The deposition conversion is estimated as the average of the lowest and highest possible conversions which, on the first time through the program, are 0 and 100%. For each iteration, the program determines if the previous conversion estimate is too high or too low by solving both the kinetic and diffusion equations, resets either the highest or lowest possible conversion to the new estimated value, and then reaverages. The conversion is soon found with a high degree of accuracy. For each conversion estimate, the bulk stream, interfacial and film compositions, and the physical properties of the bulk stream and film are recomputed.

From these values and the flow rate, the thickness of the diffusion barrier is calculated. The interfacial compositions are then determined from the Stefan-Maxwell equations. Since initially the film composition was estimated, an iterative procedure was used where the results of the previous iteration were used as the estimated interfacial composition for the next iteration. When two successive iterations agree, this set of interfacial compositions is used to calculate the deposition rate from the kinetic equations for the particular system. If this kinetic rate agrees with the rate calculated from the estimated deposition conversion, the program is completed and the interfacial compositions, conversions, etc., are printed out. If there is poor agreement, the deposition conversion is estimated again to give better agreement, and the iterative procedures repeated.

If the kinetic expression is unknown and the deposition rate is known to be diffusion controlled, such as with the tungsten–hexafluoride-hydrogen system, the test for high or low deposition rate can be a sign test on interfacial compositions. For all positive values of film composition, the deposition conversion is obviously too low, while a negative value for the concentration of any component indicates the conversion is too high. In estimating rates in systems where no experimental kinetic data are available, thermodynamic equilibria have also been employed to test if efficiency was either too high or too low.

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An Experimental Study of Nonequimolal Diffusion in Ternary Gas Mixtures

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This work is an experimental test of the Stefan-Maxwell equations as applied to cocurrent, steady state gaseous diffusion of two species through a stagnant third component. The Stefan capillary tube method was used to measure the diffusion rates. The use of constant evaporating binary liquid mixtures made possible boundary conditions that were invariant with time. Total molar losses were compared with the predictions of the theory to demonstrate the validity of the equations under conditions of a significant convective flux.

This paper describes experimental measurements of diffusion rates in three ternary gas systems in which two gases are simultaneously diffusing through a third species. The results are used to check the validity of the Stefan-Maxwell equations under these conditions.

The Stefan-Maxwell equations describe in differential form diffusion in isothermal, isobaric ideal gas mixtures (*1* to *4*). Whereas the number of cases for which these equations have been solved is limited to a few restrictive situations in ternary systems (*5* to *10*), even fewer actual experimental tests of the validity of the solutions are available (*6*, *9* to *11*). Thus although the recent extensive work of Duncan and Toor with ternary equimolal countercurrent diffusion (*11*) does offer very convincing proof of the applicability of the Stefan-Maxwell equations in real gas systems, we wish to present further evidence of this fact from a study of cocurrent diffusion of two gases through a stagnant third species.

Cocurrent diffusion of one or more gaseous species through an additional stagnant gas can be easily studied by application of the Stefan capillary tube method of measuring diffusion coefficients (*12*). In the present work this technique was utilized to study diffusion in both binary and ternary systems at 35.0°C. involving the organic compounds methyl alcohol, ethyl alcohol, chloroform, carbon tetrachloride, and benzene, and an invariant stagnant gas, air. Since both the theoretical and experimental aspects of the capillary tube method have been discussed in detail for binary systems by Lee and Wilke (*12*), only the unique features of the present work will be described here.

EXPERIMENTAL CONSIDERATIONS

A schematic diagram of the apparatus used here appears in Figure 1 and a drawing of the diffusion unit itself is

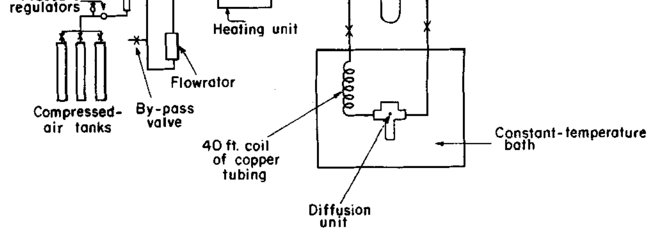

Fig. 1. Schematic diagram of the apparatus.

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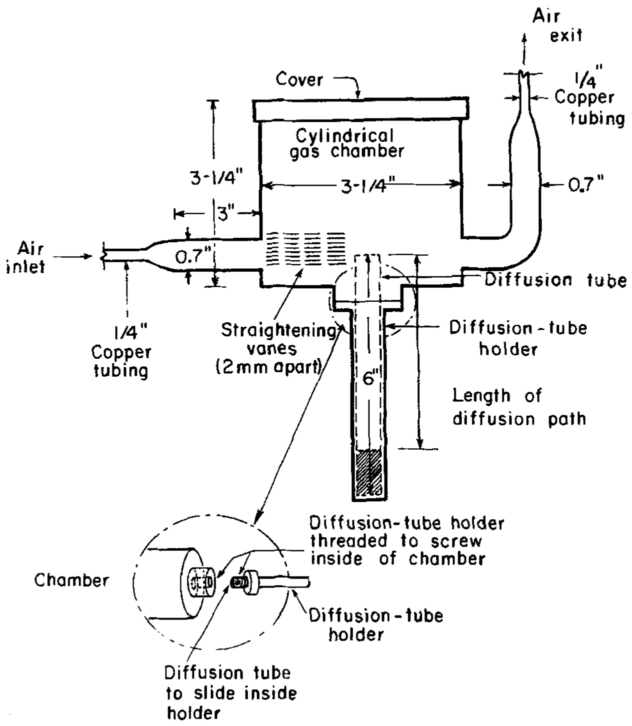

Fig. 2. Diffusion unit.

shown in Figure 2. An air flow rate of 1,890 cc./min. was found to meet the conditions stated by Lee and Wilke for the absence of either excess turbulence or stagnation at the mouth of the diffusion tube. A specially built 6-in. column of magnesium perchlorate eliminated any trace quantities of water from the gas. After passing through a flowrator, the air was heated preliminarily to within approximately 1° of the bath temperature by a heating element consisting of two heating tapes wrapped about numerous coils of the ¼-in. copper tubing through which the gas flowed and surrounded by several layers of asbestos insulating strips. The air was then directed by the tubing into the constant-temperature bath, where it passed through a 40-ft. coil to bring its temperature to 35 ± 0.1°C. before entering the suspended diffusion unit. The air and dilute organic vapors were then led by tubing from the bath to a blower and exhausted outside the building. Experimental runs generally lasted 10 hr. or longer.

The brass diffusion unit, tubes, and tube holders were similar to those described by Lee and Wilke. The dimensions of the two diffusion tubes used were:

	Large tube	Small tube
Inside diameter	2.40 cm.	1.44 cm.
Wall thickness	0.031 in.	0.031 in.
Depth	15.25 cm.	15.31 cm.

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 was 0.123 in.

In all cases gravimetric calibration curves of the depth x_A vs. the combined weight of the sample and diffusion tube were utilized. A small correction was made for thermal expansion of the liquids by using data from Perry (*13*). 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.

The work with ternary systems utilized the liquid mixtures methyl alcohol–benzene, methyl alcohol–carbon tetrachloride, and ethyl alcohol–chloroform. Since the quasi steady state aspect of the capillary tube technique requires boundary conditions that are invariant with time, it was necessary to locate liquid mixtures at 35.0°C. in which the composition of the vapor leaving the liquid was equal to that of the liquid for all time. Hence constant evaporating liquid mixtures were first determined for these three systems and then were used throughout this work to obtain ternary data.

Late in the experimental work, it was decided to condense and analyze at least one vapor sample to confirm the assumption of equal vapor and liquid composition. 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 this latter unit could be removed from the apparatus without halting the air flow whenever an analysis was desired.

Compositions of the binary liquid were determined from indexes of refraction. Initially, calibration curves showing the index of refraction vs. 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 the reference thesis (*14*).

Benzene, carbon tetrachloride, methyl alcohol, and chloroform were A.C.S. standard purity chemicals. The chloroform was vacuum distilled over magnesium perchlorate to minimize the water content, and the ethyl alcohol was vacuum distilled over sodium to decrease the water content to 0.424 wt. %. The compressed air had a maximum water content of 220 p.p.m.

The bath temperature of 35.0°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 have been published by Scatchard and co-workers for mixtures of methyl alcohol–benzene (*15*), methyl alcohol–carbon tetrachloride (*16*), and ethyl alcohol–chloroform (*17*) at 35°C. and these values were used for this work. From this data partial pressure vs. concentration curves were drawn and the values shown at the bottom of Table 1 were read for use in the calculations. It is felt that the uncertainty introduced in plotting the data and reading the curves for use in the calculations is of the order of 0.5 mm. Hg.

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 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.

In the capillary tube method plug flow is assumed in the diffusion tube (that is, no radial concentration gradients). A recent study made by Heinzelmann et al. (*18*) confirms this assumption.

It should also 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 various species into oxygen and nitrogen.

The Gilliland solution of the Stefan-Maxwell equation for the case of diffusion of two species through a third stagnant gas is expressed in terms of two complex simultaneous algebraic equations (*5*). These equations were solved by a trial and error iteration procedure for comparison with the experimental results of this study.

RESULTS

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, the apparent diffusion coefficient, against $1/x_A$ for each run, according to the technique of Lee and Wilke (*12*), and extrapolating to infinite x_A as shown in Figure 3 for the methyl alcohol–air system. A least squares treatment was employed to locate accurately the dotted lines and the true diffusion coefficient in all cases. The following values, corrected to 1 atm. total pressure, were obtained in the small diffusion tube at 35.0°C.

$D_{C_6H_6\text{-air}}$ = 0.107 sq.cm./sec.
$D_{CCl_4\text{-air}}$ = 0.0894
$D_{CH_3OH\text{-air}}$ = 0.191
$D_{C_2H_5OH\text{-air}}$ = 0.144
$D_{CHCl_3\text{-air}}$ = 0.101

These values are from 2 to 10% larger than those calculated by the modified Hirschfelder, Bird, and Spotz (HBS) equation (*19*) using "collision diameters" taken from the tables of Hirschfelder, Curtiss, and Bird (*3*). Since measurements with the large diffusion tube used gave similar results (cf. Figure 3), only the smaller tube was utilized in the ternary runs.

The interaction coefficients D_{AB} between two organic vapors, which are also needed in calculations with the ternary systems, were obtained as follows: (1) the measured binary diffusion coefficients were combined with the force constant ϵ/k for air (97.0°K.) in the modified HBS equation to calculate an ϵ/k value for each of the organic compounds; and (2) the same theoretical equation was used to calculate the various D_{AB}'s from these semiempirical ϵ/k values. The results are

$D_{CH_3OH\text{-}C_6H_6}$ = 0.0809 sq.cm./sec.
$D_{CH_3OH\text{-}CCl_4}$ = 0.0676
$D_{C_2H_5OH\text{-}CHCl_3}$ = 0.0566

As mentioned earlier the use of constant evaporating binary liquid mixtures was an important factor in this work. These mixtures were estimated for the three systems of interest (methyl alcohol–benzene, methyl alcohol–carbon tetrachloride, and ethyl alcohol–chloroform) by an approximate technique (*20*) and then accurately determined by a series of trial and error experimental runs.

The approximate constant evaporating mixtures located at 35.0°C. and 756 mm. Hg 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 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.

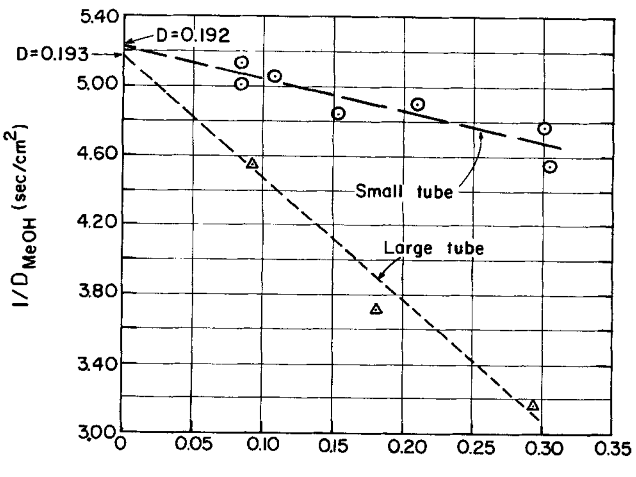

Fig. 3. Experimental diffusion coefficients for methyl alcohol in a methyl alcohol–air system.

A further assurance of the accuracy of this method of determining the vapor composition was offered by the condensation analysis described earlier. The system methyl alcohol–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 methyl alcohol and the composition of the condensed vapor was 0.596 methanol.

The ternary runs were carried out in the same manner as the binary experiments reported above. Since the liquid composition was constant during the experimental periods, it was only necessary to weigh the sample before and after each run to determine the rate of evaporation of each species. An extension of the treatment of Lee and Wilke to multicomponent systems resulted in the calculation of true effective diffusion coefficients D_A'' and D_B'' for each system (see reference *20*). The true diffusion path length x for any run was then determined by subtracting the mole fraction average of the correction factor Δx for components A and B in the ternary mixtures from x_A in each case (*14*).

With this information the Gilliland equations were solved for the flux of components A and B for all cases with a diffusion path length greater than 6 cm. Since runs with the longest path length are most reliable, we have presented in Table 1 a comparison between the theoretical predictions of the Stefan-Maxwell equations (Gilliland solution) and the experimental results for the largest value of x used in each system. A more extensive comparison can be found in the reference thesis (*14*).

The experimental values in Table 1 appear to be in satisfactory agreement with the theoretical predictions.

TABLE 1. COMPARISON OF CALCULATED AND EXPERIMENTAL RESULTS

	Theoretical		Experimental		Deviation of theory from experiment	
Path length, x cm.	Moles of A exaporated, × 10^2	Moles of B evaporated, × 10^2	Moles of A exaporated, × 10^2	Moles of B evaporated, × 10^2	For component A, %	For component B, %
13.87*	1.280	0.629	1.192	0.650	+7.4	—3.2
13.81†	1.297	0.765	1.215	0.772	+6.7	—0.9
12.32‡	0.214	1.454	0.202	1.470	+5.9	—1.1

* Methyl alcohol (A)–benzene (B)–air (C) system $(P_A)_1 = 170.2$ mm.Hg; $(P_B)_1 = 122.3$ mm. Hg; $(P_A)_2 = (P_B)_2 = 0$.
† Methyl alcohol (A)–carbon tetrachloride (B)–air (C) system $(P_A)_1 = 170.0$ mm. Hg; $(P_B)_1 = 155.0$ mm. Hg; $(P_A)_2 = (P_B)_2 = 0$.
‡ Ethyl alcohol (A)–chloroform (B)–air (C) system $(P_A)_1 = 32.3$ mm. Hg; $(P_B)_1 = 272.5$ mm. Hg; $(P_A)_2 = (P_B)_2 = 0$.

Similar agreement was observed in other experiments as is evident from the fact that average deviations in the total number of moles evaporated ($A + B$) of +3.1, +3.0, and −0.7% were found for the three systems over a large number of runs. It should be noted at this point that careful consideration has been given to the question of the sensitivity of the predictions of the Gilliland equations to small errors in the measured diffusion coefficients D_{AC} and D_{BC} and in the semiempirically determined values of D_{AB}. This analysis has indicated that the observed agreement between theory and experiment would not be significantly affected by errors in the diffusion coefficients of the order of the difference between experimental and modified HBS values. Thus it is felt that these comparisons provide further evidence of the validity of the Stefan-Maxwell equations in multicomponent systems, and in the presence of a significant convective flux.

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A Stochastic Mixing Model for Homogeneous, Turbulent, Tubular Reactors

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A stochastic mixing model is developed for turbulent flow in homogeneous plug-flow reactors. The model is based on random coalescence and redispersion of fluid elements. Of special significance is its applicability when mixing and reaction rates are comparable, as well as when either rate dominates. The model's parameters may be determined by measuring conversion with instantaneous reactions. Experimental results reported by others are successfully simulated.

Mixing is an important factor in many chemical reaction processes, both heterogeneous and homogeneous. This paper considers homogeneous reactions occurring in turbulent flow tubular reactors where the reactants are fed separately. If the rate of reaction is very rapid compared with the rate of mixing, or vice versa, then the performance of the reactor can be calculated by well-developed techniques (*1* to *3*). However, the general case where the rate of reaction and the rate of mixing are comparable has not been extensively studied.

Of particular importance to this paper is the experimental work of Vassilatos and Toor (*4*). They measured conversion in an isothermal tubular reactor, using reactions which were rapid, intermediate, and slow in comparison with the rate of mixing. For the limiting cases of rapid and slow reactions, they successfully predicted conversion, but they experienced difficulty in predicting the results of intermediate speed reactions.

A simple stochastic mixing model is developed here for turbulent tubular reactors. It is shown capable of simulating the experimental results reported by Vassilatos and Toor. The model is based on random collisions and redispersions between elements of fluid. These notions have been used previously by others, especially Curl (*5*) and

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