University of California

Ernest O. Lawrence Radiation Laboratory

STEADY-STATE DIFFUSION IN TERNARY GAS MIXTURES

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STEADY-STATE DIFFUSION IN TERNARY GAS MIXTURES

Richard W. Getzinger
(M.S. Thesis)

January 17, 1962
# STEADY-STATE DIFFUSION IN TERNARY GAS MIXTURES

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ABSTRACT

The Stefan diffusion-tube approach was utilized to experimentally determine the rate of mass transfer in three ternary systems in which two gases were simultaneously diffusing into a third stagnant gas. Constant evaporating binary liquid mixtures were used. The experimentally determined values were compared with the quantities predicted by the Gilliland, or exact, solution of the Stefan-Maxwell equations. Similar comparisons were made with several approximate sets of equations from the literature for typical experimental runs.

Results of these comparisons indicate that: (a) unless the interacting influence of the two diffusing gases upon each other is considered, any predictive method will be seriously in error; (b) the validity of the Stefan-Maxwell equations has been established under experimental conditions more stringent than any that have been employed previously. These results, together with earlier data for stagnant gas mixtures, provide some proof of the applicability of the Stefan-Maxwell equations to diffusion in complex, multicomponent, gas systems.
INTRODUCTION

In recent years a number of different sets of equations have been proposed to describe the phenomenon of diffusion in multicomponent mixtures of gases. Each of these methods is based upon the well-known film theory of mass transfer, and each attempts to express in some manner the effect of interactions between the different gases upon the total mass-transfer rate. In addition to these approximate equations, if one restricts himself to ternary systems, exact solutions are available to the Stefan-Maxwell equations for diffusion in ideal multicomponent gases. However, little work has been done in verifying these exact solutions or in comparing the predictions of the exact solutions with those of the various approximate relationships.

This report describes recent work completed by the author upon ternary systems with one gas stagnant and compares the experimentally measured values with those predicted under these conditions by each of the methods mentioned above. The system used for this work is that of capillary diffusion from a binary liquid solution whose composition approximates that of a mixture evaporating constantly into a stream of air at 35°C and 756 mm Hg. Methyl alcohol-benzene, methyl alcohol-carbon tetrachloride, and ethyl alcohol-chloroform mixtures were used.
THEORY

Stefan-Maxwell Equations

The equations for diffusion in isothermal, nonflow systems of ideal gas mixtures were developed by Stefan\(^7,8\) and Maxwell\(^9,10\) and have since been derived more rigorously from kinetic theory by Curtis and Hirschfelder\(^11\). For a mixture of \(n\) components, these equations take the form

\[
- \frac{dp_i}{dx} = \sum_{j \neq i} a_{ij} c_i c_j (u_i - u_j),
\]

where

\[
a_{ij} = a_{ji} = \frac{R^2 T}{D_{ij} P}
\]

and

\[
i, j = 1, 2, \ldots, n.
\]

Equation (1) can easily be transformed into

\[
- \frac{P}{RT} \frac{dy_i}{dx} = \sum_{j \neq i} \frac{N_i y_j - N_j y_i}{D_{ij}}
\]

A similar expression can be written for each component in a multi-component mixture although, as pointed out by Toor\(^2\) for \(n\) components, there are only \(n-1\) independent equations since we have \(\sum y_i = 1\), and the total pressure is assumed constant. However, by adding another restriction—for example, letting \(N_i = 0\) for one of the components, as in the case of a stagnant gas—the system becomes determinate.

Gilliland's solution of the diffusion equations (3) for a ternary system with \(N_c = 0\) was of particular interest in this experiment and takes the form of two simultaneous equations:\(^3\)
These relationships will be referred to hereafter as the exact solution of the Stefan-Maxwell equations.

The use of Eqs. (4) and (5) requires a trial-and-error solution, making them too cumbersome for general engineering purposes. In addition, because of their complexity these equations appear to have no physical significance. For these reasons it is desirable to have available approximate, less complicated equations relating the mass-transfer rates to the basic binary properties for such ternary systems.

Approximate Solutions of the Diffusion Equations

It has been shown that for a binary mixture in which neither $u_A$ nor $u_B$ is equal to zero, Eq. (1) can be transformed into

$$N_A = -\frac{D_{AB}P}{RT} \frac{dy_A}{dx} + (N_A + N_B) y_A,$$

which is the definition of the binary diffusion coefficient. This expression introduces the mathematical concept of equimolal diffusion plus bulk flow, in which each term, respectively, on the right side of Eq. (6) can be viewed as the transport rate due to these two effects.
Following this form, Wilke has defined an expression analogous to Eq. (6) for a multicomponent mixture:

\[ N_A = -\frac{D_A}{RT} \frac{dy_A}{dx} + N_t y_A, \]  

(7)

where \( D_A \) is an effective diffusion coefficient for component A in the mixture, and \( N_t = \Sigma N_i \) is the total mass-transfer rate. If a constant average diffusion coefficient is assumed, integration of Eq. (7) gives

\[ N_A = \frac{D_A}{RT} \left(\frac{P}{\Sigma (p_f)_A}\right) (P_A - P_2), \]  

(8)

where \((p_f)_A\) is the diffusion-film-pressure factor, which accounts for the effect of bulk movement of the gas mixture, due to simultaneous motion of all the components, upon the component in question. It is defined as

\[ (p_f)_A = \frac{P}{\phi_A} (\phi_A - y_A)_L \]  

(9)

where

\[ (\phi_A - y_A)_L = \frac{\phi_A - y_A_2 - (\phi_A - y_A_1)}{\ln \frac{\phi_A - y_A_2}{\phi_A - y_A_1}}, \]  

(10)

and

\[ \phi_A = \frac{N_A}{N_t} \]  

(11)

Similar equations may be written for the other components in the mixture. The two different ways proposed for defining the coefficient \( D_A \),
combined with Eq. (8), constitute what will be referred to in this report as Wilke's first and second methods, respectively. These methods will be developed in the following paragraphs.

It was shown by Wilke in the same paper that for the diffusion of component A into a mixture of stagnant gases (i.e., \( u_B = u_C = \ldots = 0 \)) Eq. (1) can be rearranged to yield

\[
N_A = \frac{-(1 - y_A) P}{\frac{y_B}{D_{AB}} + \frac{y_C}{D_{AC}} + \frac{y_D}{D_{AD}} + \ldots} \frac{dp_A}{dx}, \tag{12}
\]

where \( p_i = P - p_A \). This expression, which contains no approximations beyond those in Eq. (1), indicates that the effective diffusion coefficient, \( D_A' \), in Eq. (7) (where \( N_t = N_A \)) should be defined as

\[
D_A' = \frac{1 - y_A}{\frac{y_B}{D_{AB}} + \frac{y_C}{D_{AC}} + \frac{y_D}{D_{AD}} + \ldots}. \tag{13}
\]

Therefore, as a first approximation for \( D_A'' \), Wilke chose to use the equation based upon the arithmetic-mean average compositions in the film. For a ternary system, the resulting expression for component A is

\[
D_A'' = \frac{1 - y_A'}{\frac{y_B'}{D_{AB}} + \frac{y_C'}{D_{AC}}}, \tag{14}
\]

where any \( y_i' \) is defined by

\[
y_i' = \frac{y_{i1} + y_{i2}}{2}. \tag{15}
\]
Early experimental results presented in the same paper indicate that this expression does not completely account for the effects of simultaneous diffusion by several components. Therefore, at the same time Wilke introduced a more complex and "somewhat arbitrary" definition of $D_A''$ which seems to better describe his ternary data. When applied to a three-component system, the expression takes the form

$$D_A'' = \frac{1}{\frac{y_B}{D_{AB}} + \frac{y_C}{D_{AC}}}$$

where

$$y_B'' = \frac{(p_f)_{AB}}{(p_f)_{AB} + (p_f)_{AC}}$$

$$y_C'' = \frac{(p_f)_{AC}}{(p_f)_{AB} + (p_f)_{AC}}$$

$$(p_f)_{AB} = \frac{P}{(\phi_{AB})} (y_A' + y_B')(\phi_{AB} - y_{AB})$$

$$(p_f)_{AC} = \frac{P}{(\phi_{AC})} (y_A' + y_C')(\phi_{AC} - y_{AC})$$

$$y_{AB}' = \frac{y_A'}{y_A + y_B}$$

$$y_{AC}' = \frac{y_A'}{y_A + y_C}$$

$$\phi_{AB} = \frac{N_A}{N_A + N_B}$$

$$\phi_{AC} = \frac{N_A}{N_A + N_C}$$
and \( y_A' \), \( y_B' \), and \( y_C' \) are the arithmetic-mean film compositions defined by Eq. (15). Similar expressions can be written for components B and C.

The significance of the various terms is explained in the reference article, and it need only be added here that in this second method, \( D_i'' \) is based upon effective partial pressures, or partial film-pressure factors, of the components rather than on their true average partial pressures in the mixture. Shain later showed that this definition of \( D_i'' \) is exact at any single point, provided negative partial film-pressure factors are used when they arise, but that it becomes approximate in averaging over the diffusion path. If \( D_i'' \) changes sign over the path, the concept is particularly difficult to use.

The chief disadvantage of Wilke's methods are that they both require trial-and-error solutions. In addition, while the first method appears to lack sufficient accuracy even for engineering calculations, the second is extremely cumbersome and may yield negative partial film-pressure factors from Eq. (19) and (20), hence losing all physical significance. For this latter case Wilke suggested assuming these values equal to zero, while Toor indicates that they should be retained for greater accuracy. This latter procedure seems preferable in view of the studies by Toor and by Shain.

In his paper, Toor also introduced an approximate method of describing the rate of mass transfer in a ternary system with one gas stagnant. He assumed \( D_{AC} = D_{BC} \) in the Gilliland Eq. (4) and (5), and simplified and combined the resulting expressions to obtain

\[
N_A = \frac{D_{AC}P}{RTx} \phi_C \left( \delta M y_A - y_A \right)
\]

(25)

and

\[
N_B = \frac{D_{BC}P}{RTx} \phi_C \left( \delta M y_B - y_B \right),
\]

(26)
where

\[
\delta_M' = \left( \frac{y_{C_2}}{y_{C_1}} \right)^{D_M/D_{AB}}
\]

(27)

\[
\phi_C' = \frac{\ln \left( \frac{y_{C_1}}{y_{C_2}} \right)}{(1-y_{C_2}) - \delta_M (1-y_{C_1})}
\]

(28)

and

\[
D_M = \frac{1}{2} (D_{AC} + D_{BC}).
\]

(29)

This result can be solved directly for \( N_A \) and \( N_B \) without a trial-and-error procedure, but, of course, the accuracy of the value obtained would be expected to decrease as the dissimilarity between the diffusion coefficients for pure A and B into C increases.

Shain has recently introduced another approach to this problem by first transforming Eq. (1) into the form

\[
N_i = - \left[ \frac{P}{RT \sum_{j \neq i} (y_j - y_i) \phi_{ij} \frac{1}{D_{ij}}} \right] \frac{dy_i}{dx}. \]

(30)

By then noting that the denominator of Eq. (30) is approximately linear in \( y_i \), he integrated to obtain the relation

\[
N_i \approx \frac{P(y_{i_1} - y_{i_2})}{RT \sum_{j \neq i} (y_j - y_i) \phi_{ij} \frac{1}{D_{ij}}} \]

(31)
which can be applied to a mixture containing any number of components. Solution of this equation also involves an iteration procedure, but the results appear to be comparable in accuracy to those of the Gilliland expressions.

One other set of equations is used for comparative purposes in this thesis. It was shown earlier that for the diffusion of component A into a mixture of stagnant gases (hence, no interaction between component A and the other components in the mixture) Eqs. (12) and (13) were exact at any point in the film. Therefore, by again assuming a constant average diffusion coefficient of the form of Eq. (14), one can integrate Eq. (12) for the case \( N_A = N_t \), which yields

\[
N_A = \frac{D_A \frac{P}{RT \times (P_B)^{LM}}}{(P - P_{A_1}) (P - P_{A_2})}\]

(32)

where

\[
(P_B)^{LM} = \frac{(P - P_{A_2}) - (P - P_{A_1})}{\ln \left( \frac{P - P_{A_2}}{P - P_{A_1}} \right)}
\]

(33)

This expression, which represents the situation where only the diffusion of A molecules creates a bulk-flow effect upon the mass-transfer rate of component A, will hereafter be referred to as the case of B assumed stagnant.
EXPERIMENTAL PROCEDURE

Theory of the Stefan-tube Apparatus

The theory of the Stefan capillary-tube method for measuring diffusion coefficients in a binary system is covered fully in a paper by Lee and Wilke; the highlights of their work are summarized here. The process is one of steady-state evaporation and diffusion from a pure liquid into a passing stream of gas, in which the partial pressure of the diffusing substance is kept at a minimum, as shown in Fig. 1. It should be noted that these authors found that steady-state conditions were reached in less than 15 minutes of operation and that experimental runs of 10 hr. or longer were used in their work.

Lee and Wilke have introduced two end corrections, $\Delta x_e$ and $\Delta x_s$, which account respectively for the effects of eddies or turbulence at the open end of the tube, and for the curvature of the liquid surface due to surface tension. They have shown that the sum of these corrections, $\Delta x$, must be subtracted from the apparent depth measured at the center line of the tube, $x_A$, in order to obtain the true film thickness (i.e., $x = x_A - \Delta x$) used in the equation

$$N_A = \frac{DP}{RT(p_B)LMx} \Delta p_A$$

which applies in such a binary system.

These same authors proceed to point out that the use of $x_A$ in Eq. (34), combined with the known weight loss and experimental period (to obtain $N_A$) will yield only an apparent diffusion coefficient, $D_A$. By equating

$$N_A = \frac{DP}{RT(p_B)LMx} \Delta p_A = \frac{D_A p}{RT(p_B)LMx_A} \Delta p_A$$

(35)
Fig. 1. Model for the theory of Lee and Wilke.
and simplifying, they have shown that the expression

$$\frac{1}{D_A} = - \left( \frac{\Delta x}{D} \right) \frac{1}{x_A} + \frac{1}{D}$$  \hspace{1cm} (36)$$

may be used to determine $\Delta x$ and $D$ from a series of measured values of $D_A$ versus $x_A$, if a plot of $1/D_A$ versus $1/x_A$ is extrapolated to $1/x_A = 0$. In addition, they have indicated that $\Delta x$ and $D$ may alternatively be determined by using a least-squares treatment involving the solution of the simultaneous equations

$$D \Sigma \frac{x_A}{D_A} - n \Delta x - \Sigma x_A = 0$$ \hspace{1cm} (37)

and

$$D \Sigma \left( \frac{x_A}{D_A} \right)^2 - \Delta x \Sigma \frac{x_A}{D_A} - \Sigma \left( \frac{x_A}{D_A} \right)^2 = 0,$$ \hspace{1cm} (38)

where $n$ equals the number of measurements of $D_A$ versus $x_A$.

In the present work, the technique of Lee and Wilke was used to measure the true binary coefficients of the different organic substances in air.

It should be noted here that in this approach plug flow is assumed in the diffusion tube (i.e., no radial concentration gradients). The agreement between kinetic theory and the previous data of Lee and Wilke and others for binary systems appears to validate this assumption.
APPARATUS

The apparatus used for this work is shown schematically in Fig. 2 and, as it actually appeared, in Figs. 3 and 4. Air enters the system at room temperature at a positive pressure of some 7 to 7-1/2 in. of water from three parallel tanks of the compressed gas. A constant flow rate of 0.0668 cfm (1890 cc/min) is maintained by three pressure regulators. (The method of determination of this flow rate is discussed in the following section, Procedure). It then passes through a specially built 6-in. column of magnesium perchlorate to eliminate any trace quantities of water from the gas. After passing through a flowrator, the air is heated preliminarily to within approximately one degree of the bath temperature by a heating element consisting of two heating tapes wrapped about numerous coils of the 1/4-in. copper tubing through which the gas flows and surrounded by several layers of asbestos insulating strips. The current through the tapes is regulated by a Variac, and hence the air temperature is easily controlled. The air is then directed by the tubing into the constant-temperature bath, where it passes through a 40-ft coil to bring its temperature to exactly 35°C before entering the suspended diffusion unit. The air and dilute organic vapors are then lead by tubing from the bath to a blower and exhausted outside the building.

The constant-temperature bath of water in a 12-in. -diam. by 16-in. -deep Pyrex jar is maintained at 35.0 ± 0.1°C by a mercury thermoregulator connected to a specially built electrical controller and a heating element. The bath is continuously agitated by a 1/5-hp variable-speed General Electric motor and a specially constructed extended impeller. A Variac is used to control the speed of the motor. The Pyrex jar is surrounded on all sides by 2 to 3 in. of Styrofoam insulation and located inside a large 22 by 19-in. wooden box constructed for this purpose. Holes were drilled through the box cover and the attached insulation to permit passage of the copper tubing, the impeller shaft, and the control units into the bath.
Fig. 2. Schematic diagram of the apparatus.
Fig. 3. View of the working area and apparatus.
Fig. 4. View of the experimental apparatus.
The heart of the apparatus is the diffusion unit. Figure 5 is a drawing of this unit and Fig. 6 is a photograph of the unit and adjacent submerged pieces of copper tubing. The air entering the unit first passes through copper straightening vanes spaced 2 mm apart to eliminate all turbulence accompanying the transition into the chamber, before it flows over the capillary diffusion tube itself. All parts of the unit other than the entrance and exit tubing and the vanes are constructed of brass to achieve the combination of strength and good thermal conductivity.

The diffusion tubes and corresponding tube holders were built so as to be interchangeable. The dimensions of the tubes are:

<table>
<thead>
<tr>
<th></th>
<th>Large tube</th>
<th>Small tube</th>
</tr>
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<tbody>
<tr>
<td>Inside diameter</td>
<td>2.40 cm</td>
<td>1.44 cm</td>
</tr>
<tr>
<td>Wall thickness</td>
<td>0.031 in.</td>
<td>0.031 in.</td>
</tr>
<tr>
<td>Depth</td>
<td>15.25 cm</td>
<td>15.31 cm</td>
</tr>
</tbody>
</table>

The tube holders were built to leave a minimum of clearance (0.001 in.) between the holder and tube, but still permit the latter to be removed when desired. The thickness of the diffusion tube holders is 0.123 in. Both of the diffusion tubes and their holders, as well as the brass supporting unit for the straightening vanes, are shown clearly in Fig. 6, as are the supports used to suspend the entire unit from the rim of the Pyrex jar. A precision electric timer was used to accurately determine the length of each run to within 0.01 min.

Late in the experimental work, it was decided to condense and analyze at least one vapor sample as confirmation of one of the basic assumptions involved in this type of apparatus. Therefore two acetone-dry-ice glass traps were located in series just after the second thermometer well. Connections between the traps and the copper tubing of the original system were designed so that the experimenter could easily remove this latter unit from the apparatus without halting the air flow whenever an analysis was desired.
Fig. 5. Diffusion unit.
Fig. 6. Components of the diffusion unit.
In all cases, gravimetric calibration curves of the depth, $x_A$, versus the combined weight of the sample and diffusion tube were utilized. In this manner a given sample could be weighed at the beginning and at the end of each run and a mean $x_A$ chosen for calculation purposes. For this calibration, the distance between the liquid surface at the center of the tube and the rim of the tube was determined for samples of different weights. The surface was first pierced by a pointed probe, and this distance (apparent path length) was observed. The samples were then weighed at room temperature on a Braun-Knecht-Heimann balance on which a weight difference of 0.0001 g is readily discernible. Most of the samples weighed 40 to 70 g. Finally, before plotting the calibration curve, the measured values of $x_A$ were corrected for the volume change with temperature, according to the data of Perry.13

Compositions of the binary liquid were determined from indexes of refraction measured in the analytical laboratory located in Building 70 of the Lawrence Radiation Laboratory. Initially, calibration curves showing the index of refraction versus mole fraction were determined for the narrow range of interest in each case. During the experiment, readings were taken on the binary samples immediately before and after each run, and a mean composition was determined. The calibration curves were also used for the condensed-vapor analysis. These curves are given in Appendix C of this report.

The type and purity of the chemicals used in this work are described in Appendix B.
PROCEDURE

Before full-scale experimental work was initiated, the proper operating conditions were determined. The bath temperature of $35.0^\circ C$ was chosen as a compromise between a desire to obtain high vapor pressures for the pure components and the mixtures—thus increasing the rate at which material is lost and hence shortening the required running time—and the difficulties involved in constructing the proper heater for the air stream and in locating reliable partial-pressure data for several common binary mixtures. Such data has been published by Scatchard and his co-workers for mixtures of methyl alcohol-benzene, methyl alcohol-carbon tetrachloride, and ethyl alcohol-chloroform at $35.0^\circ C$, and these values were used for this work. Curves showing Scatchard's data are located in Appendix E of this report. It is felt that the uncertainty introduced in plotting the data and picking values off the curves for use in the calculations is of the order of 0.5 mm Hg or less.

The proper air flow rate was determined by experimentation. Too low a value will produce stagnation in the gas chamber of the diffusion unit, hence reducing the driving force and consequently the rate of mass transfer through the film. Conversely, too large a value will increase the turbulence in the film until $\Delta x_e$ (Fig. 1) reaches the liquid surface level and turbulent diffusion becomes the chief mode of mass transport. Experimentation and an examination of the early results at several different rates indicated the proper range of operation. The flow rate thus selected produced a velocity of 73.4 cm/sec and a Reynolds number of 95.5 in the copper vanes of the diffusion unit. This rate also fixed the operating pressure of the system at 7 to 7-1/2 in of water above atmospheric pressure, since the blower vacuum was found to be of negligible influence. It should be noted that air was treated as a single component in this work, since exact calculations showed that there was essentially no difference between the diffusion coefficients of the various species into oxygen and nitrogen.
Once the proper operating conditions were selected, the true binary coefficients for the diffusion of each of the five organic compounds into air were measured by the technique of Lee and Wilke for the small diffusion tube, and several of the values were checked by experimentation with the large tube. All later work utilized the small tube exclusively, however, because generally the results obtained from its application were more consistent with calculated values (to be demonstrated later under Results) and included a smaller total $\Delta x$ effect.

As mentioned earlier, an important factor in the work with ternary systems (binary liquid evaporating and diffusing into stagnant air) is the constant-evaporating mixture, because the composition of the vapor leaving the diffusion unit must be known in order to ascertain how much of each liquid component has been lost. In addition, for steady-state operation a constant driving force is needed for each component.

A constant-evaporating mixture is one in which the combination of diffusion coefficients and partial vapor pressures of the two components is such that the liquid composition is always constant for the case of evaporation by molecular diffusion, and is therefore equal to the composition of the vapor leaving the mixture.

In this work, approximate component ratios for the constant-evaporating mixtures were calculated for the three systems (i.e., methyl alcohol-benzene, methyl alcohol-carbon tetrachloride, and ethyl alcohol-chloroform) by using Wilke's second method. The exact values were then approached by experimentally observing the direction and size of composition changes indicated by the refractometer analysis for various initial compositions within the range of expectation. Once the value for a given mixture was correctly ascertained, a series of 10 to 12 runs was conducted and the next mixture was considered. In this manner, results were obtained for all three mixtures.

Finally, since the constant-evaporating mixtures could not always be exactly located and maintained, and also as a matter of scientific
interest, it was decided to attempt to condense and analyze the vapors leaving the diffusion unit. For this operation, the equipment described earlier was used, and the resulting liquid was examined on the refractometer.
RESULTS

As mentioned earlier, the first quantities determined experimentally in this work were the true diffusion coefficients for the organic compounds in air. These values were obtained by plotting the reciprocal of \( D_A \) against \( 1/x_A \) for each run, according to the technique of Lee and Wilke, and extrapolating to infinite \( x_A \) as shown in Fig. 7 for the methyl alcohol-air system. The least-squares treatment utilizing Eqs. (37) and (38) was employed to accurately locate the dotted lines and the true diffusion coefficient in all cases. The results of this work are shown in Table I, where the figures in the last column are the values obtained by calculations based upon the equation of Hirschfelder, Bird, and Spotz, including the constant coefficient correlation presented by Wilke and Lee\(^{17}\) (the modified Hirschfelder, Bird, and Spotz equation).\(^{17}\) The values for the "collision diameters", \( r_0 \) or \( \sigma \), for each of the substances involved were taken from the tables in Hirschfelder, Curtiss, and Bird.\(^{11}\) The discrepancies between observed and calculated diffusion coefficients will be considered later in the Discussion section.

In addition to these values, the interaction coefficients, \( D_{AB} \) between the two organic vapors were needed for calculations with the ternary systems. By combining the measured binary coefficients listed in Table I with the force constant, \( \epsilon/k \) for air (97.0\(^{0}\)K), the corresponding \( \epsilon/k \) values for each of the organic compounds were calculated from the modified Hirschfelder, Bird, and Spotz equation. Once these values were known, it was possible to use this same equation to determine an experimental \( D_{AB} \) for each of the three vapor interactions. The values thus obtained are compared in Table II with the coefficients calculated from tabulated force constants.\(^{11}\)
Fig. 7. Experimental diffusion coefficients for methyl alcohol in a methyl alcohol-air system.
Table I. Experimental and calculated results at 35.0°C.

<table>
<thead>
<tr>
<th>System</th>
<th>Tube</th>
<th>$\Delta x$ (cm)</th>
<th>D(measured) (cm²/sec)</th>
<th>D(a) (cm²/sec)</th>
<th>D(calculated) (cm²/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₆-air</td>
<td>L</td>
<td>0.22</td>
<td>0.114</td>
<td>0.113</td>
<td>0.101</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>0.35</td>
<td>0.107</td>
<td>0.107</td>
<td></td>
</tr>
<tr>
<td>CCl₄-air</td>
<td>L</td>
<td>0.20</td>
<td>0.0931</td>
<td>0.0926</td>
<td>0.0877</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>0.15</td>
<td>0.0898</td>
<td>0.0894</td>
<td></td>
</tr>
<tr>
<td>CH₃OH-air</td>
<td>L</td>
<td>1.36</td>
<td>0.193</td>
<td>0.192</td>
<td>0.173</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>0.35</td>
<td>0.192</td>
<td>0.191</td>
<td></td>
</tr>
<tr>
<td>C₂H₅OH-air</td>
<td>S</td>
<td>0.19</td>
<td>0.145</td>
<td>0.144</td>
<td>0.136</td>
</tr>
<tr>
<td>CHCl₃-air</td>
<td>S</td>
<td>0.05</td>
<td>0.101</td>
<td>0.101</td>
<td>0.0985</td>
</tr>
</tbody>
</table>

a Measured D. corrected to 760 mm Hg.

b At 760 mm Hg.
Table II. Force constants and interaction coefficients.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Tabular Values</th>
<th>Experimental Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\epsilon_A^a$</td>
<td>$\epsilon_B^a$</td>
</tr>
<tr>
<td></td>
<td>($\kappa_K^a$)</td>
<td>($\kappa_K^b$)</td>
</tr>
<tr>
<td>CH$_3$OH-C$_6$H$_6$</td>
<td>507</td>
<td>440</td>
</tr>
<tr>
<td>CH$_3$OH-CCl$_4$</td>
<td>507</td>
<td>327</td>
</tr>
<tr>
<td>C$_2$H$_5$OH-CHCl$_3$</td>
<td>391</td>
<td>327</td>
</tr>
</tbody>
</table>

$^a$ Values taken from reference 11.

$^b$ At 35.0°C and the total pressure of the system, 0.995 atm.
For the ternary systems, the approximate constant-evaporating mixtures located at 35.0°C and 756 mm Hg in this work were 0.651 mole fraction methanol in benzene, 0.618 mole fraction methanol in carbon tetrachloride, and 0.122 mole fraction ethanol in chloroform. Once these values had been determined, standard mixtures were made up and liquid composition changes were kept at a minimum, hence ensuring an accurate knowledge of the vapor composition. Small changes in liquid composition frequently occurred, since the figures listed above are only approximate (probably ± 0.002) and since the standard mixtures were not of exactly these compositions. However, such variations seldom exceeded 0.001 mole-fraction units. Therefore there was always a negligible concentration gradient in the liquid and always an essentially constant and known partial pressure of each component at the gas-liquid interface.

A further assurance of the accuracy of this method of determining the vapor composition was offered by the condensation analysis described earlier. The system methanol-carbon tetrachloride-air was chosen for this check. The results of the run considered showed that the mean liquid composition was 0.613 mole fraction methanol, and the composition of the condensed vapor was 0.596 methanol.

Once the ternary data had been recorded for a series of runs, it had to be put in a form convenient for later examination and comparison. It was found convenient to solve Eq. (8) for $D_A''$ and $D_B''$, and then extend the method of Lee and Wilke to this type of ternary system by plotting $1/D_i''$ versus $1/x_A$ and extrapolating to obtain a true value of $D_A''$ and $D_B''$ in the mixture. Such a procedure is valid by the same reasoning previously employed in deriving Eq. (36). These plots are shown in Figs. 8 through 13, where again the least-squares technique was used to locate the dotted lines. The resulting diffusion coefficients and total $\Delta x$ values are recorded in Table III.
Fig. 8. Experimental diffusion coefficients for methyl alcohol in a methyl alcohol-benzene-air system.
Fig. 9. Experimental diffusion coefficients for benzene in a methyl alcohol-benzene-air system.
Fig. 10. Experimental diffusion coefficients for methyl alcohol in a methyl alcohol-carbon tetrachloride-air system.
Fig. 11. Experimental diffusion coefficients for carbon tetrachloride in a methyl alcohol-carbon tetrachloride-air system.
Fig. 12. Experimental diffusion coefficients for ethyl alcohol in an ethyl alcohol-chloroform-air system.
Fig. 13. Experimental diffusion coefficients for chloroform in an ethyl alcohol-chloroform-air system.
Table III. Results of ternary runs

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Component A</th>
<th>Component B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_A$ (cm$^2$/sec)</td>
<td>$\Delta x$ (cm)</td>
</tr>
<tr>
<td>CH$_3$OH - C$_6$H$_6$</td>
<td>0.170</td>
<td>0.24</td>
</tr>
<tr>
<td>CH$_3$OH - CCl$_4$</td>
<td>0.159</td>
<td>0.05</td>
</tr>
<tr>
<td>C$_2$H$_5$OH-CHCl$_3$</td>
<td>0.125</td>
<td>-0.07</td>
</tr>
</tbody>
</table>
However, another approach was needed to compare the various exact and approximate predictive methods introduced under Theory. It was decided to use a mole-loss basis for this purpose. Therefore, the actual number of moles of component A and of component B lost by evaporation during the course of a given representative run for each of the three systems was determined, and these values, plus their sums, were compared with the results from Eqs. (32) and (33), (8) and (14), (8) and (16), (31), (4) and (5), and (25) and (26), respectively. Table IV shows the results of these calculations. A sample calculation showing the manner in which these values were obtained appears in Appendix A of this report.

The representative runs chosen for these comparisons were selected after consideration of the effect of path length and of closeness to the curves in Figs. 8 through 13. A long path length is desirable to minimize the percentage error involved in determining $x_A$ (see Discussion), and points lying near the curves for $1/D_i$ versus $1/x_A$ are assumed to indicate a more reliable run.

Because one of the main objectives of this investigation was to test the validity of the Stefan-Maxwell equations, themselves, it was felt that a more complete comparison with the experimental results was called for than the one appearing in Table IV. Therefore, the Gilliland, or exact solution, Eqs. (4) and (5) were solved for all cases in which the path length exceeded 6 cm, and the resulting predicted values of molar quantities evaporated are compared with the experimental values in Table V.

The true values of $x$ used in all of the above calculations were determined by subtracting the mole-fraction average of the total $\Delta x$ correction factors given in Table III from $x_A$ in each case.
Table IV. Summary of ternary results

<table>
<thead>
<tr>
<th></th>
<th>Mixture 1. Methyl alcohol(A)-benzene(B)-air(C)</th>
<th>Mixture 2. Methyl alcohol(A)-carbon tetrachloride(B)-air (C)</th>
<th>Mixture 3. Ethyl alcohol(A)-chloroform(B)-air (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>Total</td>
</tr>
<tr>
<td></td>
<td>(x10^2)</td>
<td>(x10^2)</td>
<td>(x10^2)</td>
</tr>
<tr>
<td>Actual</td>
<td>1.192</td>
<td>0.650</td>
<td>1.842</td>
</tr>
<tr>
<td>Predicted by stagnant-B case [Eqs. (32) and (33)]</td>
<td>1.118</td>
<td>0.465</td>
<td>1.583</td>
</tr>
<tr>
<td>Predicted by Wilke's first method [Eqs. (8) and (14)]</td>
<td>1.194</td>
<td>0.589</td>
<td>1.783</td>
</tr>
<tr>
<td>Predicted by Wilke's second method [Eqs. (8) and (16)]</td>
<td>1.285</td>
<td>0.627</td>
<td>1.912</td>
</tr>
<tr>
<td>Predicted by Shain's method [Eq. (31)]</td>
<td>1.298</td>
<td>0.630</td>
<td>1.919</td>
</tr>
<tr>
<td>Predicted by Gilliland's solution [Eqs. (4) and (5)]</td>
<td>1.280</td>
<td>0.629</td>
<td>1.909</td>
</tr>
<tr>
<td>Predicted by Toor's method [Eqs. (25) and (26)]</td>
<td>1.400</td>
<td>0.561</td>
<td>1.961</td>
</tr>
</tbody>
</table>

- Based on Run 41
- Based on Run 47
- Based on Run 53
**Table V. Comparison of calculated and experimental results**

**Mixture 1. Methyl alcohol (A) - Benzene (B) - Air (C)**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Moles of A evaporated ($\times 10^2$)</th>
<th>Moles of B evaporated ($\times 10^2$)</th>
<th>Total Moles evaporated ($\times 10^2$)</th>
<th>Moles of A evaporated ($\times 10^4$)</th>
<th>Moles of B evaporated ($\times 10^4$)</th>
<th>Total Moles evaporated ($\times 10^4$)</th>
<th>Deviation in total moles evaporated $^a$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
<td>1.328</td>
<td>0.654</td>
<td>1.982</td>
<td>1.229</td>
<td>0.665</td>
<td>1.894</td>
<td>+ 4.6</td>
</tr>
<tr>
<td>35</td>
<td>1.733</td>
<td>0.851</td>
<td>2.584</td>
<td>1.635</td>
<td>0.882</td>
<td>2.517</td>
<td>+ 2.7</td>
</tr>
<tr>
<td>37</td>
<td>2.16</td>
<td>1.062</td>
<td>3.222</td>
<td>2.030</td>
<td>1.100</td>
<td>3.130</td>
<td>+ 2.9</td>
</tr>
<tr>
<td>38</td>
<td>1.492</td>
<td>0.734</td>
<td>2.226</td>
<td>1.413</td>
<td>0.762</td>
<td>2.175</td>
<td>+ 2.3</td>
</tr>
<tr>
<td>40</td>
<td>1.313</td>
<td>0.645</td>
<td>1.958</td>
<td>1.241</td>
<td>0.672</td>
<td>1.913</td>
<td>+ 2.4</td>
</tr>
<tr>
<td>41</td>
<td>1.280</td>
<td>0.629</td>
<td>1.909</td>
<td>1.192</td>
<td>0.650</td>
<td>1.842</td>
<td>+ 3.6</td>
</tr>
<tr>
<td><strong>Avg.</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>+ 3.1</strong></td>
</tr>
</tbody>
</table>

**Mixture 2. Methyl alcohol (A) - carbon tetrachloride (B) - Air (C)**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Moles of A evaporated ($\times 10^2$)</th>
<th>Moles of B evaporated ($\times 10^2$)</th>
<th>Total Moles evaporated ($\times 10^2$)</th>
<th>Moles of A evaporated ($\times 10^4$)</th>
<th>Moles of B evaporated ($\times 10^4$)</th>
<th>Total Moles evaporated ($\times 10^4$)</th>
<th>Deviation in total moles evaporated $^a$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
<td>1.663</td>
<td>0.984</td>
<td>2.647</td>
<td>1.635</td>
<td>1.027</td>
<td>2.662</td>
<td>- 0.6</td>
</tr>
<tr>
<td>45</td>
<td>1.362</td>
<td>0.806</td>
<td>2.168</td>
<td>1.289</td>
<td>0.807</td>
<td>2.096</td>
<td>+ 3.4</td>
</tr>
<tr>
<td>47</td>
<td>1.297</td>
<td>0.765</td>
<td>2.062</td>
<td>1.215</td>
<td>0.772</td>
<td>1.987</td>
<td>+ 3.8</td>
</tr>
<tr>
<td>49</td>
<td>2.29</td>
<td>1.302</td>
<td>3.592</td>
<td>2.090</td>
<td>1.317</td>
<td>3.407</td>
<td>+ 5.4</td>
</tr>
<tr>
<td><strong>Avg.</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>+ 3.0</strong></td>
</tr>
</tbody>
</table>
### Table V. (continued)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Moles of A evaporated (x10^2)</th>
<th>Moles of B evaporated (x10^2)</th>
<th>Total Moles evaporated (x10^2)</th>
<th>Moles of A evaporated (x10^2)</th>
<th>Moles of B evaporated (x10^2)</th>
<th>Total Moles evaporated (x10^2)</th>
<th>Deviation in total moles evaporated (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>52</td>
<td>0.118</td>
<td>0.805</td>
<td>0.923</td>
<td>0.114</td>
<td>0.826</td>
<td>0.940</td>
<td>- 1.8</td>
</tr>
<tr>
<td>53</td>
<td>0.214</td>
<td>1.454</td>
<td>1.668</td>
<td>0.202</td>
<td>1.470</td>
<td>1.672</td>
<td>- 0.2</td>
</tr>
<tr>
<td>55</td>
<td>0.145</td>
<td>0.984</td>
<td>1.129</td>
<td>0.138</td>
<td>0.989</td>
<td>1.127</td>
<td>+ 0.2</td>
</tr>
<tr>
<td>57</td>
<td>0.221</td>
<td>1.504</td>
<td>1.725</td>
<td>0.212</td>
<td>1.520</td>
<td>1.732</td>
<td>- 0.4</td>
</tr>
<tr>
<td>59</td>
<td>0.266</td>
<td>1.811</td>
<td>2.077</td>
<td>0.257</td>
<td>1.841</td>
<td>2.098</td>
<td>- 1.0</td>
</tr>
<tr>
<td>60</td>
<td>0.255</td>
<td>1.758</td>
<td>2.013</td>
<td>0.248</td>
<td>1.785</td>
<td>2.033</td>
<td>- 1.0</td>
</tr>
<tr>
<td>61</td>
<td>0.248</td>
<td>1.709</td>
<td>1.957</td>
<td>0.240</td>
<td>1.732</td>
<td>1.972</td>
<td>- 0.8</td>
</tr>
</tbody>
</table>

**Avg.** - 0.7

---

*a Prediction of Eqs. (4) and (5) compared with experimental results.*
DISCUSSION

A. Possible Source of Error

Before attempting to analyze and compare the results just described, it would be best to consider the validity of the experimental values. It is felt that a number of the independent measurements used in the calculation procedure—such as room air pressure, bath temperature, vapor-pressure data, length of run, and sample weight—contributed practically no error to the results, since the instruments or data sources involved were extremely reliable. Several other measurements will be examined, however.

The readings taken on the refractometer, and the corresponding mole fractions, contain a small uncertainty because interpolation was required to obtain the important fifth figure in all of the determinations. However, the possible discrepancy involved should have been no larger than 0.001 mole-fraction units, thus making its effect extremely small.

The gravimetric calibration curves present a somewhat larger uncertainty due both to the method employed to measure \( x_A \) and to the required volume correction with the change in temperature. The estimated error is 0.05 cm, which is less than 1% for \( x_A > 6.00 \) cm; this factor should be considered for the smaller \( x_A \) values. Accordingly, more weight should be given to the runs with large path lengths, as was the case for both the least-squares approximation techniques and the method of selection of the runs chosen for comparative purposes.

Two of the important assumptions made in this experiment are that of a uniform temperature throughout the liquid sample and of steady-state operation. Lee and Wilke have investigated these assumptions for a similar apparatus and for chemicals akin (in one case identical) to those used in the present work.\(^{12} \) They found that (1) "the interfacial temperature may be assumed equal to the bath temperature for most liquids, with negligible error in the resulting diffusion coefficient" and (2) in 15 min from startup, the vaporization rate of their "slowest" liquid sample had reached 99.92% of the steady-state value. Hence both of the assumptions seem justified.
A third important assumption is that of a uniform concentration throughout the liquid and hence of the equality of the mean liquid concentration and the composition of the vapor leaving the sample. This assumption must be true if the liquid concentration is constant during the run—as was the case for many of the tests, including all of the ethanol-chloroform-air runs—but may not be so otherwise. The one condensed vapor sample that was analyzed seems to indicate that such an approximation may be fairly good but not exact, although the composition of the sample itself did change somewhat during the run and hence some discrepancy might have been expected to appear. In addition, some trace amounts of water may have escaped adsorption by the magnesium perchlorate unit and diluted the vapor sample, thus altering the reading. In any event the assumption appears to be a good approximation that should be even more accurate for smaller composition changes in the liquid sample over a run.

B. Selection of Experimental Systems

Before going any further it should be noted that the three systems utilized were chosen from a group of mixtures for which data were available at 35°C. Each of the three presents a slightly different situation for study. The methyl alcohol-benzene-air system is one in which both the pure diffusion coefficients into air and the partial pressures above the constant evaporating mixture are widely different. In the methyl alcohol-carbon tetrachloride-air system, the partial-pressure difference is greatly reduced, but the two diffusion coefficients are even further apart. The ethyl alcohol-chloroform-air system is representative of the case in which the diffusion coefficients are much more nearly equal but the partial-pressure difference is extremely large.

C. Binary Results

The binary coefficients measured in the first portion of this experiment and recorded in Table I are certainly self-consistent although they are all larger (from 2 to 10%) than those predicted by the modified
Hirschfelder, Bird, and Spotz equation. It is difficult to explain this deviation unless it is due to some peculiarity of the apparatus. The $\Delta x$ corrections, which are largely made up of the factor $\Delta x_e$, follow roughly the pattern suggested by Lee and Wilke, where $\Delta x_e$ is larger for systems of low vapor pressure.

D. Ternary Results

As noted earlier, the main objective of this work was to test the validity of the Stefan-Maxwell equations under the conditions of this experiment. Since these equations are the basis for all of the approximate methods, it is important to first determine if they are sufficiently accurate to warrant further simplification. It is therefore of value to first examine a comparison of the results predicted by the exact solution of these equations for the particular physical situation encountered in this experiment (Gilliland solution) with the actual measured experimental values.

Such a comparison is shown in Table V for all of the experimental runs with diffusion path lengths long enough to avoid the introduction of a large percentage error in the measurement of this distance. It can be seen from Table V that the agreement is satisfactory and within the limits of experimental error. It is of interest to note that predicted values of moles lost by evaporation in each case is too large for component A and too small for component B. This phenomenon may be due in part to either experimental error or some inherent feature of this particular physical arrangement, and its significance is subject to question.

Table IV is a comparison of the predictions by all of the approximate methods with those of the exact solution and the experimental values for one sample run for each of the three chemical systems studied. From this table some tentative conclusions may be drawn as to the value of these various methods, although more extensive studies and comparisons for other physical arrangements are necessary before any definite conclusions can be derived. Some observations from the comparison shown in Table IV are listed below.
a. The predictions based upon the assumption of a stagnant component B are low by a considerable amount in all three cases because they fail to include the effect of the movement of B upon A and vice versa. It is quite apparent that such interaction does occur here.

b. Wilke's first method, although fairly easy to apply, gives values that are also quite low in all three cases, hence also failing to account sufficiently for the effect of interaction upon the mass-transfer rate. It is apparent that in this type of approach the expression for $D_i^{\prime\prime}$ is more involved than that suggested in Eq. (14).

c. Several comments need be made concerning Wilke's second method. First, for greater accuracy the negative partial-film-pressure factors and effective mole fractions should be retained, as is recommended by Toor. Secondly, this method is extremely cumbersome to apply in a trial-and-error solution, probably even more so than the Gilliland expressions. Finally, its accuracy generally parallels that of Shain's method except in the case of a wide difference in volatility (mixture 3) where it continues to overestimate the total loss.

d. The Shain method and the Gilliland expressions give very similar and fairly accurate results in all cases. In addition, they are of comparable difficulty to apply.

e. The Toor approximation, although extremely easy to apply, gives values that are quite high in all three cases. However, its accuracy appears to improve as the diffusion coefficients of the two diffusing substances become more nearly equal. This is exactly the result that was expected.
CONCLUSIONS

The results of the experiment appear to point to the following conclusions:

a. In this type of experiment, interaction does occur between the simultaneously diffusing molecules, and some method of accounting for its effect is required.

b. The validity of the Stefan-Maxwell equations has been established under experimental conditions more stringent than any that have been employed previously. These results, together with earlier data for stagnant gas mixtures, provide some proof of the applicability of the Stefan-Maxwell equations to diffusion in complex multicomponent gas systems.
ACKNOWLEDGMENT

I would like to express my gratitude to Professor Charles R. Wilke for his assistance, advice, and patience, and to the Department of Chemical Engineering of the Berkeley campus for making it possible for me to pursue this work.

I would also like to acknowledge the many suggestions and the assistance given me by the personnel of the Mechanics Shop of Building 70, particularly Mr. Benjamin Kluga, and by Mr. Arthur Trips of the Analytical Laboratory.
APPENDIXES

A. Sample Calculations

These calculations are based upon a methyl alcohol (A) - benzene (B) - air (C) ternary system (run 41). One wishes to determine the actual and predicted number of moles of A and B lost from the liquid mixture during the given run.

For the number of moles $n_i$ of component $i$ lost by evaporation during the run, one can write

$$n_i = N_i (1.63) (\theta) (60),$$

where $N_i$ is the molar flux of component $i$ in g-moles/cm$^2$-sec, 1.63 is the cross-sectional area of the diffusion tube in square centimeters, and $\theta$ is the duration of the experimental run in minutes. To obtain $n_i$, in many cases one need only determine $N_i$ from the formulae and multiply by a constant. The manner of calculation is therefore as follows:

1. Experimental Result

The total weight loss and the initial and final liquid concentrations were recorded as part of the original data. From the figures, a mean percent composition was computed and it was assumed that this value was the same for both the liquid and vapor phases (constant-evaporating mixture). Hence, $n_A$ and $n_B$ were easily calculated as illustrated below:

<table>
<thead>
<tr>
<th>Data:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total weight loss</td>
<td>0.8889 g</td>
</tr>
<tr>
<td>Initial liquid composition</td>
<td>0.649 mole fraction A</td>
</tr>
<tr>
<td>Final liquid composition</td>
<td>0.646 mole fraction A</td>
</tr>
</tbody>
</table>

Therefore, from the data the mean liquid composition was 0.648 mole fraction $A = 0.430$ weight fraction $A$. Hence, 0.382 g of $A$ and 0.507 g of $B$ were lost during the run. The mole loss of $A$ was thus equal to...
1.192 \times 10^{-2} \text{ moles, and for B it was } 0.650 \times 10^{-2} \text{ moles. The total loss was therefore equal to } 1.842 \times 10^{-2} \text{ moles.}

2. Case of B Assumed Stagnant

This most crude predictive method is based upon the assumption that molecules A and B behave as though they are each diffusing into a stagnant mixture of the other and C. The basis predictive equations are:

\[ \frac{D_A'' P}{RT_x} \ln \left( \frac{1 - y_{A_2}}{1 - y_{A_1}} \right) \]

where

\[ D_A'' = \frac{1 - y_{A_1}}{\frac{y_B}{D_{AB}} + \frac{y_C}{D_{AC}}} \]

and

\[ y_A' = \frac{y_{A_1} + y_{A_2}}{2} \]

Similar equations apply to component B. Here \( y_{A_1}, y_{B_1}, \) and \( y_{C_1} \) were determined from the measured total pressure of 756 mm Hg (0.995 atm) and the equilibrium data of Scatchard and Raymond.\(^{16}\) Note that values of \( y_{A_2} = y_{B_2} = 0; \ y_{C_1} = 1.000 \) were assumed for this calculation. Coefficients \( D_{AC}^2 \) and \( D_{BC}^2 \) were measured as an earlier part of this experiment, and \( D_{AB} \) was determined from computed force constants as described earlier. The true value of \( x \) was calculated from \( x_A \) and a mole-fraction average of the \( \Delta x \) correction factors given in Table III.

Therefore one obtains

\[ D_A'' = \frac{1 - 0.112}{0.081 + 0.807 \over 0.0809 + 0.192} \]

\[ = 0.171 \text{ cm}^2/\text{sec}, \]
\[ \Delta x = 0.23 \text{ cm}, \]
\[ x = 14.10 - 0.23 = 13.87 \text{ cm}. \]

(This value will be the same for all later methods.)

and

\[
N_A = \frac{(0.171)(0.995)}{(82.057)(308.16)(13.87)} \ln \left( \frac{1.000}{1.000 - 0.225} \right) = 1.240 \times 10^{-7} \text{ g-moles/cm}^2\text{-sec.}
\]

Since \( \theta \) is 921.29 min, one can compute

\[
n_A = (1.240 \times 10^{-7})(1.63)(921.29)(60) = 1.118 \times 10^{-2} \text{ g-moles of A,}
\]

and similarly

\[
N_B = 0.516 \times 10^{-7} \text{ g-moles/cm}^2\text{-sec}
\]

and

\[
n_B = 0.465 \times 10^{-2} \text{ g-moles of B.}
\]

The total number of moles lost is \( n_A + n_B = 1.583 \times 10^{-2} \text{ g-moles.} \)

3. Wilke's First Method

One can write

\[
N_A = \frac{D_{A}'' P}{RT x (p_{fA}^{A}) (p_{A1} - p_{A2})},
\]

where

\[
(p_{fA}^{A}) = P (\phi_A - y_A)_{LM} / \phi_A \cdot D_{A}'' \text{ is defined with no interaction [Case (2)]}, \text{ and } \phi_A = N_A / N_t.
\]
This method requires a trial-and-error solution. In this and several of the following methods, the definition \( N_A' = \frac{RTx}{P} N_A = 0.0352 \times 10^7 N_A \) (also \( N_B' = 0.0352 \times 10^7 N_B \)) was found to be useful.

A sample trial-and-error calculation is as follows:

Assume \( \phi_A = 0.671 \) and \( \phi_B = 0.329 \). Therefore we have

\[
(p_f)_A = 623 \text{ mm Hg},
\]

\[
(p_f)_B = 549 \text{ mm Hg},
\]

\[
N_A' = \frac{(0.171)(170.1)}{(623)} = 0.0466
\]

and

\[
N_B' = \frac{(0.103)(122.4)}{(549)} = 0.0230,
\]

where

\[
p_A = 170.1 \text{ mm Hg, } p_B = 122.4 \text{ mm Hg},
\]

\[
N_A + N_B = 0.0696, \quad \phi_A = 0.670, \quad \text{and } \phi_B = 0.330.
\]

Hence the solution is complete. These values of \( N_A' \) and \( N_B' \) were then multiplied by the previously described constants. The resulting values of \( n_A \) and \( n_B \) are tabulated in Table V.

4. Wilke's Second Method

In the second method, we have

\[
N_A' = \frac{D_A''}{(p_f)_A (p_A - p_A_2)}
\]

where \( D_A'' \) is defined by Eqs. (16) through (24).

This method also requires an iterative solution. A sample calculation is as follows:
Assume

\[ \phi_A = \phi_{AB} = 0.673 \quad \text{and} \quad \phi_B = \phi_{BA} = 0.327. \]

Therefore we have

\[
(p_f)^{AB} = \frac{756}{0.673} (0.193)(0.093) = 20.2 \text{ mm Hg},
\]

\[
(p_f)^{AC} = \frac{756}{l} (0.918)(0.878) = 609 \text{ mm Hg},
\]

\[
\gamma_B'' = \frac{20.2}{629} = 0.0321,
\]

\[
\gamma_C'' = \frac{609}{629} = 0.968,
\]

\[
D_A'' = \frac{1}{0.0321 + 0.968} = \frac{1}{5.437} = 0.184 \text{ cm}^2/\text{sec},
\]

\[
(p_f)^{A} = \frac{756}{0.673} \frac{0.225}{\ln \frac{0.673}{0.448}} = 623 \text{ mm Hg},
\]

and

\[
N_A' = \frac{(0.184)(170.1)}{(623)} = 0.0502.
\]

Similarly one can compute

\[
N_B' = 0.0245,
\]

\[
N_A' + N_B' = 0.0747,
\]

and

\[
\phi_A = 0.672,
\]

and the solution is complete.
5. Shain's Method

We have

\[ N_i = \frac{P_i}{\sum_{i \neq j} \left( Y_j - \frac{y_i \phi_j}{\phi_i} \right) \frac{1}{D_{ij}}} \]

which also involves a trial-and-error solution. As an example, assume

\[ \phi_A = 0.672 \text{ and } \phi_B = 0.328. \]

Therefore one can write

\[
N_A' = \left( Y_A - Y_A' \right) \ln \left\{ \frac{Y_A - \frac{y_A \phi_B}{\phi_A}}{\frac{y_A \phi_B}{\phi_A}} \right\} \left[ \left( \frac{y_A \phi_B}{\phi_A} \right) \frac{1}{D_{AB}} + \left( \frac{y_C \phi_C}{\phi_A} \right) \frac{1}{D_{AC}} \right] \\
- \left[ \left( \frac{y_B \phi_B}{\phi_A} \right) \frac{1}{D_{AB}} + \left( \frac{y_C \phi_C}{\phi_A} \right) \frac{1}{D_{AC}} \right]
\]

\[
\begin{align*}
0.225 \ln \left\{ \left( \frac{0.162 - (0.225)(0.328)}{0.672} \right) \frac{1}{0.0809} + \frac{0.613}{0.0809} \right\} \\
= \left( \frac{0.162 - (0.225)(0.328)}{0.672} \right) \frac{1}{0.0809} + \frac{0.613}{0.0809} - \frac{1.000}{0.192}
\end{align*}
\]

\[ = 0.0504. \]
Similarly, one can compute

\[ N_B' = 0.0246, \]
\[ N_A' + N_B' = 0.0750, \]

and

\[ \phi_A = 0.672, \]

and the solution is complete.

6. Gilliland Solution

This solution involves two simultaneous equations, which can be reduced to the following for application in this experiment:

\[ \frac{N_A'}{D_{AC}} + \frac{N_B'}{D_{BC}} = \ln \left( \frac{p_{C_2}}{p_{C_1}} \right) \]

\[ N_A' + N_B' = D_{AB} \ln \left\{ \frac{[M]P}{[L]\left( \frac{p_{B_1}}{p_B} \right) - \left( \frac{p_{A_1}}{\phi_A} \right) + [M]P} \right\} \]

where

\[ [M] = \begin{bmatrix} \frac{1}{D_{AC}} & -\frac{1}{D_{BC}} \\ \frac{1}{D_{AB}} & -\frac{1}{D_{BC}} \end{bmatrix} = -1.37 \]

and

\[ [L] = \begin{bmatrix} \frac{1}{D_{AB}} & -\frac{1}{D_{AC}} \\ \frac{1}{D_{AB}} & -\frac{1}{D_{BC}} \end{bmatrix} = 2.37. \]
Assume $N'_A = 0.0499$. Therefore we have

$$N'_B = D_{BC} \left[ \ln(756) - \frac{0.0499}{0.192} \right] = 0.0246,$$

and accordingly

$$N'_A + N'_B = 0.0745.$$

Therefore we have

$$\phi_A = 0.669,$$

$$\phi_B = 0.331,$$

and

$$\frac{N'_A + N'_B}{D_{AB}} = 0.922.$$

It follows that

$$\ln \left\{ \frac{-1.37(756)}{(2.37)\left(\frac{122.4}{0.331}\right) - 170.1 - 1.37(756)} \right\} = 0.919.$$

Further trial yields $N'_A = 0.0500$ and $N'_B = 0.0246$ as a better combination.
7. **Toor's Method**

The approximation proposed by Toor does not require a trial-and-error solution. We have

\[ \delta_M' = \left( \frac{p_{C_2}}{p_{C_1}} \right)^{D_M/D_{AB}} \]

where

\[ D_M = \frac{1}{2} (D_{AC} + D_{BC}) \]

\[ = \frac{1}{2} (0.192 + 0.107) = 0.150. \]

It follows that

\[ \delta_M' = \left( \frac{756}{463.5} \right)^{0.150/0.0809} = 2.475. \]

We also have

\[ \phi_C' = \ln \left( \frac{y_{C_1}}{y_{C_2}} \right) \]

\[ = \frac{\ln \left( \frac{1.000}{0.613} \right)}{(1-1.000) - (2.475)(1-0.613)} \]

\[ = 0.510, \]

Hence we obtain

\[ N_A' = D_{AC} \phi_C' \left[ \left( \delta_M' y_{A_1} - y_{A_2} \right) \right] \]

\[ = (0.192)(0.510) \left[ (2.475)(0.225) - 0 \right] \]

\[ = 0.0546. \]
Similarly we compute

\[ n_B = 0.0219, \]

and \( n_A \) and \( n_B \) can be determined easily.

**B. Purity of Materials**

**Benzene** - A. C. S. standard purity. Water content determined to be 0.0227 weight percent.

**Carbon tetrachloride** - A. C. S. standard purity. Water content determined to be 0.0035 weight percent.

**Methyl alcohol** - A. C. S. standard purity. Water content determined to be 0.0910 weight percent.

**Ethyl alcohol** - Rossville Gold Shield 200-proof alcohol produced by the Commercial Solvents Corporation. Distilled with excess of sodium. Water content in final product determined to be 0.425 weight percent.

**Chloroform** - A. C. S. standard purity. Distilled with excess magnesium perchlorate. Water content in final product determined to be 0.0041 weight percent.

**Compressed air** - Liquid Carbonic water-pumped compressed air supplied by the Radiation Laboratory. Guaranteed maximum water content of 220 ppm.
C. Calibration Curves for Index-of-Refraction Measurements
Fig. 14. Calibration curve for liquid mixtures of methyl alcohol and benzene.
Fig. 15. Calibration curve for liquid mixtures of methyl alcohol and carbon tetrachloride.
Fig. 16. Calibration curve for liquid mixtures of ethyl alcohol and chloroform.
D. Vapor Analysis Data for Run 62: MeOH-CCl₄-air system

<p>| | |</p>
<table>
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<tr>
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<tr>
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<td>Total weight loss, grams</td>
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<tr>
<td>Time of run, minutes</td>
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<td>Initial index of refraction</td>
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<td>Final index of refraction</td>
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<td>Initial liquid composition (mole % A)</td>
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<tr>
<td>Final liquid composition (mole % A)</td>
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<tr>
<td>Mean liquid composition (mole % A)</td>
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<tr>
<td>Index of refraction of condensed vapor</td>
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</tr>
<tr>
<td>Composition of condensed vapor (mole % A)</td>
<td>59.6</td>
</tr>
</tbody>
</table>
E. Partial-Pressure-Data Curves
Fig. 17. Partial-pressure curve for liquid mixtures of methyl alcohol and benzene at 35°C.
Fig. 18. Partial-pressure curve for liquid mixtures of methyl alcohol and carbon tetrachloride at 35°C.
Fig. 19. Partial-pressure curve for liquid mixtures of ethyl alcohol and chloroform at 35°C.
F. Nomenclature

c_i  gas-phase concentration of component \ i
D_{A}  apparent diffusion coefficient in binary system
D_{ij}  true binary diffusion coefficient
D_{i}'  effective diffusion coefficient of \ i \ in \ gas \ mixture
D_{i}''  average diffusion coefficient across gas film
D_M  mean diffusion coefficient, defined in Eq. (29)
N_{i}  diffusion rate for component \ i
N_t  total diffusion rate
P  total pressure
p_i  partial pressure of component \ i
(p_{fi})  film pressure factor, defined in Eq. (9)
(p_{fij})  partial film pressure factor, defined in Eq. (19)
(p_B^{LM})  log-mean partial pressure
T  absolute temperature
u_i  gaseous velocity of component \ i \ molecules
x  film thickness
x_A  apparent film thickness
\Delta x_e  correction for turbulence at mouth of tube
\Delta x_s  correction for liquid surface curvature
y_i  mole fraction of component \ i \ in \ gas \ phase
y_{i1}  mole fraction of component \ i \ above \ liquid \ surface
y_{i2}  mole fraction of component \ i \ at \ mouth \ of \ tube
Y_i  arithmetic-mean mole fraction of \ i \ in \ film
effective mole fraction of component $i$

$y_i$ defined by Eq. (21)

$y_{ij}$ defined by Eq. (23)

$\phi_i$ defined by Eq. (11)

$\phi_{ij}$ defined by Eq. (23)

$\phi_C$ defined by Eq. (28)
BIBLIOGRAPHY

8. Ibid., 65, Abt. II, 323 (1872).
10. Ibid., p. 625.


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