF THE RESIDUALS.
      WRITE(6,106) SUM
      WRITE(6,108) DA(1)
C.....DA(1) IS THE STANDARD DEVIATION OF THE INITIAL CONCENTRATION IN THE BATH.
      WRITE(6,107)  DA(2)
C.....DA(2) IS THE STANDARD DEVIATION OF THE DIFFUSIVITY.
      WRITE (6,121) LIST(4)
   11 CONTINUE
      STOP
  100 FORMAT (2F18.8)
  101 FORMAT (4I5,F14.7)
  105 FORMAT(9X,26HCONCENTRATION/COUNT RATIO=,E18.8)
  106 FORMAT(9X,36HAVERAGE ABSOLUTE PERCENT DEVIATION =,E18.8)
  107 FORMAT(9X,41HSTANDARD DEVIATION OF MASS TRANSFER AREA=,E18.8)
  108 FORMAT (9X,52HSTANDARD DEVIATION OF INITIAL CONCENTRATION IN BATH=
     2,E18.8)
  109 FORMAT(1H1,9X,4HRUN=,I4,4X,7HSOLUTE=,I4,4X,8HSOLVENT=,I4,4X,
     212HTEMPERATURE=,F14.7)
  110 FORMAT(9X,14HCONCENTRATION=,E18.8,4X,5HTIME=,E18.8,4X,9HTIME**.5=,
     2E18.8)
  111 FORMAT(16X,48HPARAMETERS AND INITIAL VALUES FROM EQUATION 3.10)
  112 FORMAT(9X,30HINITIAL CONCENTRATION IN BATH=,E18.8)
  113 FORMAT (9X,22HAREA OF MASS TRANSFER=,E18.8)
  114 FORMAT(9X,38HINITIAL CONCENTRATION IN POROUS PLATE=E18.8)
  115 FORMAT(9X,12HDIFFUSIVITY=,E18.8)
  116 FORMAT(9X,32HAVERAGE VOLUME IN SOLVENT BATH =,E18.8)
  117 FORMAT (20X,20HRESULTS FROM EQN 3.9)
  118 FORMAT(9X,22HINITIAL CONC. IN BATH=,E18.8)
  119 FORMAT(9X,22HAREA OF MASS TRANSFER=,E18.8)
  120 FORMAT(9X,14HNO. OF TERMS =,I5)
  121 FORMAT (9X,13HERROR SIGNAL=,I5)
  122 FORMAT(9X,21HNUMBER OF ITERATIONS=,I5)
  123 FORMAT (9X,18HEFFECTIVE LENGTH =,E18.8)
      END
$IBFTC STND     LIST,DECK
      SUBROUTINE STDZ(R,DATA,A,DA,DY,N,J)
      DIMENSION  DATA(20,2),A(5),DA(2)
      X=DATA(J,2)
      Y=DATA(J,1)
C.....X AND Y ARE DUMMY VARIABLES USED ONLY TO PRESERVE THE DATA.
      DY=Y*DATA(J,3)
C.....DY IS THE VARIANCE OF THE CONCENTRATION.
```

```
      R=2.*A(2)*SQRT(A(4)*X)/A(5)
      DA(1)=EXP(R**2)*(1.-ERF(R))
      DA(2)=(A(1)-A(3))*((2.*R*R*DA(1)/A(2)) -(1.128379*R/A(2)))
C.....DA(1) AND DA(2) ARE THE PRATIAL DERIVATIVES OF THE REDIDUAL WITH
C     RESPECT TO THE INITIAL CONCENTRATION IN THE BATH AND THE MASS
C     TRANSFER AREA RESPECTIVELY
      R=(A(3)+((A(1)-A(3))*DA(1)))-Y
C.....R IS THE RESIDUAL OR THE FUNCTION LESS THE EXPERIMENTAL
C     VALUE OF THE CONCENTRATION
      RETURN
      END
$IBFTC STIN     LIST,DECK
      SUBROUTINE STNI(R,DATA,A,DA,DY,N,J)
      DIMENSION  DATA(20,2),A(5),DA(2)
      X=DATA(J,2)
      Y=DATA(J,1)
C.....X AND Y ARE DUMMY VARIABLES USED ONLY TO PRESERVE THE DATA.
      DY=Y*DATA(J,3)
C.....DY IS THE VARIANCE OF THE CONCENTRATION.
      DA(1)=1.0
      DA(2)=4.*A(3)*SQRT(A(4)*X/3.14159)/A(5)
C.....DA(1) AND DA(2) ARE THE PRATIAL DERIVATIVES OF THE REDIDUAL WITH
C     RESPECT TO THE INITIAL CONCENTRATION IN THE BATH AND THE MASS
C     TRANSFER AREA RESPECTIVELY
      R=A(1)+DA(2)*A(2)-Y
C.....R IS THE RESIDUAL OR THE FUNCTION LESS THE EXPERIMENTAL
C     VALUE OF THE CONCENTRATION
      RETURN
      END
$IBFTC FITS     LIST,DECK
      SUBROUTINE FITALL(RESID,X,P,DP,Q,LIST)
      DIMENSION P(1), DP(1), LIST(4), A(20,20), S(403), BB(20)
      DOUBLE PRECISION B(20), SUM
      EQUIVALENCE (S,KK),(S(2),NFIX),(S(3),KSIG),(S(4),A),(B,BB)
      DATA MAX,MMAX,CONV/20,403,0.001/
C.....INITIALIZE
      JJ=LIST(1)
      KK=LIST(2)
      LOOPS=LIST(3)
      LIST(3)=0
      NFREE=JJ-KK
      IF(LOOPS.EQ.0) GO TO 10
      MOST=2*KK
      IF(KK.LT.1.OR.NFREE.LT.0) GO TO 14
      IF(KK.GT.MAX) GO TO 15
C.....BEGIN ITERATION LOOP
    1 NFIX=KK
      DO 2 N=1,MAX
      B(N)=0.0
      DO 2 M=1,MAX
    2 A(M,N)=0.0
      DO 6 J=1,JJ
      CALL RESID(R,X,P,DP,VAR,KK,J)
      IF(VAR.NE.0.0) GO TO 4
      NFIX=NFIX+1
      IF(NFIX.GT.MAX) GO TO 15
      IF(NFIX.GT.MOST) GO TO 14
C.....CALCULATE FIX POINT ELEMENTS
      B(NFIX)=R
```

```
      DO 3  M=1,KK
      A(M,NFIX)=DP(M)
    3 A(NFIX,M)=DP(M)
      GO TO 6
C.....CALCULATE REGULAR POINT
    4 DO 5 N=1,KK
      B(N)=B(N)+R*DP(N)/VAR
      DO 5  M=N,KK
    5 A(M,N)=A(M,N)+DP(M)*DP(N)/VAR
    6 CONTINUE
C.....FINISH OFF MATRIX
      DO 7 N=1,KK
      DO 7 M=N,KK
    7 A(N,M)=A(M,N)
C.....INVERT MATRIX
      KSIG=0
      CALL MATINV(A,NFIX,KSIG)
      IF(KSIG.EQ.1.OR.KSIG.EQ.2) GO TO 16
      IF (LOOPS.EQ.-1) GO TO 10
C.....CALCULATE NEW VALUES OF PARAMETERS
      BIG=0.0
      DO 9 M=1,KK
      SUM=0.0
      DO 8  N=1,NFIX
    8 SUM=SUM-A(M,N)*B(N)
      DP(M)=SUM
      P(M)=P(M)+SUM
    9 BIG=BIG+AMAX1(ABS(SUM)-CONV*ABS(P(M)),0.0)
      LIST(3)=LIST(3)+1
      IF(BIG.EQ.0.0) GO TO 10
      IF(LIST(3).GE.LOOPS) GO TO 17
      GO TO 1
C.....CONVERGENCE ACHIEVED -- COMPUTE VARIANCES
   10 IF(LOOPS.EQ.1) GO TO 18
      Q=0.0
      IF(NFREE.EQ.0) GO TO 12
      SUM=0.0
      DO 11 J=1,JJ
      CALL RESID(R,X,P,DP,VAR,KK,J)
      IF(VAR.EQ.0.0) GO TO 11
      SUM=SUM+R*R/VAR
   11 CONTINUE
      Q=SQRT(SNGL(SUM)/FLOAT(NFREE))
   12 DO 13 K=1,KK
   13 DP(K)=SQRT(ABS(A(K,K)))
      IF(KSIG.NE.0) GO TO 19
      RETURN
   14 LIST(4)=LIST(4)+1
   15 LIST(4)=LIST(4)+1
   16 LIST(4)=LIST(4)+1
   17 LIST(4)=LIST(4)+1
   18 LIST(4)=LIST(4)+1
   19 LIST(4)=LIST(4)+1
      RETURN
C.....ENTRY FOR SAVING MATRIX
      ENTRY FITSAV(HOLD)
      DIMENSION HOLD(1)
      DO 20 N=1,MMAX
   20 HOLD(N)=S(N)
```

```
      RETURN
C.....ENTRY FOR RESTORING SAVED MATRIX
      ENTRY FITBAK(HELD)
      DIMENSION HELD(1)
      DO 21 N=1,MMAX
   21 S(N)=HELD(N)
      RETURN
C.....ENTRY FOR VARIANCE OF RESIDUAL AT XX FOLLOWS
      ENTRY FITVAR(FUNC,XX,PAR,RES,DRES,L)
      CALL FUNC(RES,XX,PAR,BB,VAR,KK,L)
      VAR=0.0
      DO 23 K=1,KK
      SUM=0.0
      DO 22 N=1,KK
   22 SUM=SUM+A(K,N)*BB(N)
   23 VAR=VAR+SUM*BB(K)
      DRES=SQRT(ABS(VAR))
      RETURN
      END
```

```
 RUN=    1      SOLUTE=     2      SOLVENT=     1      TEMPERATURE=     25.0
CONCENTRATION=      0.30630491E-05          TIME=        0.10200000E 02
CONCENTRATION=      0.40487843E-05          TIME=        0.27000000E 02
CONCENTRATION=      0.36149085E-05          TIME=        0.42000000E 02
CONCENTRATION=      0.66381519E-05          TIME=        0.19199999E 03
CONCENTRATION=      0.10483953E-04          TIME=        0.49200000E 03
CONCENTRATION=      0.13302548E-04          TIME=        0.84000000E 03
CONCENTRATION=      0.16425219E-04          TIME=        0.13560000E 04
CONCENTRATION=      0.19105843E-04          TIME=        0.20280000E 04
CONCENTRATION=      0.24144401E-04          TIME=        0.32460000E 04
CONCENTRATION=      0.27595536E-04          TIME=        0.41460000E 04
CONCENTRATION=      0.29989435E-04          TIME=        0.51419999E 04
CONCENTRATION=      0.29853037E-04          TIME=        0.60419999E 04
CONCENTRATION=      0.29714181E-04          TIME=        0.69419999E 04
CONCENTRATION=      0.33790732E-04          TIME=        0.78420000E 04
CONCENTRATION=      0.37246194E-04          TIME=        0.87420000E 04
CONCENTRATION=      0.37982825E-04          TIME=        0.96420000E 04
CONCENTRATION=      0.40054215E-04          TIME=        0.10541999E 05
CONCENTRATION=      0.42009882E-04          TIME=        0.11442000E 05
CONCENTRATION=      0.42493771E-04          TIME=        0.12443999E 05
CONCENTRATION=      0.51539584E-04          TIME=        0.63120000E 05
CONCENTRATION/COUNT RATIO=    0.40837342E-08
          PARAMETERS AND INITIAL VALUES FROM EQUATION B-27
NO. OF TERMS = 11
INITIAL CONCENTRATION IN BATH=     0.15648379E-05
AREA OF MASS TRANSFER=    0.11644274E 02
INITIAL CONCENTRATION IN POROUS PLATE=    0.11100000E-02
DIFFUSIVITY=      0.16100000E-04
AVERAGE VOLUME IN SOLVENT BATH=     0.29450000E 03
                RESULTS FROM EQN B-33
NO. OF TERMS = 11
```

```
INITIAL CONC. IN BATH=        0.15194262E-05
AREA OF MASS TRANSFER=    0.11865972E 02
EFFECTIVE LENGTH =      -0.00000000E-19
NUMBER OF ITERATIONS=       2
AVERAGE ABSOLUTE PERCENT DEVIATION =        0.44057584E 01
STANDARD DEVIATION OF INITIAL CONCENTRATION IN BATH=        0.72612161E-07
STANDARD DEVIATION OF DIFFUSIVITY=        0.90748133E-01
ERROR SIGNAL=        1
```

1. Standardization. The data obtained from the standardization runs are summarized in Table B-II as runs numbered 1 through 14 and 105 through 110. These summarized results include the run number, the number of data points used in the analysis and the corresponding average solvent bath volume, the initial concentration of the solute in the bath and its standard deviation, the area of mass transfer and its standard deviation, and the average absolute percent deviation of the residuals. For this latter term the percent deviation of the residuals is defined by,

$$\text{DEV} = 100\% \left| \frac{C_{f_i} - C'_{f_i}}{C_{f_i}} \right| \qquad \text{(B-41)}$$

All of the standardization runs were performed at 25.0°C were the diffusion coefficient of sodium chloride is $(0.161 \pm .001) \times 10^{-5}$ square centimeters per second (Harned and Owen, 1958).

The results obtained for the standardization runs are also summarized in Table B-III. The areas determined show agreement to ± 5% for any one cell. The runs numbered one through fourteen were performed at the beginning of this project and those numbered 105 through 110 at the end. The values of the area of mass transfer do not show any trends either increasing or decreasing. This indicates that during the course of this work the pores in the plates did not significantly collect any foreign particles.

While counting the samples taken from these standardization runs, it was noticed that periodically the counters being used would malfunction. This was usually noticed by an unusual drift in the count rate obtained for one sample of a series of samples. To minimize the possibility of errors

TABLE B-II

RESULTS FOR THE STANDARDIZATION RUNS

Run Number	Cell No.	Average Volume in Solvent Bath, cm^3	Number of Data Points	Initial Concentration in Bath mole/liter	Standard Deviation of Initial Concentration	Area of Mass Transfer cm^2	Standard Deviation of Area	Average Percent Deviation of Residuals
				x10^5	x10^6			
1	1	294.5	11	0.1519	0.0726	11.87	0.0907	4.41
2	1	294.5	11	0.1270	0.1130	12.12	0.1443	5.41
3	2	294.5	11	0.1424	0.1231	14.14	0.1565	15.86
4	3	295.0	10	-0.0421	0.1233	11.70	0.1565	6.65
5	2	294.5	11	-0.1018	0.0587	12.74	0.1189	13.56
6	3	295.0	10	-0.1223	0.0949	13.01	0.1125	5.66
7	4	294.5	11	-0.0318	0.0705	12.79	0.1125	7.33
8	4	294.5	11	-0.0168	0.1063	11.46	0.1581	9.83
9	5	294.5	11	-0.0826	0.0781	12.14	0.1419	10.11
10	5	294.5	11	-0.0915	0.0742	10.20	0.1398	15.10
12	1	294.5	11	-0.0736	0.0488	12.62	0.0953	6.34
13	6	294.5	11	-0.0955	0.0594	10.98	0.1287	10.87
14	6	294.5	11	-0.1452	0.0280	10.38	0.0880	5.34
105	1	295.5	9	-0.0280	0.1519	11.51	0.2141	7.59
106	2	295.0	10	-0.1014	0.1303	10.87	0.1826	6.44
107	6	295.5	9	-0.2746	0.1561	11.90	0.2398	2.18
108	3	296.0	8	-0.0328	0.1526	11.18	0.2144	4.49
109	4	296.0	8	0.0604	0.0718	11.51	0.0858	6.54
110	5	296.0	8	-0.1282	0.1137	14.58	0.1438	5.74

Solute NaCl
Solvent Water
Temperature 25.0°C
Diffusivity = $0.161(10)^{-4}$ cm^2/sec
Initial concentration of porous plate = 0.0111 moles/liter
Effective length = 0.544 cm (Wu, 1968)

TABLE B-III

STANDARDIZATION RESULTS

SUMMARIZED

Cell Number	Average Area of Mass Transfer, cm^2
1	12.03 ± 0.6
2	12.59 ± 1.6
3	11.96 ± 1.1
4	11.92 ± 0.9
5	12.31 ± 2.3
6	11.09 ± 0.9
Average of Cells:	11.98

obtained from these drifts, each sample was counted by two different counters in rapid succession. Likewise, the samples taken during the diffusivity determination runs were counted twice; however, the liquid scintillation counter used for these samples did not show this drift. This unusual drift in the count rate was probably due to the poor counters used as they were very old.

During the data analysis of the diffusivity determination runs it was noticed, by Wu (1968), that if the individual cell average area of mass transfer was used, the results did not yield a smooth Arrhenius activation energy plot of the calculated diffusivities versus reciprocal temperature. On the other hand, if the average area for all cells was used, the determined diffusivities gave a smooth Arrhenius activation energy plot. This indicates that some error was introduced during the standardization runs that was not introduced during the diffusivity determination runs. That error is probably due to the counters used as indicated above. Thus, the average area of mass transfer of 11.98 square centimeters as shown in Table B-III was used in the data analysis for all of the diffusivity determination runs.

This average area should be very close for all cells as they were all made to the same dimensions. The use of this average probably limits the accuracy of the experimentally determined diffusivities to approximately ten percent or more.

The results obtained for the area of mass transfer from the analysis by Equations B-20 and B-27 differ in most cases by less than 10%. The results of the data analysis obtained from Equation B-20 will be used here since this equation was developed by including the effects of the solute concentration increase in the solvent bath.

2. Diffusivities. The data obtained from these runs are summarized in Tables B-IV through B-IX and appear as runs 50 through 104. Shown with other data for each run are the values of the diffusivity and the initial concentrations obtained from the least squares analysis of Equation B-20. The experimentally measured diffusion coefficients at the given temperatures are summarized in Table B-X. The activation energies and the free energies of activation for each temperature are also given in Table B-X for each system. The diffusion coefficients shown in Table B-X are the average values of all the runs made for any specified solvent-solute system at the temperature indicated.

Figures B-8 and B-9 show the variation of the binary diffusion coefficients as a function of reciprocal temperature. The activation energies given in Table B-X are calculated from these data. The activation energies vary from 4.48 to 9.92 Kcal/mole. On the other hand, the free energies of activation vary only from 4.70 to 5.66 Kcal/mole.

Estimates of the entropies of activation for these six systems vary from about 0 to 17 entropy units. Bondi (1946) shows entropies of activation for viscous flow that range from -10 to 100 entropy units for the viscous materials that he investigated.

Bondi (1946) also has shown that there exists a "degree of proportionality" between the enthalpy of activation and the entropy of activation. The activation

TABLE B-IV

RESULTS FOR THE DIFFUSIVITY RUNS FOR THE DIFFUSION OF CYCLOHEXANOL INTO PROPYLENE GLYCOL

Run No.	Cell No.	Temp °C	Average Solvent Volume cm^3	Number of Data Points	Effective* Length cm	Initial Bath Concentration mole/liter $x10^4$	Standard Deviation of Initial Concentration $x10^6$	Diffusivity cm^2/sec. $x10^6$	Standard Deviation of Diffusivity $x10^8$	Average Percent Deviation of Residuals
91	3	26.6	293.0	14	0.324	0.1826	1.6704	0.2810	0.7573	8.11
92	3	26.0	292.5	15	0.325	0.0856	0.5510	0.2365	0.2678	2.05
97	6	30.0	292.5	15	0.320	0.1280	1.2657	0.3121	0.6454	2.60
98	6	30.0	292.5	15	0.322	0.1314	1.2752	0.3082	0.6433	2.89
103	3	39.9	295.0	10	0.375	0.6622	2.0126	0.5549	1.5374	3.18
104	3	39.9	295.0	10	0.373	0.6362	2.0033	0.5886	1.5934	3.10

Initial concentration in porous plate = 0.0241 moles/liter

Area of mass transfer = 11.98 cm^2

*Yu (1968)

TABLE B-V

RESULTS FOR THE DIFFUSIVITY RUNS FOR THE DIFFUSION OF CYCLOHEXANOL INTO DIETHYLENE GLYCOL

Run No.	Cell No.	Temp °C	Average Solvent Volume cm^3	Number of Data Points	Effective* Length cm	Initial Bath Concentration mole/liter x10^4	Standard Deviation of Initial Concentration x10^5	Diffusivity cm^2/sec. x10^6	Standard Deviation of Diffusivity x10^7	Average Percent Deviation of Residuals
89	5	26.6	294.5	11	0.345	0.3059	0.2221	0.4621	0.1539	2.17
90	5	26.6	294.5	11	0.344	0.2678	0.2117	0.4586	0.1488	5.70
95	2	30.0	292.5	15	0.332	0.2219	0.1579	0.4980	0.0994	2.80
96	2	30.0	292.5	15	0.333	0.2254	0.1542	0.4950	0.0974	4.24
101	5	39.9	294.0	12	0.499	0.9780	0.2645	0.8278	0.1970	2.10
102	5	39.9	295.0	10	0.462	0.9624	0.2760	0.8257	0.2511	2.85

Initial Concentration in porous plate = 0.0241 moles/liter

Area of mass transfer = 11.98 cm^2

*Wu (1968)

TABLE B-VI

RESULTS FOR THE DIFFUSIVITY RUNS FOR THE DIFFUSION OF CYCLOHEXANOL INTO ETHYLENE GLYCOL

Run No.	Cell No.	Temp °C	Average Solvent Volume cm^3	Number of Data Points	Effective Length cm	Initial Bath Concentration mole/liter x10^4	Standard Deviation of Initial Concentration x10^5	Diffusivity cm^2/sec. x10^6	Standard Deviation of Diffusivity x10^7	Average Percent Deviation of Residuals
87	4	26.6	295.5	9	0.330	0.2744	0.2573	0.5951	0.2602	6.46
88	4	26.6	295.5	9	0.325	0.2843	0.2487	0.6209	0.2580	3.64
93	1	30.0	293.5	13	0.357	0.5336	0.2778	0.6132	0.1690	3.84
94	1	30.0	293.0	14	0.356	0.4953	0.2208	0.6547	0.1551	4.52
99	4	39.9	296.0	8	0.444	0.5252	0.2965	1.0362	0.4476	2.71
100	4	39.9	295.5	9	0.474	0.4822	0.2626	1.1078	0.3489	3.24

Initial concentration in porous plate = 0.0241 moles/liter

Area of mass transfer = 11.98 cm^2

*Wu (1968)

TABLE B-VII

RESULTS FOR THE DIFFUSIVITY RUNS FOR THE DIFFUSION OF ETHYLENE GLYCOL INTO ETHYLENE GLYCOL

Run No.	Cell No.	Temp °C	Average Solvent Volume cm³	Number of Data Points	Effective* Length cm	Initial Bath Concentration mole/liter x10⁷	Standard Deviation of Initial Concentration x10⁸	Diffusivity cm²/sec. x10⁵	Standard Deviation of Diffusivity x10⁷	Average Percent Deviation of Residuals
51	4	25.0	297.0	6	0.324	0.4257	0.2191	0.0976	0.2646	10.51
52	4	25.0	297.0	6	0.339	0.4839	0.2319	0.1041	0.2864	12.43
57	1	25.0	295.5	9	0.545	0.3129	0.2201	0.0916	0.1526	2.76
58	1	25.0	295.5	9	0.536	0.2956	0.2187	0.0912	0.1519	2.22
63	4	30.0	295.5	9	0.582	0.3374	0.2184	0.1145	0.1821	4.94
64	4	30.0	296.0	8	0.558	0.3353	0.2277	0.1127	0.2131	2.19
69	1	40.0	297.0	6	0.459	0.5581	0.3478	0.1543	0.5311	4.39
70	1	40.0	297.0	6	0.502	0.4997	0.3392	0.1548	0.5227	3.06
75	4	40.0	295.5	9	0.546	0.4865	0.3592	0.1497	0.3682	2.96
76	4	40.0	295.0	10	0.568	0.4764	0.3450	0.1446	0.3057	2.09
81	1	50.0	297.0	6	0.354	0.3170	0.4054	0.2067	0.7685	3.05

Initial concentration in porous plate = 0.000036 moles/liter

Area of mass transfer = 11.98 cm^2

*Wu (1968)

TABLE B-VIII

RESULTS FOR THE DIFFUSIVITY RUNS FOR THE DIFFUSION OF ETHYLENE GLYCOL INTO DIETHYLENE GLYCOL

Run No.	Cell No.	Temp °C	Average Solvent Volume cm^3	Number of Data Points	Effective* Length cm	Initial Bath Concentration mole/liter x10^4	Standard Deviation of Initial Concentration x10^5	Diffusivity cm^2/sec. x10^5	Standard Deviation of Diffusivity x10^8	Average Percent Deviation of Residuals
59	2	25.0	294.5	11	0.475	0.5510	0.2746	0.0563	0.9013	2.83
60	2	25.0	294.5	11	0.493	0.4728	0.2597	0.0554	0.8653	3.48
65	5	30.0	293.5	13	0.740	0.5124	0.2480	0.0624	0.7627	5.40
66	5	30.0	295.0	10	0.488	0.5361	0.2756	0.0676	1.1596	3.07
77	5	40.0	295.5	9	0.409	0.9952	0.5478	0.0926	3.3147	3.61
78	5	40.0	295.5	9	0.410	0.7808	0.5175	0.1066	3.4811	2.17

Initial concentration in porous plate = 0.045 moles/liter

Area of mass transfer = 11.98 cm^2

*Wu (1968)

TABLE B-IX

RESULTS FOR THE DIFFUSIVITY RUNS FOR THE DIFFUSION OF ETHYLENE GLYCOL INTO PROPYLENE GLYCOL

Run No.	Cell No.	Temp °C	Average Solvent Value cm^3	Number of Data Points	Effective* Length cm	Initial Bath Concentration mole/liter $x10^4$	Standard Deviation of Initial Concentration $x10^5$	Diffusivity $cm^2/sec.$ $x10^6$	Standard Deviation of Diffusivity $x10^8$	Average Percent Deviation of Residuals
61	6	25.0	294.5	11	0.479	0.3245	0.2254	0.4866	0.7588	5.84
62	6	25.0	294.5	11	0.525	0.3782	0.2350	0.4772	0.7635	5.75
67	3	30.0	292.5	15	0.774	0.2545	0.1896	0.5274	0.5136	4.65
68	3	30.0	294.0	12	0.561	0.2434	0.1945	0.5368	0.6882	7.15
73	6	40.0	297.0	6	0.423	0.4187	0.2915	1.0293	3.3815	8.27
74	6	40.0	296.5	7	0.479	0.5204	0.2490	0.8189	1.7960	8.04
85	6	50.0	297.5	5	0.349	0.0710	0.3204	1.2531	3.6511	1.88
86	6	50.0	297.5	5	0.349	0.0821	0.3727	1.2657	4,2417	1.40

Initial concentration in porous plate = 0.045 moles/liter

Area of mass transfer = 11.98 cm^2

*Wu (1968)

TABLE B-X

EXPERIMENTALLY MEASURED DIFFUSION COEFFICIENTS, ACTIVATION ENERGY AND FREE ENERGY OF ACTIVATION AT THE TEMPERATURES INDICATED

Solvent	Solute	Temp °C	$D_{AB}(10)^6$ Cm^2/Sec	$E_{D_{AB}}$ (Kcal/Mole)	$\Delta F_{D_{AB}}$
Ethylene Glycol	Ethylene Glycol	25	0.961±.10	4.48	4.74
		30	1.136±.12		4.73
		40	1.509±.15		4.73
		50	2.067±.21		4.70
Diethylene Glycol	Ethylene Glycol	25	0.558±.06	5.99	5.27
		30	0.650±.07		5.28
		40	0.996±.10		5.21
Propylene Glycol	Ethylene Glycol	25	0.482±.05	6.48	5.25
		30	0.532±.06		5.29
		40	0.924±.10		5.15
		50	1.259±.13		5.14
Ethylene Glycol	Cyclo-hexanol	26.6	0.608±.06	7.07	5.04
		30	0.636±.06		5.08
		39.9	1.072±.10		4.94
Diethylene Glycol	Cyclo-hexanol	26.6	0.460±.06	7.25	5.42
		30	0.496±.05		5.44
		39.9	0.827±.09		5.32
Propylene Glycol	Cyclo-hexanol	26.6	0.259±.03	9.92	5.66
		30	0.310±.04		5.62
		39.9	0.572±.06		5.44

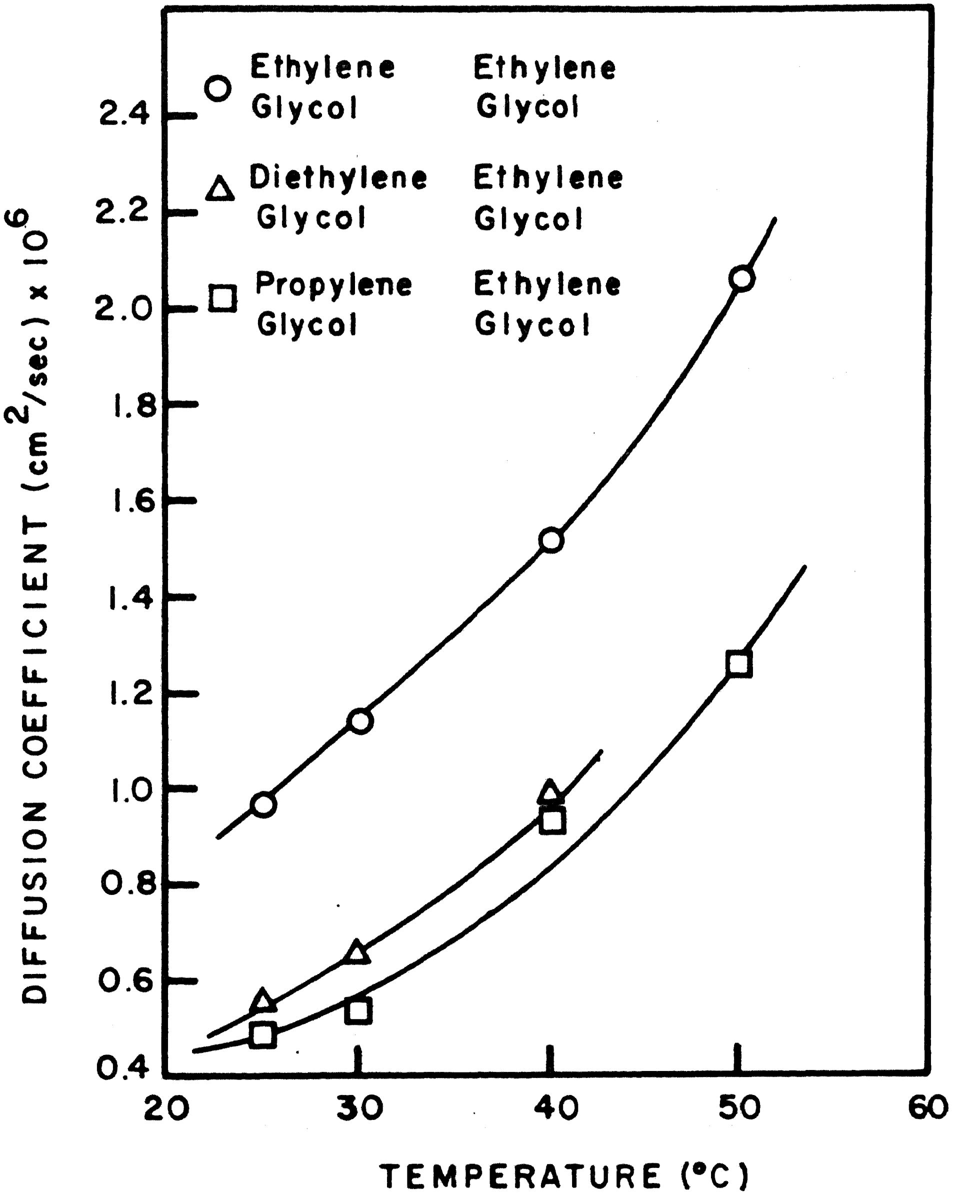

Figure B-8. Diffusivities of ethylene glycol in the solvents ethylene glycol, propylene gylcol and diethylene glycol versus temperature.

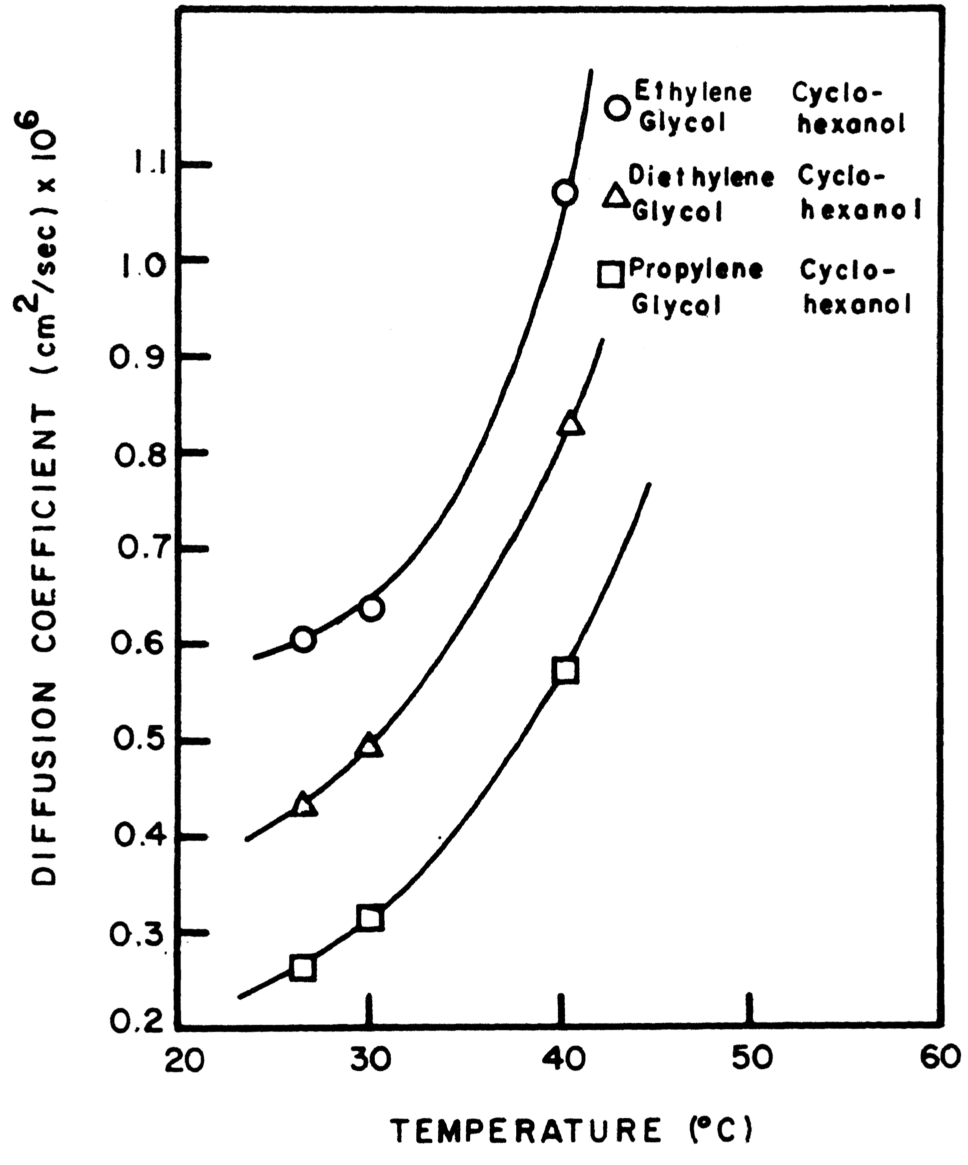

Figure B-9. Diffusivities of cyclohexanol in the solvents ethylene glycol, propylene glycol and diethylene glycol versus temperature.

energies in Table B-X are only slightly different (by less than 10%) from the enthalpy of activation. The free energy of activation defined by

$$\Delta F_{D_{AB}} = \Delta H_{D_{AB}} - T\Delta S_{D_{AB}}$$

Thus, since this degree of proportionality between the enthalpy and entropy of activation exists, one should expect the free energy of activation to deviate much less from system to system than does the activation energy. This is of course shown in Table B-X.

G. Programs

The following program was used to predict the diffusivities by the Wilke-Chang equation, the modified Gainer and Metzner equation, the Olander equation, and the equation developed in this work.

```
$ID    YGW0645 MITCHELL,R.D.  DIFGM
$TCP           TIME=2,PAGES=65
$IBJOB         GO
$IBFTC MAIN    LIST,DECK
C.....THIS PROGRAM CALCULATES THE DIFFUSION COEFFICIENTS BY THE WILKE-
C     CHANG EQUATION (DWC); BY OLANDER'S EQUATION (DO), BY GAINER'S
C     EQUATION, BUT USING THE EXPERMENTAL VALUES OF THE VISCOUS ACTIVATION
C     ENERGY (DGM'), AND BY EQUATIONS DM1,DM2,AND DM3 AS DEVELOPED IN THIS
C     WORK.
      DIMENSION  EDD(41),EDN(41)
      DIMENSION  SUM(41,60),SOM(41,60),SUME(41,60),SOME(41,60)
      DIMENSION  SOUM(41,60),RAT(41),ENH(41),EDH(41)
      DIMENSION DEN(2,41),VIS(2,41),EN(41),ED(41),ALP(41),XP(41),XM(41)
     2,Z(41),ZZ(41),DBP(41),V(41),RA(41)
      READ(5,200) IRUN
      DO 88 JRUN=1,IRUN
      READ(5,200) NWAY,NSTD,NTOT,NH2O
C.....NSTD IS THE NUMBER OF PURE LIQUIDS FOR WHICH DATA IS READ IN.
C.....NTOT IS THE NUMBER OF SYSTEMS FOR WHICH THE DIFFUSIVITIES ARE
C     CALCULATED.
      CORF=2.0**0.166667
      READ  (5,106) (RAT(I),I=1,NSTD)
C.....RAT IS THE RATIO OF THE ENTHALPY OF VAPORIZATION DUE TO DISPERSION
C     FORCE BONDS TO THE TOTAL.
      READ  (5,100) ((DEN(I,J),I=1,2),J=1,NSTD)
C.....DEN IS THE DENSITY.
      READ  (5,100) ((VIS(I,J),I=1,2),J=1,NSTD)
C.....VIS IS THE VISCOSITY.
      READ  (5,100)  (XP(I),XM(I),Z(I),ZZ(I),DBP(I),I=1,NSTD)
C.....XP IS THE SOLVENT PARAMETER FOR USE IN THE WILKE-CHANG EQUATION.
C.....XM IS THE MOLECULAR WEIGHT.
C.....Z IS XI FOR USE IN GIANER AND METZNER'S EQUATION.
C.....ZZ IS XI FOR USE IN EQUATIONS DM2 AND DM3.
C.....DBP IS THE MOLAR VOLUME AT THE BOILING POINT.
      READ(5,100) R,CK,XK,AVGN,H
C.....R IS THE UNIVERSAL GAS CONSTANT.
C.....CK IS THE CONSTANT USED IN THE WILKE-CHANG EQUATION.
C.....XK IS THE BOLTZMAN CONSTANT.
C.....AVGN IS THE AVOGADRO NUMBER.
C.....H IS THE PLANCK CONSTANT.
      WRITE (6,150) R
      WRITE (6,151) H
      WRITE (6,152) XK
      WRITE (6,153) AVGN
      WRITE (6,154) CK
      SAM=0.0
C.....SAM,AS WELL AS SUM,SOUM,SOM,SUME, AMD SOME  BELOW, ARE USED IN
C     CALCULATING THE AVERAGE ABSOLUTE FRACTIONAL DEVIATIONS .
      DO 10  J=1,NSTD
C..... J IS THE SOLVENT NUMBER, SEE LIST BELOW
      READ(5,100) T1
C.....T1 IS THE TEMPERATURE FOR WHICH THE DATA ARE USEFUL FOR THIS SOLVENT.
      T2=T1+15.
      WRITE (6,155) J
      WRITE (6,156) RAT(J)
      WRITE (6,157) XP(J)
      WRITE (6,158) XM(J)
      WRITE (6,159) Z(J),ZZ(J)
      WRITE (6,163) DBP(J)
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      WRITE(6,109) DEN(1,J),T1,DEN(2,J),T2
      WRITE(6,111) VIS(1,J),T1,VIS(2,J),T2
      EN(J)= R*(ALOG(VIS(2,J)/VIS(1,J)))/((1./T2) -(1./T1) )
C.....EN IS THE EXPERIMENTALLY DETERMINED ACTIVATION ENERGY FOR VISCOUS
C     TRANSFER.
      ALP(J)= DEN(1,J)*((1./DEN(2,J))-(1./DEN(1,J)))/ (T2 -T1)
C.....ALP IS THE COEFFICIENT OF VOLUMETRIC  EXPANSION.
      ED(J)= EN(J) -(R*T1 *( 1.- (T1* ALP(J)/3.0)))
C.....ED IS THE SELF-DIFFUSION ACTIVATION ENERGY FOR EQUATIONS DM1 AND DM3.
      WRITE (6,160) EN(J)
      WRITE (6,161) ED(J)
   10 WRITE (6,162) ALP(J)
      DO 16 I=1,NSTD
      ENH(I)= EN(I)*(1.-RAT(I))
C.....ENH IS THE ACTIVATION ENERGY FOR VISCOSITY DUE TO HYDROGEN BONDING.
      EDH(I)=ED(I)*(1.-RAT(I))
C.....EDH IS THE ACTIVATION ENERGY FOR DIFFUSION DUE TO HYDROGEN BONDING.
      EDD(I)=ED(I)*RAT(I)
C.....EDD IS THE ACTIVATION ENERGY FOR DIFFUSION DUE TO DISPERSION FORCES.
   16 EDN(I)=EN(I)*RAT(I)
C.....EDN IS THE ACTIVATION ENERGY FOR VISCOSITY DUE TO DISPERSION FORCES.
      DO 11  J=1,NTOT
      READ (5,102)  NB,NA,T1,DACT
C.....DACT IS THE EXPERIMENTALLY DETERMINED DIFFUSIVITY.
      IP=1
      DWC= (CK*T1*((XP(NB)*XM(NB))**.5)/(VIS(1,NB)*(DBP(NA)**.6)))*.0001
C.....DWC IS THE DIFFUSIVITY AS CALCULATED BY THE WILKE-CHANG EQUATION.
      V(NA)=XM(NA)/DEN(1,NA)
C.....V IS THE MOLAR VOLUME AT THE TEMPERATURE T1.
      V(NB)= XM(NB)/ DEN(1,NB)
      RA(NA)=(V(NA)/AVGN)** 0.33333
C.....RA IS THE MOLECULAR RADIUS.
      RA(NB)= (V(NB)/AVGN)** 0.33333
      RAB=(RA(NB)+RA(NA))/2.00
C.....RAB IS AN AVERAGE MOLECULAR RADIUS.
      DFBO=R*T1*ALOG(VIS(1,NB)*V(NB)/(AVGN*H))
C.....DFBO IS THE ACTIVATION FREE ENERGY OF THE SOLVENT B FOR OLANDER'S MODEL.
      DFAO=R*T1*ALOG(VIS(1,NA)*V(NA)/(AVGN*H))
C.....DFAO IS THE ACTIVATION FREE ENERGY OF THE SOLUTE  A FOR OLANDER'S MODEL.
      DEV5=(DACT-DWC)/DACT
C.....DEV5 IS THE FRACTIONAL DEVIATION IN THE WILKE-CHANG DIFFUSIVITY.
      SAM=SAM+ABS(DEV5)
C.....THIS SECTION IS HERE TO SUPPRESS UNNEEDED OUTPUT WHEN DESIRED.
      IF(NWAY)30,31,30
   30 IF(J-1)42,32,42
   32 WRITE (6,103)  NA,NB
      WRITE (6,170) T1,DACT,VIS(1,NB)
      WRITE(6,112) DWC,DEV5
      GO TO 42
   31 CONTINUE
    8 WRITE (6,103)  NA,NB
      WRITE (6,170) T1,DACT,VIS(1,NB)
      WRITE(6,112) DWC,DEV5
   42 CONTINUE
      DFB=DFBO+(R*T1*(ALOG(2.0**0.5)))
C.....DFB IS THE ACTIVATION FREE ENERGY FOR MODEL DM1 FOR SOLVENT B.
      DFA=DFAO+(R*T1*(ALOG(2.0**0.5)))
C.....DFA IS THE ACTIVATION FREE ENERGY FOR MODEL DM1 FOR SOLUTE A.
      DFAH=(1.-RAT(NA))*DFA
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C.....DFAH IS THE ACTIVATION FREE ENERGY DUE TO HYDROGEN BONDING FOR SOLUTE A.
      DFBH=(1.-RAT(NB))*DFB
C.....DFBH IS THE ACTIVATION FREE ENERGY DUE TO HYDROGEN BONDING FOR SOLVENT B.
      DFA=DFA*RAT(NA)
C.....DFA IS THE ACTIVATION FREE ENERGY FOR SOLUTE A DUE TO DISPERSION
C     FORCE BONDS.
      DFB=DFB*RAT(NB)
C.....DFB IS THE ACTIVATION FERE ENERGY FOR SOLVENT B DUE TO DISPERSION
C     FORCE BONDS.
      X=R*T1*(1.-(T1*ALP(NB)/3.))
      XY=   -SQRT(((RA(NB)*RA(NA)/((RAB)**2))**12)*ZZ(NA)*EDD(NA)*EDD(NB)
     2/ZZ(NB))
      XZX= - SQRT (RA(NA)*EDH(NA)*RA(NB)*EDH(NB)*ZZ(NB)/(RAB*RAB*
     2ZZ(NB)))
      XZY=-Z(NA)*SQRT(RA(NB)*RA(NA)*ENH(NA)  *ENH(NB)/(RAB*RAB))/Z(NB)
      XX=-Z(NA)*SQRT((RA(NB)*RA(NA)/((RAB)**2))**12*EDN(NB)*EDN(NA))/
     2Z(NB)
      XZZ=-2.*V(NA)*SQRT((ED(NA)*ED(NB)/(V(NA)*V(NB))))
C.....X, XY, XZX, XZY, XX AND XZZ ARE GROUPS OF TERMS TO BE USED IN THE
C     EXPONENTS OF THE VARIUS EQUATIONS BELOW.
      TANT = RA(NB)/SQRT((RA(NA)**2)+(2.*RA(NA)*RA(NB)))
C.....TANT IS THE TANGENT OF THE ANGLE THETA, SEE DERIVATION OF EQUATION DM3.
      ZP= 3.14159/ ATAN( TANT)
C.....ZP IS THE NUMBER OF B MOLECULES THAT WILL FIT AROUND THE CENTRAL A
C     MOLECULE.
      ZP=(2.*ZP-1.)/11.
      DO 12 IP=1,40
      F=IP
      F=0.025*F
C.....F IS THAT FRACTION OF THE ACTIVATION  (FREE) ENERGY DUE TO THE
C     HOLE FORMATION STEP.
      AF=1.-F
C.....AF IS THAT FRACTION OF THE ACTIVATION  (FREE) ENERGY DUE TO THE
C     JUMP STEP.
      DO=(XK*T1/(RA(NB)*5.6))*EXP(AF*(DFBO-SQRT(DFBO*DFAO))/(R*T1))
     2/VIS(1,NB)
C.....DO IS THE DIFFUSIVITY AS CALCULATED BY OLANDER'S MODEL.
      ZG=(F*DFB/RAT(NB))-(DFB*V(NA)*(1.-F)/(V(NB)*RAT(NB)))+(2.*V(NA)*
     2(1.-F)*SQRT(DFA*DFB/(V(NA)*V(NB)*RAT(NA)*RAT(NB))))
      XDGM=(1.-F)*(EN(NB)+XX+XZY)
      XDM1= (F*X)+(1.-F)*ZP*(XY+XZX)
      XDM2=(F*X)+    ((1.-F)*(EN(NB)+((V(NA)/V(NB))*ED(NB))+(XZZ)))
C.....ZG, XDGM, XDM1, AND XDM2 ARE TERMS USED IN THE EXPONENTS OF THE
C     EQUATIONS BELOW.
      DGM= (XK*T1/(Z(NA)*VIS(1,NB)))*(EXP(XDGM/(R*T1)))/ RA(NB)
C.....DGM IS THE DIFFUSIVITY AS CALCULATED BY THE MODIFIED GAINER MODEL.
      DM3= (XK*T1/(ZZ(NB)*VIS(1,NB)))*(EXP( XDM1/(R*T1)))/(RA(NB)*CORF)
C.....DM3 IS THE DIFFUSIVITY AS CALCULATED BY THE EQUATION DM3.
      DM2= (XK*T1/(ZZ(NB)*VIS(1,NB)))*(EXP(XDM2/ (R*T1)))/(RA(NB)*CORF)
C.....DM2 IS THE DIFFUSIVITY AS CALCULATED BY EQUATION DM2.
      DM1=(((RA(NB)*CORF)**2    )*XK*T1/ Z(NB))*EXP(-ZG/(R*T1))
      DM1=1.07*DM1/H
C.....DM1 IS THE DIFFUSIVITY AS CALCULATED BY EQUATION DM1.
      SUM(IP,J)=(DACT-DO)/DACT
      SOM(IP,J)=(DACT-DGM)/DACT
      SUME(IP,J)=(DACT-DM1)/DACT
      SOME(IP,J)=(DACT-DM2)/DACT
      SOUM(IP,J)=(DACT-DM3)/DACT
C.....THIS SECTION IS HERE TO SUPPRESS UNNEEDED OUTPUT WHEN DESIRED.
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      IF(NWAY)20,21,20
   20 IF(J-1)12,22,12
   22 WRITE (6,104) F,DO,DGM,DM1,DM2,DM3
      WRITE(6,105)SUM(IP,J),SOM(IP,J),SUME(IP,J),SCME( IP,J),SOUM(IP,J)
      GO TO 12
   21 CONTINUE
      WRITE (6,104) F,DO,DGM,DM1,DM2,DM3
      WRITE(6,105)SUM(IP,J),SOM(IP,J),SUME(IP,J),SCME( IP,J),SOUM(IP,J)
   12 CONTINUE
   11 CONTINUE
      WRITE (6,171)
      DO 15 J=1,40
      F=J
      F=0.025*F
      WW=0.0
      W=0.0
      X=0.0
      Y=0.0
      U=0.0
C.....WW, W, X, Y AND U ARE THE AVERAGE DEVIATIONS OF THE DIFFUSIVITIES.
      DO 14 I=1,NTOT
      WW=WW+ABS(SOUM(J,I))
      W=W + ABS(SUM(J,I))
      X=X + ABS(SOM(J,I))
      Y=Y + ABS(SUME(J,I))
   14 U=U + ABS(SOME(J,I))
      XYZ=NTOT
      W=W/XYZ
      X=X/XYZ
      Y=Y/XYZ
      U=U/XYZ
      WW=WW/XYZ
   15 WRITE(6,172)F,W,X,Y,U,WW
      SAM=SAM/XYZ
      WRITE (6,173)  SAM
   88 CONTINUE
      STOP
  100 FORMAT (4E18.8)
  101 FORMAT (4E18.8)
  102 FORMAT (2I6,2E18.8)
  103 FORMAT (1X,14H SOLUTE CODE =,I3,5X,15H SOLVENT CODE =,I3)
  106 FORMAT(8F9.5)
  104 FORMAT(5X,5H F = ,F5.3,8H   DO = ,E12.5,9H   DGM = ,E12.5,9H   DM1
     2 = ,E12.5,9H   DM2 = ,E12.5,9H   DM3 = ,E12.5)
  105 FORMAT(15X,8H  DDO = ,F11.7,9H  DDGM = ,F11.7,9H  DDM1 = ,F11.7,
     29H  DDM2 = ,F11.7,9H  DDM3 = ,F11.7)
  109 FORMAT (10X,11H DENSITY = ,F7.5,3H AT,F6.1,6H DEG C,6X,11H DENSITY
     2 = ,F7.5,3H AT,F6.1,18H DEG C, IN GRAM/CC)
  111 FORMAT (10X,13H VISCOSITY = ,F7.5,3H AT,F6.1,6H DEG C,4X,13H VISCO
     2SITY = ,F7.5,3H AT,F6.1,16H DEG C, IN POISE)
  112 FORMAT (6X,4HDWC=,E18.8,6X,5HDDWC=,F9.5)
  150 FORMAT(1H1,10X,28H UNIVERSAL GAS CONSTANT,R = ,F10.5,13H CAL/DEG*M
     2OLE)
  151 FORMAT(10X,21H PLANCK CONSTANT,H = ,F18.8,8H ERG*SEC)
  152 FORMAT(10X,24H BOLTZMAN CONSTANT,XK = ,E18.8,8H ERG/DEG)
  153 FORMAT(10X,24H AVOGADRO NUMBER,AVGN = ,E18.8,7H 1/MOLE)
  154 FORMAT(10X,50H EMPERICAL CONSTANT FOR WILKE-CHANG EQUATION,CK = ,
     2E18.8)
  155 FORMAT(1HC,10X,18H SOLVENT NUMBER = ,I3)
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156 FORMAT(10X,83H FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUT
   2ED TO DISPERSION FORCE BONDS = ,F6.3)
157 FORMAT(10X,58H SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUAT
   2ION = ,F5.2)
158 FORMAT(10X,34H MOLECULAR WEIGHT OF SOLVENT,XM = ,F8.3,10H GRAM/MOL
   2E)
159 FORMAT(10X,23H XI FOR EQUATION DGM = ,F5.2,36H  AND XI FOR EQUATIO
   2N DM2 AND DM3 = ,F5.2)
160 FORMAT(10X,32H VISCOUS ACTIVATION ENERGY,EN = ,F12.5,13H CAL/DEG*M
   2OLE)
161 FORMAT(10X,64H SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 A
   2ND DM3,ED = ,F12.5, 13H CAL/DEG*MOLE)
162 FORMAT(10X,43H COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP = ,F12.7,
   26H 1/DEG)
163 FORMAT(10X,41H MOLAR VOLUME AT THE BOILING POINT,DBP = ,F10.5,
   28H CC/MOLE)
170 FORMAT(10X,14H TEMPERATURE = ,F6.2,6H DEG C,18H    DIFFUSIVITY = ,
   2F12.5,10H CM**2/SEC,15H   VISCOSITY = ,F8.5,6H POISE)
171 FORMAT(5X,49H THE FOLLOWING DEVIATIONS ARE AVERAGES FOR EACH F)
172 FORMAT(5X,5H F = ,F5.3,8H  DDO = ,F11.8,9H  DDGM = ,F11.8,9H  DDM1
   2 = ,F11.8,9H  DDM2 = ,F11.8,9H  DDM3 = ,F11.8)
173 FORMAT(5X,8H DDWC = ,F9.5)
200 FORMAT(4I5)
    END
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YGW0645 MITCHELL,R.D.
     UNIVERSAL GAS CONSTANT,R =     1.98700 CAL/DEG*MOLE
    PLANCK CONSTANT,H =      0.66250000E-26 ERG*SEC
    BOLTZMAN CONSTANT,XK =      0.13805400E-15 ERG/DEG
    AVOGADRO NUMBER,AVGN =      0.60225200E 24 1/MOLE
    EMPERICAL CONSTANT FOR WILKE-CHANG EQUATION,CK =      0.74000000E-05

     SOLVENT NUMBER =    1
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.331
    SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
    MOLECULAR WEIGHT OF SOLVENT,XM =    62.100 GRAM/MOLE
    XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
    MOLAR VOLUME AT THE BOILING POINT,DBP =    66.60000 CC/MOLE
    DENSITY = 1.10620 AT 303.0 DEG C        DENSITY = 1.09580 AT 318.0 DEG C, IN GRAM/CC
    VISCOSITY = 0.13560 AT 303.0 DEG C      VISCOSITY = 0.07980 AT 318.0 DEG C, IN POISE
    VISCOUS ACTIVATION ENERGY,EN =   6767.12933 CAL/DEG*MOLE
    SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3, ED =   6203.54272 CAL/DEG*MOLE
    COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =    0.0006327 1/DEG

     SOLVENT NUMBER =    2
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.331
    SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
    MOLECULAR WEIGHT OF SOLVENT,XM =    62.100 GRAM/MOLE
    XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
    MOLAR VOLUME AT THE BOILING POINT,DBP =    66.60000 CC/MOLE
    DENSITY = 1.11320 AT 293.0 DEG C        DENSITY = 1.10280 AT 308.0 DEG C, IN GRAM/CC
    VISCOSITY = 0.20620 AT 293.0 DEG C      VISCOSITY = 0.11300 AT 308.0 DEG C, IN POISE
    VISCOUS ACTIVATION ENERGY,EN =   7190.03223 CAL/DEG*MOLE
    SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3, ED =   6643.58966 CAL/DEG*MOLE
    COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =    0.0006287 1/DEG

     SOLVENT NUMBER =    3
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.454
    SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
    MOLECULAR WEIGHT OF SOLVENT,XM =    76.100 GRAM/MOLE
    XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
    MOLAR VOLUME AT THE BOILING POINT,DBP =    88.80000 CC/MOLE
    DENSITY = 1.02920 AT 303.0 DEG C        DENSITY = 1.01770 AT 318.0 DEG C, IN GRAM/CC
    VISCOSITY = 0.32630 AT 303.0 DEG C      VISCOSITY = 0.15500 AT 318.0 DEG C, IN POISE
    VISCOUS ACTIVATION ENERGY,EN =   9501.19177 CAL/DEG*MOLE
    SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3, ED =   8944.93945 CAL/DEG*MOLE
    COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =    0.0007533 1/DEG

     SOLVENT NUMBER =    4
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.568
    SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
    MOLECULAR WEIGHT OF SOLVENT,XM =  106.100 GRAM/MOLE
    XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
    MOLAR VOLUME AT THE BOILING POINT,DBP =  118.40000 CC/MOLE
    DENSITY = 1.10920 AT 303.0 DEG C        DENSITY = 1.09850 AT 318.0 DEG C, IN GRAM/CC
    VISCOSITY = 0.21610 AT 303.0 DEG C      VISCOSITY = 0.12000 AT 318.0 DEG C, IN POISE
    VISCOUS ACTIVATION ENERGY,EN =   7508.23508 CAL/DEG*MOLE
    SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3, ED =   6945.66211 CAL/DEG*MOLE
    COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =    0.0006494 1/DEG

     SOLVENT NUMBER =    5
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.914
    SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
    MOLECULAR WEIGHT OF SOLVENT,XM =  150.200 GRAM/MOLE
    XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
    MOLAR VOLUME AT THE BOILING POINT,DBP =  170.20000 CC/MOLE
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YGW0645 MITCHELL,R.D.
    DENSITY = 1.13880 AT 273.0 DEG C         DENSITY = 1.12730 AT 288.0 DEG C, IN GRAM/CC
    VISCOSITY = 1.60000 AT 273.0 DEG C       VISCOSITY = 0.56000 AT 288.0 DEG C, IN POISE
    VISCOUS ACTIVATION ENERGY,EN =  10933.96008 CAL/DEG*MOLE
    SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3,ED =  10425.08044 CAL/DEG*MOLE
    COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =     0.0006801 1/DEG

     SOLVENT NUMBER =    6
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.666
    SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
    MOLECULAR WEIGHT OF SOLVENT,XM =  100.200 GRAM/MOLE
    XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
    MOLAR VOLUME AT THE BOILING POINT,DBP =  136.90000 CC/MOLE
    DENSITY = 0.94155 AT 303.0 DEG C         DENSITY = 0.92994 AT 318.0 DEG C, IN GRAM/CC
    VISCOSITY = 0.41070 AT 303.0 DEG C       VISCOSITY = 0.17190 AT 318.0 DEG C, IN POISE
    VISCOUS ACTIVATION ENERGY,EN =  11116.53943 CAL/DEG*MOLE
    SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3,ED =  10565.08972 CAL/DEG*MOLE
    COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =     0.0008323 1/DEG

     SOLVENT NUMBER =    7
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.372
    SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
    MOLECULAR WEIGHT OF SOLVENT,XM =   92.100 GRAM/MOLE
    XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
    MOLAR VOLUME AT THE BOILING POINT,DBP =   96.20000 CC/MOLE
    DENSITY = 1.25830 AT 298.0 DEG C         DENSITY = 1.24900 AT 313.0 DEG C, IN GRAM/CC
    VISCOSITY = 9.50000 AT 298.0 DEG C       VISCOSITY = 2.45000 AT 313.0 DEG C, IN POISE
    VISCOUS ACTIVATION ENERGY,EN =  16744.48413 CAL/DEG*MOLE
    SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3,ED =  16181.55505 CAL/DEG*MOLE
    COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =     0.0004964 1/DEG

     SOLVENT NUMBER =    8
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.368
    SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
    MOLECULAR WEIGHT OF SOLVENT,XM =   92.100 GRAM/MOLE
    XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
    MOLAR VOLUME AT THE BOILING POINT,DBP =   96.20000 CC/MOLE
    DENSITY = 1.26130 AT 293.0 DEG C         DENSITY = 1.25190 AT 308.0 DEG C, IN GRAM/CC
    VISCOSITY = 4.80000 AT 293.0 DEG C       VISCOSITY = 3.82000 AT 308.0 DEG C, IN POISE
    VISCOUS ACTIVATION ENERGY,EN =  16190.65710 CAL/DEG*MOLE
    SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3,ED =  15636.92896 CAL/DEG*MOLE
    COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =     0.0005005 1/DEG

     SOLVENT NUMBER =    9
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.368
    SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
    MOLECULAR WEIGHT OF SOLVENT,XM =   92.100 GRAM/MOLE
    XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
    MOLAR VOLUME AT THE BOILING POINT,DBP =   96.20000 CC/MOLE
    DENSITY = 1.26080 AT 294.0 DEG C         DENSITY = 1.25130 AT 309.0 DEG C, IN GRAM/CC
    VISCOSITY = 3.60000 AT 294.0 DEG C       VISCOSITY = 3.49000 AT 309.0 DEG C, IN POISE
    VISCOUS ACTIVATION ENERGY,EN =  16368.35339 CAL/DEG*MOLE
    SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3,ED =  15813.15161 CAL/DEG*MOLE
    COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =     0.0005061 1/DEG

     SOLVENT NUMBER =   10
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.754
    SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
    MOLECULAR WEIGHT OF SOLVENT,XM =  102.200 GRAM/MOLE
    XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
    MOLAR VOLUME AT THE BOILING POINT,DBP =  148.00000 CC/MOLE
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YGW0645 MITCHELL,R.D.
    DENSITY = 0.81560 AT 298.0 DEG C       DENSITY = 0.81524 AT 313.0 DEG C, IN GRAM/CC
    VISCOSITY = 0.00437 AT 298.0 DEG C     VISCOSITY = 0.00287 AT 313.0 DEG C, IN POISE
    VISCOUS ACTIVATION ENERGY,EN =   5194.95399 CAL/DEG*MOLE
    SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3,ED =   4604.56952 CAL/DEG*MOLE
    COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =    0.0000294 1/DEG

     SOLVENT NUMBER =  11
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.750
    SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
    MOLECULAR WEIGHT OF SOLVENT,XM =  102.200 GRAM/MOLE
    XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
    MOLAR VOLUME AT THE BOILING POINT,DBP =  148.00000 CC/MOLE
    DENSITY = 0.83285 AT 273.0 DEG C       DENSITY = 0.82239 AT 288.0 DEG C, IN GRAM/CC
    VISCOSITY = 0.00880 AT 273.0 DEG C     VISCOSITY = 0.00577 AT 288.0 DEG C, IN POISE
    VISCOUS ACTIVATION ENERGY,EN =   4395.98468 CAL/DEG*MOLE
    SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3,ED =   3895.39035 CAL/DEG*MOLE
    COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =    0.0008479 1/DEG

     SOLVENT NUMBER =  12
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.100
    SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  2.60
    MOLECULAR WEIGHT OF SOLVENT,XM =   18.000 GRAM/MOLE
    XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
    MOLAR VOLUME AT THE BOILING POINT,DBP =   75.60000 CC/MOLE
    DENSITY = 0.99723 AT 293.0 DEG C       DENSITY = 0.99406 AT 308.0 DEG C, IN GRAM/CC
    VISCOSITY = 0.01005 AT 293.0 DEG C     VISCOSITY = 0.00722 AT 308.0 DEG C, IN POISE
    VISCOUS ACTIVATION ENERGY,EN =   3953.50595 CAL/DEG*MOLE
    SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3,ED =   3383.40332 CAL/DEG*MOLE
    COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =    0.0002126 1/DEG

     SOLVENT NUMBER =  13
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.395
    SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.90
    MOLECULAR WEIGHT OF SOLVENT,XM =   32.000 GRAM/MOLE
    XI FOR EQUATION DGM =  8.00  AND XI FOR EQUATION DM2 AND DM3 = 16.00
    MOLAR VOLUME AT THE BOILING POINT,DBP =   35.80000 CC/MOLE
    DENSITY = 0.79030 AT 294.0 DEG C       DENSITY = 0.77610 AT 309.0 DEG C, IN GRAM/CC
    VISCOSITY = 0.00576 AT 294.0 DEG C     VISCOSITY = 0.00476 AT 309.0 DEG C, IN POISE
    VISCOUS ACTIVATION ENERGY,EN =   2294.77390 CAL/DEG*MOLE
    SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3,ED =   1780.42723 CAL/DEG*MOLE
    COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =    0.0012198 1/DEG

     SOLVENT NUMBER =  14
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.365
    SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
    MOLECULAR WEIGHT OF SOLVENT,XM =   92.100 GRAM/MOLE
    XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
    MOLAR VOLUME AT THE BOILING POINT,DBP =   96.20000 CC/MOLE
    DENSITY = 1.27370 AT 273.0 DEG C       DENSITY = 1.26440 AT 288.0 DEG C, IN GRAM/CC
    VISCOSITY = 1.00000 AT 273.0 DEG C     VISCOSITY = 2.67000 AT 288.0 DEG C, IN POISE
    VISCOUS ACTIVATION ENERGY,EN =  17442.60132 CAL/DEG*MOLE
    SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3,ED =  16924.35547 CAL/DEG*MOLE
    COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =    0.0004903 1/DEG

     SOLVENT NUMBER =  15
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.668
    SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
    MOLECULAR WEIGHT OF SOLVENT,XM =   88.200 GRAM/MOLE
    XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
    MOLAR VOLUME AT THE BOILING POINT,DBP =  125.80000 CC/MOLE
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YGW0645 MITCHELL,R.O.
    DENSITY = 0.80760 AT 303.0 DEG C          DENSITY = 0.79700 AT 318.0 DEG C, IN GRAM/CC
    VISCOSITY = 0.02980 AT 303.0 DEG C      VISCOSITY = 0.01880 AT 318.0 DEG C, IN POISE
    VISCOUS ACTIVATION ENERGY,EN =    5879.61444 CAL/DEG*MOLE
    SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3,ED =    5331.46954 CAL/DEG*MOLE
    COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =     0.0008867 1/DEG

     SOLVENT NUMBER =  16
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  1.000
    SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
    MOLECULAR WEIGHT OF SOLVENT,XM =   86.200 GRAM/MOLE
    XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
    MOLAR VOLUME AT THE BOILING POINT,DBP =  140.60000 CC/MOLE
    DENSITY = 0.65050 AT 303.0 DEG C          DENSITY = 0.63720 AT 318.0 DEG C, IN GRAM/CC
    VISCOSITY = 0.00278 AT 303.0 DEG C      VISCOSITY = 0.00227 AT 318.0 DEG C, IN POISE
    VISCOUS ACTIVATION ENERGY,EN =   2586.83170 CAL/DEG*MOLE
    SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3,ED =    2069.38553 CAL/DEG*MOLE
    COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =     0.0013915 1/DEG

     SOLVENT NUMBER =  17
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  1.000
    SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
    MOLECULAR WEIGHT OF SOLVENT,XM =  240.400 GRAM/MOLE
    XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
    MOLAR VOLUME AT THE BOILING POINT,DBP =  340.20000 CC/MOLE
    DENSITY = 1.04800 AT 295.0 DEG C          DENSITY = 1.03850 AT 310.0 DEG C, IN GRAM/CC
    VISCOSITY = 4.50000 AT 295.0 DEG C      VISCOSITY = 5.70000 AT 310.0 DEG C, IN POISE
    VISCOUS ACTIVATION ENERGY,EN =  17664.82959 CAL/DEG*MOLE
    SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3,ED =  17113.81616 CAL/DEG*MOLE
    COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =     0.0006099 1/DEG

     SOLVENT NUMBER =  18
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.668
    SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
    MOLECULAR WEIGHT OF SOLVENT,XM =  102.200 GRAM/MOLE
    XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
    MOLAR VOLUME AT THE BOILING POINT,DBP =  148.00000 CC/MOLE
    DENSITY = 0.81660 AT 296.4 DEG C          DENSITY = 0.80610 AT 311.4 DEG C, IN GRAM/CC
    VISCOSITY = 0.04760 AT 296.4 DEG C      VISCOSITY = 0.02970 AT 311.4 DEG C, IN POISE
    VISCOUS ACTIVATION ENERGY,EN =   5767.08197 CAL/DEG*MOLE
    SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3,ED =    5228.66431 CAL/DEG*MOLE
    COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =     0.0008684 1/DEG

     SOLVENT NUMBER =  19
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.668
    SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
    MOLECULAR WEIGHT OF SOLVENT,XM =   88.200 GRAM/MOLE
    XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
    MOLAR VOLUME AT THE BOILING POINT,DBP =  125.80000 CC/MOLE
    DENSITY = 0.81240 AT 296.4 DEG C          DENSITY = 0.80170 AT 311.4 DEG C, IN GRAM/CC
    VISCOSITY = 0.03610 AT 296.4 DEG C      VISCOSITY = 0.02310 AT 311.4 DEG C, IN POISE
    VISCOUS ACTIVATION ENERGY,EN =   5458.65180 CAL/DEG*MOLE
    SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3,ED =    4921.48920 CAL/DEG*MOLE
    COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =     0.0008898 1/DEG

     SOLVENT NUMBER =  20
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  1.000
    SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
    MOLECULAR WEIGHT OF SOLVENT,XM =  142.300 GRAM/MOLE
    XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
    MOLAR VOLUME AT THE BOILING POINT,DBP =  229.40000 CC/MOLE
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YGW0645 MITCHELL,R.D.
     DENSITY = 0.72850 AT 295.0 DEG C       DENSITY = 0.71710 AT 310.0 DEG C, IN GRAM/CC
     VISCOSITY = 0.00906 AT 295.0 DEG C     VISCOSITY = 0.00703 AT 310.0 DEG C, IN POISE
     VISCOUS ACTIVATION ENERGY,EN =   3073.12799 CAL/DEG*MOLE
     SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3, ED =   2548.05078 CAL/DEG*MOLE
     COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =     0.0010598 1/DEG

      SOLVENT NUMBER =  21
     FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  1.000
     SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
     MOLECULAR WEIGHT OF SOLVENT,XM =  418.800 GRAM/MOLE
     XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
     MOLAR VOLUME AT THE BOILING POINT,DBP =  658.60000 CC/MOLE
     DENSITY = 0.93020 AT 295.0 DEG C       DENSITY = 0.92090 AT 310.0 DEG C, IN GRAM/CC
     VISCOSITY = 0.00000 AT 295.0 DEG C     VISCOSITY = 8.10000 AT 310.0 DEG C, IN POISE
     VISCOUS ACTIVATION ENERGY,EN =  19346.36548 CAL/DEG*MOLE
     SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3, ED =  18799.00659 CAL/DEG*MOLE
     COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =     0.0006732 1/DEG

      SOLVENT NUMBER =  22
     FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.668
     SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
     MOLECULAR WEIGHT OF SOLVENT,XM =  102.200 GRAM/MOLE
     XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
     MOLAR VOLUME AT THE BOILING POINT,DBP =  148.00000 CC/MOLE
     DENSITY = 0.81750 AT 295.0 DEG C       DENSITY = 0.80710 AT 310.0 DEG C, IN GRAM/CC
     VISCOSITY = 0.04980 AT 295.0 DEG C     VISCOSITY = 0.03100 AT 310.0 DEG C, IN POISE
     VISCOUS ACTIVATION ENERGY,EN =   5742.40869 CAL/DEG*MOLE
     SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3, ED =   5205.75854 CAL/DEG*MOLE
     COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =     0.0008590 1/DEG

      SOLVENT NUMBER =  23
     FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.696
     SOLVENT ASSOCIATION PARAMETER FOR WILKE-CHANG EQUATION =  1.00
     MOLECULAR WEIGHT OF SOLVENT,XM =  130.200 GRAM/MOLE
     XI FOR EQUATION DGM =  6.00  AND XI FOR EQUATION DM2 AND DM3 = 12.00
     MOLAR VOLUME AT THE BOILING POINT,DBP =  192.40000 CC/MOLE
     DENSITY = 0.82730 AT 295.0 DEG C       DENSITY = 0.81710 AT 310.0 DEG C, IN GRAM/CC
     VISCOSITY = 0.08220 AT 295.0 DEG C     VISCOSITY = 0.04760 AT 310.0 DEG C, IN POISE
     VISCOUS ACTIVATION ENERGY,EN =   6618.19275 CAL/DEG*MOLE
     SELF DIFFUSION ACTIVATION ENERGY FOR EQUATION DM2 AND DM3, ED =   6079.99603 CAL/DEG*MOLE
     COEFFIEIENT OF VOLUMETRIC EXPANSION,ALP =     0.0008322 1/DEG
SOLUTE CODE = 18       SOLVENT CODE = 17
     TEMPERATURE =296.40 DEG C    DIFFUSIVITY =  0.19300E-06 CM**2/SEC   VISCOSITY = 24.50000 POISE
  DWC=    0.69223576E-08        DDWC=  0.96413
  F = 0.025   DO  =  0.20043E-06   DGM =  0.50717E-01   DM1 =  0.29170E-05   DM2 =  0.40717E 01   DM3 =  0.39173E-13
              DDO =  -0.0384964   DDGM = 779.6289063  DDM1 = -14.1138405  DDM2 = 927.0000000  DDM3 =   0.9999998
  F = 0.050   DO  =  0.18142E-06   DGM =  0.33309E-01   DM1 =  0.24578E-05   DM2 =  0.23978E 01   DM3 =  0.52775E-13
              DDO =   0.0599955   DDGM = 585.4804688  DDM1 = -11.7345685  DDM2 = 835.8750000  DDM3 =   0.9999997
  F = 0.075   DO  =  0.16421E-06   DGM =  0.21876E-01   DM1 =  0.20709E-05   DM2 =  0.14120E 01   DM3 =  0.71100E-13
              DDO =   0.1491462   DDGM = 348.6542969  DDM1 =  -9.7298512  DDM2 = 311.6875000  DDM3 =   0.9999996
  F = 0.100   DO  =  0.14864E-06   DGM =  0.14368E-01   DM1 =  0.17449E-05   DM2 =  0.83155E 00   DM3 =  0.95787E-13
              DDO =   0.2298418   DDGM = 443.6640625  DDM1 =  -8.0407223  DDM2 = 524.4375000  DDM3 =   0.9999995
  F = 0.125   DO  =  0.13454E-06   DGM =  0.94364E-02   DM1 =  0.14702E-05   DM2 =  0.48969E 00   DM3 =  0.12905E-12
              DDO =   0.3028842   DDGM = 892.0410156  DDM1 =  -6.6175014  DDM2 = 260.1875000  DDM3 =   0.9999993
  F = 0.150   DO  =  0.12178E-06   DGM =  0.61975E-02   DM1 =  0.12387E-05   DM2 =  0.28838E 00   DM3 =  0.17386E-12
              DDO =   0.3689992   DDGM = 110.4914551  DDM1 =  -5.4183297  DDM2 = 174.4062500  DDM3 =   0.9999991
  F = 0.175   DO  =  0.11023E-06   DGM =  0.40703E-02   DM1 =  0.10437E-05   DM2 =  0.16982E 00   DM3 =  0.23422E-12
              DDO =   0.4288438   DDGM = 088.8647451  DDM1 =  -4.4079341  DDM2 = 908.4687500  DDM3 =   0.9999988
  F = 0.200   DO  =  0.99779E-07   DGM =  0.26733E-02   DM1 =  0.87942E-06   DM2 =  0.10001E 00   DM3 =  0.31555E-12
              DDO =   0.4830127   DDGM = 850.1945801  DDM1 =  -3.5565996  DDM2 = 171.5507813  DDM3 =   0.9999984
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 YGW0645 MITCHELL,R.D.
F = 0.225   D0 =  0.90315E-07   DGM =  0.17557E-02   DM1 =  0.74098E-06   DM2 =  0.58894E-01   DM3 =  0.42512E-12
           DD0 =   0.5320442  DDGM = 096.0515137  DDM1 =  -2.8392844  DDM2 = 147.2695313  DDM3 =   0.9999978
F = 0.250   D0 =  0.81750E-07   DGM =  0.11531E-02   DM1 =  0.62433E-06   DM2 =  0.34682E-01   DM3 =  0.57274E-12
           DD0 =   0.5764255  DDGM = 973.6721802  DDM1 =  -2.2348919  DDM2 = 698.7285156  DDM3 =   0.9999970
F = 0.275   D0 =  0.73997E-07   DGM =  0.75733E-03   DM1 =  0.52605E-06   DM2 =  0.20424E-01   DM3 =  0.77161E-12
           DD0 =   0.6165976  DDGM = 922.9860535  DDM1 =  -1.7256443  DDM2 = 822.9179688  DDM3 =   0.9999960
F = 0.300   D0 =  0.66979E-07   DGM =  0.49739E-03   DM1 =  0.44324E-06   DM2 =  0.12028E-01   DM3 =  0.10395E-11
           DD0 =   0.6529598  DDGM = 576.1573181  DDM1 =  -1.2965643  DDM2 = 317.9746094  DDM3 =   0.9999946
F = 0.325   D0 =  0.60626E-07   DGM =  0.32667E-03   DM1 =  0.37346E-06   DM2 =  0.70829E-02   DM3 =  0.14005E-11
           DD0 =   0.6858733  DDGM = 691.5998588  DDM1 =  -0.9350315  DDM2 = 698.2177734  DDM3 =   0.9999927
F = 0.350   D0 =  0.54877E-07   DGM =  0.21455E-03   DM1 =  0.31467E-06   DM2 =  0.41711E-02   DM3 =  0.18858E-11
           DD0 =   0.7156653  DDGM = 110.6490021  DDM1 =  -0.6304123  DDM2 = 610.9130859  DDM3 =   0.9999902
F = 0.375   D0 =  0.49672E-07   DGM =  0.14091E-03   DM1 =  0.26513E-06   DM2 =  0.24563E-02   DM3 =  0.25419E-11
           DD0 =   0.7426319  DDGM = 729.0978317  DDM1 =  -0.3737477  DDM2 = 726.1079102  DDM3 =   0.9999868
F = 0.400   D0 =  0.44961E-07   DGM =  0.92545E-04   DM1 =  0.22340E-06   DM2 =  0.14465E-02   DM3 =  0.34246E-11
           DD0 =   0.7670409  DDGM = 478.5064812  DDM1 =  -0.1574877  DDM2 = 493.9051514  DDM3 =   0.9999823
F = 0.425   D0 =  0.40697E-07   DGM =  0.60781E-04   DM1 =  0.18823E-06   DM2 =  0.85184E-03   DM3 =  0.46137E-11
           DD0 =   0.7891349  DDGM = 313.9255562  DDM1 =   0.0247279  DDM2 = 412.6983643  DDM3 =   0.9999761
F = 0.450   D0 =  0.36837E-07   DGM =  0.39919E-04   DM1 =  0.15860E-06   DM2 =  0.50164E-03   DM3 =  0.62157E-11
           DD0 =   0.8091335  DDGM = 205.8336906  DDM1 =   0.1782585  DDM2 = 598.1961670  DDM3 =   0.9999678
F = 0.475   D0 =  0.33344E-07   DGM =  0.26218E-04   DM1 =  0.13363E-06   DM2 =  0.29542E-03   DM3 =  0.83739E-11
           DD0 =   0.8272354  DDGM = 134.8421822  DDM1 =   0.3076197  DDM2 = 529.6486664  DDM3 =   0.9999566
F = 0.500   D0 =  0.30181E-07   DGM =  0.17219E-04   DM1 =  0.11259E-06   DM2 =  0.17397E-03   DM3 =  0.11282E-10
           DD0 =   0.8436205  DDGM = -88.2170954  DDM1 =   0.4166165  DDM2 = 900.3884430  DDM3 =   0.9999415
F = 0.525   D0 =  0.27319E-07   DGM =  0.11309E-04   DM1 =  0.94868E-07   DM2 =  0.10245E-03   DM3 =  0.15199E-10
           DD0 =   0.8584517  DDGM = -57.5951347  DDM1 =   0.5084546  DDM2 = 529.8215561  DDM3 =   0.9999212
F = 0.550   D0 =  0.24728E-07   DGM =  0.74273E-05   DM1 =  0.79934E-07   DM2 =  0.60331E-04   DM3 =  0.20475E-10
           DD0 =   0.8718762  DDGM = -37.4835300  DDM1 =   0.5858353  DDM2 = 311.5970688  DDM3 =   0.9998939
F = 0.575   D0 =  0.22383E-07   DGM =  0.48780E-05   DM1 =  0.67350E-07   DM2 =  0.35529E-04   DM3 =  0.27586E-10
           DD0 =   0.8840276  DDGM = -24.2748334  DDM1 =   0.6510346  DDM2 = 183.0862560  DDM3 =   0.9998571
F = 0.600   D0 =  0.20260E-07   DGM =  0.32038E-05   DM1 =  0.56748E-07   DM2 =  0.20923E-04   DM3 =  0.37165E-10
           DD0 =   0.8950265  DDGM = -15.5997583  DDM1 =   0.7059698  DDM2 = 107.4071255  DDM3 =   0.9998074
F = 0.625   D0 =  0.18338E-07   DGM =  0.21041E-05   DM1 =  0.47814E-07   DM2 =  0.12321E-04   DM3 =  0.50070E-10
           DD0 =   0.9049823  DDGM =  -9.9022254  DDM1 =   0.7522570  DDM2 = -62.8402071  DDM3 =   0.9997406
F = 0.650   D0 =  0.16599E-07   DGM =  0.13819E-05   DM1 =  0.40287E-07   DM2 =  0.72558E-05   DM3 =  0.67456E-10
           DD0 =   0.9139938  DDGM =  -6.1602561  DDM1 =   0.7912575  DDM2 = -36.5950570  DDM3 =   0.9996505
F = 0.675   D0 =  0.15025E-07   DGM =  0.90761E-06   DM1 =  0.33945E-07   DM2 =  0.42729E-05   DM3 =  0.90878E-10
           DD0 =   0.9221507  DDGM =  -3.7025421  DDM1 =   0.8241185  DDM2 = -21.1394691  DDM3 =   0.9995291
F = 0.700   D0 =  0.13600E-07   DGM =  0.59609E-06   DM1 =  0.28601E-07   DM2 =  0.25163E-05   DM3 =  0.12243E-09
           DD0 =   0.9295340  DDGM =  -2.0885549  DDM1 =   0.8518063  DDM2 = -12.0377806  DDM3 =   0.9993556
F = 0.725   D0 =  0.12310E-07   DGM =  0.39149E-06   DM1 =  0.24099E-07   DM2 =  0.14818E-05   DM3 =  0.16495E-09
           DD0 =   0.9362170  DDGM =  -1.0284707  DDM1 =   0.8751355  DDM2 =  -6.6778589  DDM3 =   0.9991454
F = 0.750   D0 =  0.11143E-07   DGM =  0.25712E-06   DM1 =  0.20305E-07   DM2 =  0.87264E-06   DM3 =  0.22222E-09
           DD0 =   0.9422663  DDGM =  -0.3322391  DDM1 =   0.8947921  DDM2 =  -3.5214381  DDM3 =   0.9988486
F = 0.775   D0 =  0.10086E-07   DGM =  0.16887E-06   DM1 =  0.17109E-07   DM2 =  0.51389E-06   DM3 =  0.29938E-09
           DD0 =   0.9477418  DDGM =   0.1250251  DDM1 =   0.9113542  DDM2 =  -1.6626438  DDM3 =   0.9984488
F = 0.800   D0 =  0.91293E-08   DGM =  0.11091E-06   DM1 =  0.14415E-07   DM2 =  0.30263E-06   DM3 =  0.40334E-09
           DD0 =   0.9526980  DDGM =   0.4253427  DDM1 =   0.9253092  DDM2 =  -0.5680123  DDM3 =   0.9979102
F = 0.825   D0 =  0.82635E-08   DGM =  0.72842E-07   DM1 =  0.12146E-07   DM2 =  0.17821E-06   DM3 =  0.54339E-09
           DD0 =   0.9571842  DDGM =   0.6225822  DDM1 =   0.9370672  DDM2 =   0.0766084  DDM3 =   0.9971845
F = 0.850   D0 =  0.74797E-08   DGM =  0.47840E-07   DM1 =  0.10234E-07   DM2 =  0.10495E-06   DM3 =  0.73207E-09
           DD0 =   0.9612448  DDGM =   0.7521233  DDM1 =   0.9469743  DDM2 =   0.4562210  DDM3 =   0.9962069
F = 0.875   D0 =  0.67704E-08   DGM =  0.31420E-07   DM1 =  0.86229E-08   DM2 =  0.61804E-07   DM3 =  0.98626E-09
           DD0 =   0.9649204  DDGM =   0.8372020  DDM1 =   0.9553218  DDM2 =   0.6797723  DDM3 =   0.9948898
F = 0.900   D0 =  0.61283E-08   DGM =  0.20636E-07   DM1 =  0.72654E-08   DM2 =  0.36396E-07   DM3 =  0.13287E-08
           DD0 =   0.9682474  DDGM =   0.8930791  DDM1 =   0.9623552  DDM2 =   0.8114201  DDM3 =   0.9931154
F = 0.925   D0 =  0.55470E-08   DGM =  0.13553E-07   DM1 =  0.61217E-08   DM2 =  0.21433E-07   DM3 =  0.17901E-08
           DD0 =   0.9712588  DDGM =   0.9297775  DDM1 =   0.9682814  DDM2 =   0.8889466  DDM3 =   0.9907249
F = 0.950   D0 =  0.50210E-08   DGM =  0.89012E-08   DM1 =  0.51580E-08   DM2 =  0.12622E-07   DM3 =  0.24117E-08
           DD0 =   0.9739847  DDGM =   0.9538800  DDM1 =   0.9732746  DDM2 =   0.9346014  DDM3 =   0.9875044
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 YGW0645 MITCHELL,R.D.
F = 0.975   D0 =   0.45448E-08   DGM =  0.58450E-08   DM1 =  0.43460E-08   DM2 =  0.74330E-08   DM3 =  0.32491E-08
            DD0 =   0.9764520  DDGM =     0.9697097  DDM1 =    0.9774818  DDM2 =    0.9614872  DDM3 =    0.9831655
F = 1.000   D0 =   0.41137E-08   DGM =  0.38395E-08   DM1 =  0.36618E-08   DM2 =  0.43772E-08   DM3 =  0.43772E-08
            DD0 =    0.9786853  DDGM =    0.9801063  DDM1 =    0.9810267  DDM2 =    0.9773201  DDM3 =    0.9773201
THE FOLLOWING DEVIATIONS ARE AVERAGES FOR EACH F
F = 0.025  DD0 =    1.65865356   DDGM = 27.75000000   DDM1 = 92.26376343   DDM2 = 02.00000000   DDM3 =    0.99999908
F = 0.050  DD0 =    1.37729990   DDGM = 12.93750000   DDM1 = 73.99202728   DDM2 = 22.00000000   DDM3 =    0.99999882
F = 0.075  DD0 =    1.14017498   DDGM = 55.00000000   DDM1 = 59.31576729   DDM2 = 70.00000000   DDM3 =    0.99999848
F = 0.100  DD0 =    0.93074922   DDGM = 59.84375000   DDM1 = 47.52472353   DDM2 = 92.00000000   DDM3 =    0.99999805
F = 0.125  DD0 =    0.74576373   DDGM = 84.17187500   DDM1 = 38.04944420   DDM2 = 44.00000000   DDM3 =    0.99999748
F = 0.150  DD0 =    0.58946943   DDGM = 29.15625000   DDM1 = 30.43323445   DDM2 = 40.00000000   DDM3 =    0.99999577
F = 0.175  DD0 =    0.49626194   DDGM = 60.56250000   DDM1 = 24.30980206   DDM2 = 13.00000000   DDM3 =    0.99999583
F = 0.200  DD0 =    0.46577707   DDGM = 78.03125000   DDM1 = 19.38528967   DDM2 = 90.00000000   DDM3 =    0.99999461
F = 0.225  DD0 =    0.44083787   DDGM = 65.81835938   DDM1 = 15.42391348   DDM2 = 46.00000000   DDM3 =    0.99999303
F = 0.250  DD0 =    0.44296414   DDGM = 05.04394531   DDM1 = 12.23643601   DDM2 = 20.00000000   DDM3 =    0.99999098
F = 0.275  DD0 =    0.46626471   DDGM = 62.01220703   DDM1 =    9.67095101  DDM2 = 84.00000000   DDM3 =    0.99998832
F = 0.300  DD0 =    0.48704123   DDGM = 52.90573828   DDM1 =    7.60549861  DDM2 = 80.00000000   DDM3 =    0.99998485
F = 0.325  DD0 =    0.50557975   DDGM = 55.30200195   DDM1 =    5.94212973  DDM2 = 04.50000000   DDM3 =    0.99998034
F = 0.350  DD0 =    0.52213231   DDGM = 44.82849121   DDM1 =    4.60217041  DDM2 = 95.25000000   DDM3 =    0.99997447
F = 0.375  DD0 =    0.53692125   DDGM = 34.13366599   DDM1 =    3.52241054  DDM2 = 98.62500000   DDM3 =    0.99996583
F = 0.400  DD0 =    0.55485131   DDGM = 65.84503174   DDM1 =    2.65204880  DDM2 = 72.25000000   DDM3 =    0.99995685
F = 0.425  DD0 =    0.60434055   DDGM = 13.77014160   DDM1 =    1.95849553  DDM2 = 23.15625000   DDM3 =    0.99994384
F = 0.450  DD0 =    0.64827291   DDGM = 06.64602661   DDM1 =    1.44360960  DDM2 = 07.43750000   DDM3 =    0.99992584
F = 0.475  DD0 =    0.68727867   DDGM = 24.09223175   DDM1 =    1.02999598  DDM2 = 49.51953125   DDM3 =    0.99990463
F = 0.500  DD0 =    0.72191589   DDGM = 35.12725067   DDM1 =    0.74142119  DDM2 = 16.45117188   DDM3 =    0.99987559
F = 0.525  DD0 =    0.75267876   DDGM = 61.79987717   DDM1 =    0.55258001  DDM2 = 75.59863281   DDM3 =    0.99983758
F = 0.550  DD0 =    0.78000502   DDGM = 57.65475082   DDM1 =    0.55715361  DDM2 = 96.73828125   DDM3 =    0.99978782
F = 0.575  DD0 =    0.80428241   DDGM = 94.96650124   DDM1 =    0.56750688  DDM2 = 72.84399414   DDM3 =    0.99972263
F = 0.600  DD0 =    0.82585452   DDGM = 57.16279984   DDM1 =    0.57773541  DDM2 = 27.58215332   DDM3 =    0.99963711
F = 0.625  DD0 =    0.84502582   DDGM = 34.32223558   DDM1 =    0.58753534  DDM2 = 40.71170044   DDM3 =    0.99952494
F = 0.650  DD0 =    0.86206615   DDGM = 20.49532366   DDM1 =    0.59671942  DDM2 = 08.40029907   DDM3 =    0.99937768
F = 0.675  DD0 =    0.87721471   DDGM = 12.10827839   DDM1 =    0.64330213  DDM2 = 33.89511871   DDM3 =    0.99918422
F = 0.700  DD0 =    0.89068362   DDGM =  7.01056957   DDM1 =    0.71058223  DDM2 = 36.36324692   DDM3 =    0.99892990
F = 0.725  DD0 =    0.90266092   DDGM =  3.90573530   DDM1 =    0.76507033  DDM2 = 04.77280235   DDM3 =    0.99859542
F = 0.750  DD0 =    0.91331343   DDGM =  2.01073077   DDM1 =    0.80921657  DDM2 = 46.38111687   DDM3 =    0.99815522
F = 0.775  DD0 =    0.92278911   DDGM =  0.89335089   DDM1 =    0.84499863  DDM2 = 20.36279583   DDM3 =    0.99757554
F = 0.800  DD0 =    0.93121926   DDGM =  0.38716839   DDM1 =    0.87401339  DDM2 =  8.70919156   DDM3 =    0.99681176
F = 0.825  DD0 =    0.93872035   DDGM =  0.32253550   DDM1 =    0.89755070  DDM2 =  3.48133612   DDM3 =    0.99580485
F = 0.850  DD0 =    0.94539572   DDGM =  0.56370550   DDM1 =    0.91665281  DDM2 =  1.48485030   DDM3 =    0.99447574
F = 0.875  DD0 =    0.95133719   DDGM =  0.72939942   DDM1 =    0.93216220  DDM2 =  0.89812953   DDM3 =    0.99272395
F = 0.900  DD0 =    0.95662618   DDGM =  0.83182425   DDM1 =    0.94476010  DDM2 =  0.72592238   DDM3 =    0.99040957
F = 0.925  DD0 =    0.96133505   DDGM =  0.89527132   DDM1 =    0.95499766  DDM2 =  0.77373958   DDM3 =    0.98735210
F = 0.950  DD0 =    0.96552804   DDGM =  0.93465442   DDM1 =    0.96332079  DDM2 =  0.88794309   DDM3 =    0.98331095
F = 0.975  DD0 =    0.96926218   DDGM =  0.95914985   DDM1 =    0.97009057  DDM2 =  0.94343496   DDM3 =    0.97796716
F = 1.000  DD0 =    0.97258817   DDGM =  0.97441562   DDM1 =    0.97559939  DDM2 =  0.97089747   DDM3 =    0.97089747
DDWC =    0.94836

*01* UNIT05, EOF.                                                                  REC=  00000 FIL=  00002
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The following program was used to predict the diffusivities for the original Gainer and Metzner equation.

```
$ID    YGW0645 MITCHELL,R.D.  DIFGM
$IBJOB         GO
$IBLDR MAIN                                  000336     12/19/69    MAIN0000
$TEXT  MAIN                                  000336     12/19/69    MAIN0001
C.....THIS PROGRAM CALCULATES THE DIFFUSION COEFFICIENTS FOR THE
C     ORIGINAL GAINER AND METZNER MODEL.
      DIMENSION H(30),HH(30),D(30),Z(30),XM(30),V(30),R(30),DE(30)
      DIMENSION E(30),EH(30),ED(30),SUM(40,30)
      READ(5,200) IRUN
      DO 88 JRUN=1,IRUN
      READ(5,200) NWAY,NTOT,NSYS
C.....NTOT IS THE NUMBER OF LIQUIDS FOR WHICH DATA IS READ IN.
C.....NSYS IS THE NUMBER OF SYSTEMS.
      READ (5,100) XR,XK,XN
C.....XR IS THE UNIVERSAL GAS CONSTANT.
C.....XK IS THE BOLTZMAN CONSTANT.
C.....XN IS THE AVOGADRO NUMBER.
      WRITE (6,150) XR
      WRITE (6,152) XK
      WRITE (6,153) XN
      DO 1 I=1,NTOT
      READ(5,101) H(I),HH(I),D(I),Z(I),XM(I),V(I),T
C.....H IS THE ENTHALPY OF VAPORIZATION.
C.....HH IS THE RATIO OF THE ENTHALPY OF VAPORIZATION DUE TO DISPERSION
C     FORCE BONDS TO THE  TOTAL.
C.....D IS THE DENSITY.
C.....Z IS XI FOR THE GAINER-METZNER MODEL.
C.....XM IS THE MOLECULAR WEIGHT.
C.....V IS THE VISCOSITY.
C.....T IS THE TEMPERATURE.
      R(I)=(XM(I)/(D(I)*XN))**0.3333
C.....R IS THE MOLECULAR RADIUS.
      DE(I)=H(I)-XR*T
C.....DE IS THE ENERGY OF VAPORIZATION.
      E(I)=XR*T*ALOG(V(I)*DE(I)*((XM(I)/D(I))**0.6667)/(0.00109*(SQRT(
     2XM(I)))*(T**1.5)))
C..... E IS THE ACTIVATION ENERGY  FOR VISCOUS TRANSFER FOR THE ORIGINAL
C     GAINER MODEL.
      ED(I)=E(I)*HH(I)
C.....ED IS THE ACTIVATION ENERGY DUE TO DISPERSION FORCE BONDS.
      EH(I)=E(I)-ED(I)
C.....EH IS THE ACTIVATION ENERGY DUE TO HYDROGEN BONDS.
      WRITE (6,155) I
      WRITE (6,120) H(I)
      WRITE (6,156) HH(I)
      WRITE (6,151) D(I)
      WRITE (6,159) Z(I)
      WRITE (6,158) XM(I)
      WRITE(6,111) V(I),T
    1 WRITE (6,160) E(I)
      UU=NSYS
      DO 2 I=1,NSYS
      READ (5,102) NB,NA,T,DACT
C.....DACT IS THE EXPERIMENTALLY DETERMINED DIFFUSIVITY.
      WRITE (6,103) NA,NB
      WRITE (6,170) T,DACT,V(NB)
      DO 2 IP=1,40
      F=IP
      F=0.025*F
```

```
C.....F IS THAT FRACTION OF THE ACTIVATION ENERGY DUE TO THE HOLE
C     FORMATION TERM.
      A=1.-F
C.....A IS THAT FRACTION OF THE ACTIVATION ENERGY DUE TO THE JUMP TERM.
      RAB=(R(NA)+R(NB))/2.
C.....RAB IS THE AVERAGE RADIUS OF THE TWO MOLECULES IN EACH SYSTEM.
      RAB=R(NB)*R(NA)/(RAB**2)
      DELE=(E(NB)*A )-(Z(NA)/Z(NB))*(SQRT(A*A *RAB*EH(NA)*EH(NB))
     2+SQRT(A*A *(RAB**12)*ED(NA)*ED(NB)))
C.....DELE IS PART OF THE EXPONENTIAL TERM FOR THE ORIGINAL GAINER MODEL.
      DX=XK*T*(EXP(DELE/(XR*T)))/(Z(NA)*V(NB)*R(NB))
C.....DX IS THE DIFFUSIVITY AS CALCULATED BY THE ORIGINAL GAINER MODEL.
      SUM(IP,I)=(DACT-DX)/DACT
C.....SUM IS THE FRACTIONAL DEVIATION.
C.....THIS SECTION IS HERE TO SUPPRESS UNNEEDED OUTPUT WHEN DESIRED.
      IF(NWAY)20,21,20
   20 IF(I-1) 2,22, 2
   22 WRITE (6,121) F,DX,SUM(IP,I)
      GO TO 2
   21 CONTINUE
      WRITE (6,103) NA,NB
      WRITE (6,170) T,DACT,V(NB)
      WRITE (6,121) F,DX,SUM(IP,I)
    2 CONTINUE
      DO 4 J=1,40
      F=J
      F=0.025*F
      U=0.0
      DO 3 I=1,NSYS
    3 U=U+ABS(SUM(J,I))
      U=U/UU
C.....U IS THE AVERAGE FRACTIONAL DEVIATION.
    4 WRITE (6,104) F,U
   88 CONTINUE
      STOP
  100 FORMAT (4F18.8)
  101 FORMAT (7F10.5)
  102 FORMAT (2I6,4E18.8)
  103 FORMAT (1X,14H SOLUTE CODE =,I3,5X,15H SOLVENT CODE =,I3)
  104 FORMAT(10X,5H F = ,F5.3,32H AVERAGE FRACTIONAL DEVIATION = ,F8.5)
  111 FORMAT (10X,13H VISCOSITY = ,F7.5,3H AT,F6.1,6H DEG C)
  120 FORMAT(10X,30H ENTHALPY OF VAPORIZATION,H = ,F10.3,9H CAL/MOLE)
  121 FORMAT(10X,5H F = ,F5.3,9H    DGM = ,E12.5,10H    DDGM = ,F8.5)
  150 FORMAT(1H1,10X,28H UNIVERSAL GAS CONSTANT,XR= ,F10.5,13H CAL/DEG*M
     2OLE)
  151 FORMAT (10X,11H DENSITY = ,F8.5,8H GRAM/CC)
  152 FORMAT(10X,24H BOLTZMAN CONSTANT,XK = ,E18.8,8H ERG/DEG)
  153 FORMAT(10X,24H AVOGADRO NUMBER, XN  = ,E18.8,7H 1/MOLE)
  155 FORMAT(1H0,10X,18H SOLVENT NUMBER = ,I3)
  156 FORMAT(10X,83H FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUT
     2ED TO DISPERSION FORCE BONDS = ,F6.3)
  158 FORMAT(10X,34H MOLECULAR WEIGHT OF SOLVENT,XM = ,F8.3,10H GRAM/MOL
     2E)
  159 FORMAT(10X,34H XI FOR GAINER-METZNER EQUATION = ,F4.2)
  160 FORMAT(10X,32H VISCOUS ACTIVATION ENERGY,E  = ,F12.5,13H CAL/DEG*M
     2OLE)
  170 FORMAT(10X,14H TEMPERATURE = ,F6.2,6H DEG C,18H     DIFFUSIVITY = ,
     2E12.5,10H CM**2/SEC,15H    VISCOSITY = ,F8.5,6H POISE)
  200 FORMAT(3I5)
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END

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YGW0645 MITCHELL,R.D.
     UNIVERSAL GAS CONSTANT,XR=     1.98700 CAL/DEG*MOLE
    BOLTZMAN CONSTANT,XK =      0.13803000E-15 ERG/DEG
    AVOGADRO NUMBER, XN  =      0.60230000E 24 1/MOLE

     SOLVENT NUMBER =    1
    ENTHALPY OF VAPORIZATION,H =   8100.000 CAL/MOLE
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  1.000
    DENSITY =  0.88420 GRAM/CC
    XI FOR GAINER-METZNER EQUATION = 6.20
    MOLECULAR WEIGHT OF SOLVENT,XM =   78.110 GRAM/MOLE
    VISCOSITY = 0.00696 AT 288.0 DEG C
    VISCOUS ACTIVATION ENERGY,E  =   1770.82449 CAL/DEG*MOLE

     SOLVENT NUMBER =    2
    ENTHALPY OF VAPORIZATION,H =   8840.000 CAL/MOLE
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  1.000
    DENSITY =  0.87160 GRAM/CC
    XI FOR GAINER-METZNER EQUATION = 6.00
    MOLECULAR WEIGHT OF SOLVENT,XM =   92.130 GRAM/MOLE
    VISCOSITY = 0.00623 AT 288.0 DEG C
    VISCOUS ACTIVATION ENERGY,E  =   1782.29398 CAL/DEG*MOLE

     SOLVENT NUMBER =    3
    ENTHALPY OF VAPORIZATION,H =   7540.000 CAL/MOLE
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  1.000
    DENSITY =  0.66380 GRAM/CC
    XI FOR GAINER-METZNER EQUATION = 5.40
    MOLECULAR WEIGHT OF SOLVENT,XM =   86.170 GRAM/MOLE
    VISCOSITY = 0.00337 AT 288.0 DEG C
    VISCOUS ACTIVATION ENERGY,E  =   1430.33037 CAL/DEG*MOLE

     SOLVENT NUMBER =    4
    ENTHALPY OF VAPORIZATION,H =   8950.000 CAL/MOLE
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.495
    DENSITY =  0.79609 GRAM/CC
    XI FOR GAINER-METZNER EQUATION = 8.10
    MOLECULAR WEIGHT OF SOLVENT,XM =   32.040 GRAM/MOLE
    VISCOSITY = 0.00623 AT 288.0 DEG C
    VISCOUS ACTIVATION ENERGY,E  =   1723.67773 CAL/DEG*MOLE

     SOLVENT NUMBER =    5
    ENTHALPY OF VAPORIZATION,H =  10400.000 CAL/MOLE
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.555
    DENSITY =  0.80749 GRAM/CC
    XI FOR GAINER-METZNER EQUATION = 6.50
    MOLECULAR WEIGHT OF SOLVENT,XM =   60.090 GRAM/MOLE
    VISCOSITY = 0.02522 AT 288.0 DEG C
    VISCOUS ACTIVATION ENERGY,E  =   2669.75595 CAL/DEG*MOLE

     SOLVENT NUMBER =    6
    ENTHALPY OF VAPORIZATION,H =  10240.000 CAL/MOLE
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.540
    DENSITY =  0.78916 GRAM/CC
    XI FOR GAINER-METZNER EQUATION = 6.40
    MOLECULAR WEIGHT OF SOLVENT,XM =   60.090 GRAM/MOLE
    VISCOSITY = 0.02859 AT 288.0 DEG C
    VISCOUS ACTIVATION ENERGY,E  =   2740.89523 CAL/DEG*MOLE

     SOLVENT NUMBER =    7
    ENTHALPY OF VAPORIZATION,H =  10530.000 CAL/MOLE
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YGW0645 MITCHELL,R.D.
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.611
    DENSITY =  0.81337 GRAM/CC
    XI FOR GAINER-METZNER EQUATION = 6.10
    MOLECULAR WEIGHT OF SOLVENT,XM =   74.120 GRAM/MOLE
    VISCOSITY = 0.03379 AT 288.0 DEG C
    VISCOUS ACTIVATION ENERGY,E  =   2861.92545 CAL/DEG*MOLE

     SOLVENT NUMBER =   8
    ENTHALPY OF VAPORIZATION,H =  10460.000 CAL/MOLE
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.598
    DENSITY =  0.80576 GRAM/CC
    XI FOR GAINER-METZNER EQUATION = 6.00
    MOLECULAR WEIGHT OF SOLVENT,XM =   74.120 GRAM/MOLE
    VISCOSITY = 0.04703 AT 288.0 DEG C
    VISCOUS ACTIVATION ENERGY,E  =   3050.67550 CAL/DEG*MOLE

     SOLVENT NUMBER =   9
    ENTHALPY OF VAPORIZATION,H =   5030.000 CAL/MOLE
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.910
    DENSITY =  1.05310 GRAM/CC
    XI FOR GAINER-METZNER EQUATION = 6.00
    MOLECULAR WEIGHT OF SOLVENT,XM =   60.050 GRAM/MOLE
    VISCOSITY = 0.01314 AT 288.0 DEG C
    VISCOUS ACTIVATION ENERGY,E  =   1742.87024 CAL/DEG*MOLE

     SOLVENT NUMBER =  10
    ENTHALPY OF VAPORIZATION,H =  12200.000 CAL/MOLE
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  1.000
    DENSITY =  1.49845 GRAM/CC
    XI FOR GAINER-METZNER EQUATION = 6.00
    MOLECULAR WEIGHT OF SOLVENT,XM =  119.390 GRAM/MOLE
    VISCOSITY = 0.00596 AT 288.0 DEG C
    VISCOUS ACTIVATION ENERGY,E  =   1770.09784 CAL/DEG*MOLE

     SOLVENT NUMBER =  11
    ENTHALPY OF VAPORIZATION,H =   7830.000 CAL/MOLE
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  1.000
    DENSITY =  1.60370 GRAM/CC
    XI FOR GAINER-METZNER EQUATION = 5.80
    MOLECULAR WEIGHT OF SOLVENT,XM =  153.840 GRAM/MOLE
    VISCOSITY = 0.01038 AT 288.0 DEG C
    VISCOUS ACTIVATION ENERGY,E  =   1815.15852 CAL/DEG*MOLE

     SOLVENT NUMBER =  12
    ENTHALPY OF VAPORIZATION,H =   8900.000 CAL/MOLE
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  1.000
    DENSITY =  1.11172 GRAM/CC
    XI FOR GAINER-METZNER EQUATION = 6.00
    MOLECULAR WEIGHT OF SOLVENT,XM =  122.550 GRAM/MOLE
    VISCOSITY = 0.00844 AT 288.0 DEG C
    VISCOUS ACTIVATION ENERGY,E  =   1894.55584 CAL/DEG*MOLE

     SOLVENT NUMBER =  13
    ENTHALPY OF VAPORIZATION,H =   9200.000 CAL/MOLE
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  1.000
    DENSITY =  1.50170 GRAM/CC
    XI FOR GAINER-METZNER EQUATION = 6.00
    MOLECULAR WEIGHT OF SOLVENT,XM =  157.020 GRAM/MOLE
    VISCOSITY = 0.01196 AT 288.0 DEG C
    VISCOUS ACTIVATION ENERGY,E  =   2023.21459 CAL/DEG*MOLE
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YGW0645 MITCHELL,R.D.
  SOLVENT NUMBER =  14
 ENTHALPY OF VAPORIZATION,H =  10000.000 CAL/MOLE
 FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.463
 DENSITY =  0.79367 GRAM/CC
 XI FOR GAINER-METZNER EQUATION = 8.30
 MOLECULAR WEIGHT OF SOLVENT,XM =   46.070 GRAM/MOLE
 VISCOSITY = 0.01330 AT 288.0 DEG C
 VISCOUS ACTIVATION ENERGY,E  =   2261.04739 CAL/DEG*MOLE

  SOLVENT NUMBER =  15
 ENTHALPY OF VAPORIZATION,H =   6620.000 CAL/MOLE
 FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.900
 DENSITY =  0.71925 GRAM/CC
 XI FOR GAINER-METZNER EQUATION = 6.00
 MOLECULAR WEIGHT OF SOLVENT,XM =   74.120 GRAM/MOLE
 VISCOSITY = 0.00247 AT 288.0 DEG C
 VISCOUS ACTIVATION ENERGY,E  =   1126.48972 CAL/DEG*MOLE

  SOLVENT NUMBER =  16
 ENTHALPY OF VAPORIZATION,H =  13100.000 CAL/MOLE
 FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.384
 DENSITY =  0.79526 GRAM/CC
 XI FOR GAINER-METZNER EQUATION = 6.00
 MOLECULAR WEIGHT OF SOLVENT,XM =   58.110 GRAM/MOLE
 VISCOSITY = 0.00355 AT 288.0 DEG C
 VISCOUS ACTIVATION ENERGY,E  =   1689.27315 CAL/DEG*MOLE

  SOLVENT NUMBER =  17
 ENTHALPY OF VAPORIZATION,H =  10250.000 CAL/MOLE
 FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.100
 DENSITY =  0.99913 GRAM/CC
 XI FOR GAINER-METZNER EQUATION = 6.10
 MOLECULAR WEIGHT OF SOLVENT,XM =   18.000 GRAM/MOLE
 VISCOSITY = 0.01104 AT 288.0 DEG C
 VISCOUS ACTIVATION ENERGY,E  =   1991.95358 CAL/DEG*MOLE

  SOLVENT NUMBER =  18
 ENTHALPY OF VAPORIZATION,H =   6500.000 CAL/MOLE
 FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.910
 DENSITY =  0.79452 GRAM/CC
 XI FOR GAINER-METZNER EQUATION = 6.00
 MOLECULAR WEIGHT OF SOLVENT,XM =   72.100 GRAM/MOLE
 VISCOSITY = 0.00365 AT 303.0 DEG C
 VISCOUS ACTIVATION ENERGY,E  =   1316.59459 CAL/DEG*MOLE

  SOLVENT NUMBER =  19
 ENTHALPY OF VAPORIZATION,H =   7050.000 CAL/MOLE
 FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  1.000
 DENSITY =  0.76928 GRAM/CC
 XI FOR GAINER-METZNER EQUATION = 6.00
 MOLECULAR WEIGHT OF SOLVENT,XM =   84.200 GRAM/MOLE
 VISCOSITY = 0.00820 AT 298.0 DEG C
 VISCOUS ACTIVATION ENERGY,E  =   1870.58045 CAL/DEG*MOLE

  SOLVENT NUMBER =  20
 ENTHALPY OF VAPORIZATION,H =   8100.000 CAL/MOLE
 FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  1.000
 DENSITY =  0.86844 GRAM/CC
 XI FOR GAINER-METZNER EQUATION = 6.20
 MOLECULAR WEIGHT OF SOLVENT,XM =   78.100 GRAM/MOLE
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YGW0645 MITCHELL,R.D.
    VISCOSITY = 0.00569 AT 303.0 DEG C
    VISCOUS ACTIVATION ENERGY,E  =   1700.72380 CAL/DEG*MOLE

     SOLVENT NUMBER =  21
    ENTHALPY OF VAPORIZATION,H =   8100.000 CAL/MOLE
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  1.000
    DENSITY =  0.87368 GRAM/CC
    XI FOR GAINER-METZNER EQUATION = 5.20
    MOLECULAR WEIGHT OF SOLVENT,XM =   78.100 GRAM/MOLE
    VISCOSITY = 0.00599 AT 298.0 DEG C
    VISCOUS ACTIVATION ENERGY,E  =   1716.27121 CAL/DEG*MOLE

     SOLVENT NUMBER =  22
    ENTHALPY OF VAPORIZATION,H =  13100.000 CAL/MOLE
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  0.384
    DENSITY =  0.78250 GRAM/CC
    XI FOR GAINER-METZNER EQUATION = 6.00
    MOLECULAR WEIGHT OF SOLVENT,XM =   58.100 GRAM/MOLE
    VISCOSITY = 0.00302 AT 298.0 DEG C
    VISCOUS ACTIVATION ENERGY,E  =   1627.29918 CAL/DEG*MOLE

     SOLVENT NUMBER =  23
    ENTHALPY OF VAPORIZATION,H =   8840.000 CAL/MOLE
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  1.000
    DENSITY =  0.85770 GRAM/CC
    XI FOR GAINER-METZNER EQUATION = 6.00
    MOLECULAR WEIGHT OF SOLVENT,XM =   92.100 GRAM/MOLE
    VISCOSITY = 0.00523 AT 303.0 DEG C
    VISCOUS ACTIVATION ENERGY,E  =   1728.13130 CAL/DEG*MOLE

     SOLVENT NUMBER =  24
    ENTHALPY OF VAPORIZATION,H =   8840.000 CAL/MOLE
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  1.000
    DENSITY =  0.86220 GRAM/CC
    XI FOR GAINER-METZNER EQUATION = 6.00
    MOLECULAR WEIGHT OF SOLVENT,XM =   92.100 GRAM/MOLE
    VISCOSITY = 0.00555 AT 298.0 DEG C
    VISCOUS ACTIVATION ENERGY,E  =   1748.25450 CAL/DEG*MOLE

     SOLVENT NUMBER =  25
    ENTHALPY OF VAPORIZATION,H =  10400.000 CAL/MOLE
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  1.000
    DENSITY =  0.79730 GRAM/CC
    XI FOR GAINER-METZNER EQUATION = 6.50
    MOLECULAR WEIGHT OF SOLVENT,XM =   50.100 GRAM/MOLE
    VISCOSITY = 0.01970 AT 298.0 DEG C
    VISCOUS ACTIVATION ENERGY,E  =   2589.70453 CAL/DEG*MOLE

     SOLVENT NUMBER =  26
    ENTHALPY OF VAPORIZATION,H =   7540.000 CAL/MOLE
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  1.000
    DENSITY =  0.65055 GRAM/CC
    XI FOR GAINER-METZNER EQUATION = 5.40
    MOLECULAR WEIGHT OF SOLVENT,XM =   86.200 GRAM/MOLE
    VISCOSITY = 0.00278 AT 303.0 DEG C
    VISCOUS ACTIVATION ENERGY,E  =   1348.61570 CAL/DEG*MOLE

     SOLVENT NUMBER =  27
    ENTHALPY OF VAPORIZATION,H =   7830.000 CAL/MOLE
    FRACTION OF TOTAL ENTHALPY OF VAPORIZATION ATTRIBUTED TO DISPERSION FORCE BONDS =  1.000
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 YGW0645 MITCHELL,R.D.
      DENSITY =  1.58200 GRAM/CC
      XI FOR GAINER-METZNER EQUATION = 5.80
      MOLECULAR WEIGHT OF SOLVENT,XM =  153.800 GRAM/MOLE
      VISCOSITY = 0.00910 AT 298.0 DEG C
      VISCOUS ACTIVATION ENERGY,E  =    1774.70470 CAL/DEG*MOLE
SOLUTE CODE = 17       SOLVENT CODE =  8
      TEMPERATURE =288.00 DEG C    DIFFUSIVITY =  0.30000E-05 CM**2/SEC   VISCOSITY =  0.04703 POISE
      F  = 0.050   DGM =  0.19021E-04   DDGM = -5.34020
      F  = 0.100   DGM =  0.17125E-04   DDGM = -4.70835
      F  = 0.150   DGM =  0.15418E-04   DDGM = -4.13946
      F  = 0.200   DGM =  0.13882E-04   DDGM = -3.62727
      F  = 0.250   DGM =  0.12498E-04   DDGM = -3.16612
      F  = 0.300   DGM =  0.11253E-04   DDGM = -2.75093
      F  = 0.350   DGM =  0.10131E-04   DDGM = -2.37712
      F  = 0.400   DGM =  0.91217E-05   DDGM = -2.04056
      F  = 0.450   DGM =  0.82126E-05   DDGM = -1.73754
      F  = 0.500   DGM =  0.73942E-05   DDGM = -1.46472
      F  = 0.550   DGM =  0.66573E-05   DDGM = -1.21909
      F  = 0.600   DGM =  0.59938E-05   DDGM = -0.99794
      F  = 0.650   DGM =  0.53965E-05   DDGM = -0.79883
      F  = 0.700   DGM =  0.48587E-05   DDGM = -0.61956
      F  = 0.750   DGM =  0.43745E-05   DDGM = -0.45816
      F  = 0.800   DGM =  0.39385E-05   DDGM = -0.31284
      F  = 0.850   DGM =  0.35460E-05   DDGM = -0.18200
      F  = 0.900   DGM =  0.31926E-05   DDGM = -0.06421
      F  = 0.950   DGM =  0.28744E-05   DDGM =  0.04185
      F  = 1.000   DGM =  0.25880E-05   DDGM =  0.13734
      F  = 1.050   DGM =  0.16867E-05   DDGM =  0.45777
      F  = 1.100   DGM =  0.10993E-05   DDGM =  0.63358
      F  = 1.150   DGM =  0.71644E-06   DDGM =  0.75119
      F  = 1.200   DGM =  0.46693E-06   DDGM =  0.84436
      F  = 1.250   DGM =  0.30431E-06   DDGM =  0.89856
      F  = 1.300   DGM =  0.19833E-06   DDGM =  0.93389
      F  = 1.350   DGM =  0.12926E-06   DDGM =  0.95691
      F  = 1.400   DGM =  0.84244E-07   DDGM =  0.97192
      F  = 1.450   DGM =  0.54905E-07   DDGM =  0.98170
      F  = 1.500   DGM =  0.35783E-07   DDGM =  0.98807
      F  = 1.550   DGM =  0.23321E-07   DDGM =  0.99223
      F  = 1.600   DGM =  0.15199E-07   DDGM =  0.99493
      F  = 1.650   DGM =  0.99060E-08   DDGM =  0.99570
      F  = 1.700   DGM =  0.64561E-08   DDGM =  0.99785
      F  = 1.750   DGM =  0.42077E-08   DDGM =  0.99850
      F  = 1.800   DGM =  0.27423E-08   DDGM =  0.99909
      F  = 1.850   DGM =  0.17873E-08   DDGM =  0.99940
      F  = 1.900   DGM =  0.11648E-08   DDGM =  0.99961
      F  = 1.950   DGM =  0.75915E-09   DDGM =  0.99975
      F  = 2.000   DGM =  0.49477E-09   DDGM =  0.99984
SOLUTE CODE = 17       SOLVENT CODE = 14
      TEMPERATURE =288.00 DEG C    DIFFUSIVITY =  0.10200E-04 CM**2/SEC   VISCOSITY =  0.01330 POISE
SOLUTE CODE = 17       SOLVENT CODE =  4
      TEMPERATURE =288.00 DEG C    DIFFUSIVITY =  0.17500E-04 CM**2/SEC   VISCOSITY =  0.00623 POISE
SOLUTE CODE = 17       SOLVENT CODE =  5
      TEMPERATURE =288.00 DEG C    DIFFUSIVITY =  0.38000E-05 CM**2/SEC   VISCOSITY =  0.02659 POISE
SOLUTE CODE = 17       SOLVENT CODE =  5
      TEMPERATURE =288.00 DEG C    DIFFUSIVITY =  0.61000E-05 CM**2/SEC   VISCOSITY =  0.02522 POISE
SOLUTE CODE =  9       SOLVENT CODE =  4
      TEMPERATURE =288.00 DEG C    DIFFUSIVITY =  0.15400E-04 CM**2/SEC   VISCOSITY =  0.00623 POISE
SOLUTE CODE = 14       SOLVENT CODE = 10
      TEMPERATURE =288.00 DEG C    DIFFUSIVITY =  0.22000E-04 CM**2/SEC   VISCOSITY =  0.00596 POIS-
SOLUTE CODE = 15       SOLVENT CODE = 10
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     YGW0645 MITCHELL,R.D.
          TEMPERATURE =288.00 DEG C    DIFFUSIVITY =  0.20700E-04 CM**2/SEC   VISCOSITY =  0.00596 POISE
SOLUTE CODE = 16      SOLVENT CODE = 10
          TEMPERATURE =288.00 DEG C    DIFFUSIVITY =  0.23500E-04 CM**2/SEC   VISCOSITY =  0.00596 POISE
SOLUTE CODE = 10      SOLVENT CODE = 15
          TEMPERATURE =288.00 DEG C    DIFFUSIVITY =  0.44000E-04 CM**2/SEC   VISCOSITY =  0.00247 POISE
SOLUTE CODE = 10      SOLVENT CODE = 14
          TEMPERATURE =288.00 DEG C    DIFFUSIVITY =  0.16300E-04 CM**2/SEC   VISCOSITY =  0.01330 POISE
SOLUTE CODE = 10      SOLVENT CODE = 16
          TEMPERATURE =288.00 DEG C    DIFFUSIVITY =  0.39200E-04 CM**2/SEC   VISCOSITY =  0.00355 POISE
          F  = 0.025 AVERAGE FRACTIONAL DEVIATION =  2.83343
          F  = 0.050 AVERAGE FRACTIONAL DEVIATION =  2.55815
          F  = 0.075 AVERAGE FRACTIONAL DEVIATION =  2.30530
          F  = 0.100 AVERAGE FRACTIONAL DEVIATION =  2.07293
          F  = 0.125 AVERAGE FRACTIONAL DEVIATION =  1.85927
          F  = 0.150 AVERAGE FRACTIONAL DEVIATION =  1.66270
          F  = 0.175 AVERAGE FRACTIONAL DEVIATION =  1.48174
          F  = 0.200 AVERAGE FRACTIONAL DEVIATION =  1.31506
          F  = 0.225 AVERAGE FRACTIONAL DEVIATION =  1.16143
          F  = 0.250 AVERAGE FRACTIONAL DEVIATION =  1.01975
          F  = 0.275 AVERAGE FRACTIONAL DEVIATION =  0.88900
          F  = 0.300 AVERAGE FRACTIONAL DEVIATION =  0.76827
          F  = 0.325 AVERAGE FRACTIONAL DEVIATION =  0.65671
          F  = 0.350 AVERAGE FRACTIONAL DEVIATION =  0.55356
          F  = 0.375 AVERAGE FRACTIONAL DEVIATION =  0.45900
          F  = 0.400 AVERAGE FRACTIONAL DEVIATION =  0.37356
          F  = 0.425 AVERAGE FRACTIONAL DEVIATION =  0.30566
          F  = 0.450 AVERAGE FRACTIONAL DEVIATION =  0.24940
          F  = 0.475 AVERAGE FRACTIONAL DEVIATION =  0.21894
          F  = 0.500 AVERAGE FRACTIONAL DEVIATION =  0.21477
          F  = 0.525 AVERAGE FRACTIONAL DEVIATION =  0.29707
          F  = 0.550 AVERAGE FRACTIONAL DEVIATION =  0.42230
          F  = 0.575 AVERAGE FRACTIONAL DEVIATION =  0.55937
          F  = 0.600 AVERAGE FRACTIONAL DEVIATION =  0.66712
          F  = 0.625 AVERAGE FRACTIONAL DEVIATION =  0.74769
          F  = 0.650 AVERAGE FRACTIONAL DEVIATION =  0.80818
          F  = 0.675 AVERAGE FRACTIONAL DEVIATION =  0.85375
          F  = 0.700 AVERAGE FRACTIONAL DEVIATION =  0.88820
          F  = 0.725 AVERAGE FRACTIONAL DEVIATION =  0.91433
          F  = 0.750 AVERAGE FRACTIONAL DEVIATION =  0.93420
          F  = 0.775 AVERAGE FRACTIONAL DEVIATION =  0.94936
          F  = 0.800 AVERAGE FRACTIONAL DEVIATION =  0.96095
          F  = 0.825 AVERAGE FRACTIONAL DEVIATION =  0.96984
          F  = 0.850 AVERAGE FRACTIONAL DEVIATION =  0.97666
          F  = 0.875 AVERAGE FRACTIONAL DEVIATION =  0.98192
          F  = 0.900 AVERAGE FRACTIONAL DEVIATION =  0.98597
          F  = 0.925 AVERAGE FRACTIONAL DEVIATION =  0.98910
          F  = 0.950 AVERAGE FRACTIONAL DEVIATION =  0.99152
          F  = 0.975 AVERAGE FRACTIONAL DEVIATION =  0.99339
          F  = 1.000 AVERAGE FRACTIONAL DEVIATION =  0.99485

*01* UNIT05, EOF.                                                                     REC=  00000 FIL=  00002
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VIII. NOMENCLATURE

A = proportionality constant in Equation 37

A_T = effective mass transfer area on surface of porous plate, cm^2

A'_1, A'_2 = constants defined by Equation B-11

b_n = the nth root of Equation B-31

C = solute concentration in porous plate, mole/liter

$\bar{C}$ = Laplace transform of C

C_o = initial solute concentration in porous plate, mole/liter

C_f = solute concentration in solvent bath, mole/liter

$\bar{C}_f$ = Laplace transform of C_f

C_f^o = initial solute concentration in solvent bath, mole/liter

C_{f_i} = solute concentration of sample number i removed from the solvent bath, mole/liter

C'_{f_i} = solute concentration calculated using the curvefitted parameters for sample number i removed from the solvent bath, mole/liter

C_1, C_2 = constants in Equation 8

D_{AB} = binary diffusion coefficients, cm^2/sec.

D_{BB}, D_{XX} = self diffusion coefficients, cm^2/sec.

D_{GM} = binary diffusion coefficient calculated by the original Gainer and Metzner model, cm^2/sec.

D'_{GM} = binary diffusion coefficient calculated by the modified Gainer and Metzner model, cm^2/sec.

D_M = binary diffusion coefficient calculated by Equations 29 and 13, cm^2/sec.

D_O = binary diffusion coefficient calculated by Olander's model, cm^2/sec.

D_{WC} = binary diffusion coefficient calculated by the Wilke-Chang equation, cm^2/sec.

DEV = percent deviation of calculated from experimental diffusivity.

$E_{D_{AB}}$, $E_{D_{BB}}$ = activation energy for diffusion, Kcal/mole

$E_{D_{BB-H}}$ = activation energy for diffusion due to hydrogen bonding, Kcal/mole

$E_{D_{BB-D}}$ = activation energy for diffusion due to "dispersion force" bonds, Kcal/mole

E_{η_B} = activation energy for viscosity, Kcal/mole

$E_{\eta_{B-H}}$ = activation energy for viscosity due to hydrogen bonding, Kcal/mole

$E_{\eta_{B-D}}$ = activation energy for viscosity due to "dispersion force" bonds, Kcal/mole

ΔE^{vap} = energy of vaporization, Kcal/mole

$\overline{\Delta E}^{vap}_{AB}$ = partial molar energy of vaporization of a solute A from solvent, B, Kcal/mole

f = the ratio of the activation (free) energies due to hole formation to the total,

f' = the ratio of the activation (free) energies due to the jump step to the total (=1-f)

$\Delta F_{D_{AB}}, \Delta F_{D_{BB}}, \Delta F_{D_{AA}}$ = activation free energy for diffusion, Kcal/mole

$\Delta F_{\eta_B}, \Delta F_{\eta_X}$ = activation free energy for viscosity, Kcal/mole

h = the Planck constant, 6.6242 (10^{-27}) erg/sec

ΔH^{vap} = enthalpy of vaporization, Kcal/mole

ΔH^{vap}_{X-H} = enthalpy of vaporization due to hydrogen bonding, Kcal/mole

ΔH^{vap}_{X-D} = enthalpy of vaporization due to dispersion force bonds, Kcal/mole

$\overline{\Delta H}^{mix}_{AB}$ = partial molar enthalpy of mixing of A in B, Kcal/mole

$\Delta H_{D_{AB}}, \Delta H_{D_{BB}}$ = enthalpy of activation for diffusion, Kcal/mole

k = the Boltzman constant, 1.3805 (10^{-16})

k, k' = constants of proportionality in Equations 19 and 21

K = $2\, A_T \sqrt{D_{AB}}/V_f$, sec.$^{-1/2}$

L_{eff} = effective pore length in porous plate, cm

M = molecular weight, grams/mole

N = the Avagadro number, 6.023×10^{23} molecules/mole

N = the number of samples taken for analysis during any one run

Q_{AB} = partition function for equilibrium state

$Q_{\pm AB}$ = partition function for activated state

R = the universal gas constant, 1.987 $(10)^{-3}$ Kcal/mole ^{o}K

R_A, R_B = approximate molecular radius, cm

R_{AB} = arithmetic average of R_A and R_B

s = Laplace transform variable

S = the weighted sum of the square of the deviation of the actual concentration of sample i from the concentration of sample i calculated using the curve fit parameters

T = temperature, ^{o}K

T_c = critical temperature, ^{o}K

t = time, sec

$t_{\frac{1}{2}}$ = half-life, hr^{-1}

$\bar{V}$ = molar volume, cm^3/mole

V_f = average volume of solvent in solvent bath during a run, milliliters

W_i = weighting factor

x = length, cm

Y = variable defined by Equation 39a

Z = proportionality constant in Equation 23

Greek Letters

α = ratio of volume of solvent bath to void volume of porous plate

α_x = thermal coefficient of volumetric expansion, $^{o}C^{-1}$

δ = defined by Equation 39b

δA_T = correction to A_T calculated in least squares program

δC^{o}_{f} = correction to C^{o}_{f} calculated in least squares program

Δ = absolute percent deviation of predicted diffusivity from experimental diffusivity

ϵ = Lennard-Jones force constant

ϵ'_o, $\epsilon'_{o_{AB}}$, $\epsilon'_{o_{AA}}$, $\epsilon'_{o_{BB}}$ = zero point energy difference

η_B, η_X = coefficient of viscosity, poise

λ_1, λ_2, λ_3 = the distance between neighboring molecules in the ith direction, cm

λ = the distance between equilibrium positions in the direction of motion, cm

ξ, ξ_A, ξ_B, ξ_X = a lattice parameter in the rate theory equation

σ = the standard deviation of the sample equation

Subscripts

i = sample number i

p = at constant pressure

v = at constant volume

A, B, X = components A, B, and X

boiling, 1, 2 = boiling temperature, temperature 1 and temperature 2 all in ^{o}K.

Superscripts

h = due to the hole formation process

j = due to the jump process

o = refers to initial estimate of variable used in iterative least squares program

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