Dependence of the Diffusion Coefficient on Composition in Binary Gaseous Systems

ROBERT V. MRAZEK, CHARLES E. WICKS, and K. N. S. PRABHU
Chemical Engineering Department, Oregon State University, Corvallis, Ore. 97331

Diffusion coefficients are presented for the chloroform-air system at 50° C. and 1 atm. and the methanol-air system at 55° C. and 1 atm. for a range in gas-phase composition. The dependence of the diffusion coefficient on concentration was pronounced for the chloroform-air system.

IT IS A WELL ACCEPTED FACT that the diffusion coefficients for binary liquid systems depend upon composition (*2*). However, few experimental data are available for the effect of composition on the diffusion coefficient in the gas phase (*1, 6, 9*). The purpose of this work was to investigate the variation of gas-phase diffusion coefficients with composition.

APPARATUS AND EXPERIMENTAL METHOD

Diffusion coefficients were determined by measuring the rate of evaporation of a liquid into a gas stream of known composition, by weighing the diffusion tube before and after an experiment. One of the components, in the liquid state, was placed in the bottom of a vertical tube, and a gas was passed over the top of the tube at a rate sufficient to keep the partial pressure of the vapor in the gas stream at its initial value. The diffusion cell is described by Lee and Wilke (*5*) and by Larson (*4*). It was housed in a constant temperature bath which was maintained to ±0.005° C. of the desired temperature by a Thermotrol control unit. The temperature of the air stream was brought to the bath temperature by allowing the air to pass through a 40-foot coil of ⅛-inch copper tubing contained in the bath before it passed across the top of the diffusion tube. The air flow was controlled by a pressure regulator and a needle valve on the air line; flow rates were indicated on a rotameter. In addition, the pressure in the diffusion cell was indicated on a water manometer. The 0.373-inch i.d. stainless steel diffusion tube was 6½ inches long.

The initial concentration of the vapor in the gas stream was fixed by saturating the gas stream with the desired vapor in an equilibrium cell at a temperature lower than that of the diffusion cell, and then heating the gas-vapor mixture to the temperature of the diffusion cell. The partial pressure of the vapor in the gas-vapor stream was taken to be the vapor pressure of the liquid at the temperature of the equilibrium cell. The degree of saturation of the exit stream from the equilibrium cell was checked by measuring the air flow rate and the amount of liquid evaporated during a given period of time. Within experimental accuracy, the exit stream was saturated with the desired vapor. A complete description of the equilibrium cell is given by Prabhu (*7*). The equilibrium cell was contained in a second constant temperature bath controlled by a mercury thermoregulator to within ±0.01° C. of the desired temperature.

The rate of evaporation of liquid from the diffusion cell into the gas stream of known composition was determined by measuring the amount of liquid evaporated during 10 to 12 hours. The experiments were of sufficient duration so that the effect of any initial transient behavior was negligible (*5, 7*). This was verified experimentally by the consistency of the results for experiments with the same average apparent path length, but of different duration.

In addition, corrections were made for the difference between the actual diffusion path length in the diffusion cell and the apparent path length. These differences are caused by the shape of the liquid meniscus and the existence of eddies at the mouth of the diffusion tube. The correction was made by taking data for several apparent path lengths and extrapolating them to infinite path length by the method of Lee and Wilke (*5*).

The chloroform-air system at 50° C. and 1 atm. and the methanol-air system at 55° C. and 1 atm. were investigated. The chloroform and methanol used were Baker reagent grade materials of better than 99.8% purity.

EXPERIMENTAL RESULTS

Quasi-steady-state conditions were assumed, and in this case the apparent diffusion coefficient for an experiment is given by the expression (*5*)

$$D_a = \frac{W_A R T z_a}{\theta S P M_A \ln\left(\frac{1 - x_{A2}}{1 - x_{A1}}\right)} \tag{1}$$

The proper apparent path length to be used in this expression is the arithmetic average of the apparent path lengths at the beginning and end of each experiment.

Equation 1 is based upon the assumption of a constant diffusion coefficient. Since the diffusion coefficient is a function of concentration, Equation 1 actually yields a concentration average value of the apparent diffusion coefficient for the concentration range between x_{A1} and x_{A2}. Conversion of this average value to a point function of concentration is dealt with in the discussion.

The apparent diffusion coefficient was determined for the chloroform-air system at 50° C. and 1 atm. and for the methanol-air system at 55° C. and 1 atm. Data were taken for several apparent path lengths at each of several values of the concentration of vapor in the air-vapor stream passing across the top of the diffusion cell, x_{A2}. These data are presented in Table I along with the corresponding apparent path lengths, z_a, and concentrations, x_{A1} and x_{A2}.

For each value of x_{A2}, the data in Table I were extrapolated to infinite apparent path length to correct for end effects. This procedure gives a true value of the concentration-average diffusion coefficient for the range of concentration between x_{A1} and x_{A2}. This true concentration-average diffusion coefficient, $\bar{D}_{AB}$, is given in Table II; the values of x_{A1} and x_{A2} in Table II are the arithmetic averages of the appropriate values in Table I.

DISCUSSION

The concentration-average diffusion coefficients for each of the two systems for the case of pure air flowing across the top of the diffusion tube ($x_{A2} = 0$) were corrected to 25° C. with the Hirschfelder, Bird, and Spotz equation (*3*) for comparison to published values. The data for the case of $x_{A2} = 0$ were used, since this represents the case for which other experimental values are available. The values are given in Table III; the agreement with other investigators is good.

The reproducibility of the experimental data also was satisfactory. This can be seen by comparing values in Table I at the same concentrations and path length. The accuracy of the true concentration-average diffusion coefficients given in Table II is estimated to be ±2.5%, based upon the reproducibility and accuracy of the original measurements, the accuracy of the extrapolation to infinite path length, and the assumption to ideal gases. This second effect depends upon the error involved in fitting a straight line to the original data.

Table I. Summary of Experimental Data

Concentration		Apparent Path Length, z_a, Cm.	Apparent Diffusion Coefficient, D_a, Sq. Cm./Sec.
At liquid surface, x_{A1}	In air stream, x_{A2}		
Chloroform-Air System at 50° C. and 1 Atm.			
0.681	0.000	10.405	0.1110
0.679	0.000	6.960	0.1174
0.682	0.000	6.955	0.1140
0.683	0.000	8.390	0.1127
0.682	0.000	10.355	0.1116
0.681	0.000	10.890	0.1110
0.680	0.000	10.620	0.1108
0.680	0.174	10.760	0.1139
0.685	0.174	7.670	0.1159
0.684	0.174	6.575	0.1171
0.680	0.173	8.620	0.1148
0.678	0.172	6.080	0.1182
0.683	0.174	10.345	0.1129
0.685	0.174	7.615	0.1153
0.685	0.174	9.335	0.1140
0.686	0.174	6.510	0.1180
0.683	0.257	8.200	0.1205
0.680	0.261	6.655	0.1232
0.681	0.255	8.155	0.1203
0.682	0.256	8.970	0.1191
0.680	0.255	9.855	0.1177
0.685	0.257	10.850	0.1174
0.679	0.363	11.605	0.1195
0.678	0.364	8.045	0.1243
0.678	0.363	8.320	0.1235
0.684	0.366	9.425	0.1231
0.682	0.365	10.025	0.1213
0.683	0.437	11.280	0.1220
0.682	0.434	9.100	0.1253
0.683	0.434	10.690	0.1230
0.683	0.435	9.730	0.1199
0.683	0.436	5.290	0.1389
0.683	0.565	8.290	0.1370
0.682	0.565	7.145	0.1432
0.684	0.568	11.090	0.1314
0.683	0.567	7.950	0.1384
Methanol-Air System at 55° C. and 1 Atm.			
0.666	0.000	12.920	0.2191
0.666	0.000	8.425	0.2136
0.665	0.000	8.840	0.2128
0.666	0.000	10.440	0.2091
0.666	0.000	10.335	0.2093
0.667	0.000	6.215	0.2226
0.665	0.000	7.850	0.2144
0.666	0.000	6.335	0.2193
0.666	0.148	9.725	0.2121
0.663	0.147	8.115	0.2161
0.663	0.148	9.460	0.2130
0.668	0.148	8.650	0.2170
0.666	0.148	6.945	0.2208
0.666	0.241	6.970	0.2232
0.667	0.242	9.720	0.2146
0.665	0.242	7.645	0.2124
0.665	0.242	10.320	0.2137
0.663	0.241	7.645	0.2209
0.666	0.475	10.875	0.2181
0.665	0.473	8.495	0.2258
0.665	0.473	7.640	0.2298
0.666	0.473	8.455	0.2252
0.666	0.473	9.325	0.2222

Table II shows that the total variation of the diffusion coefficient over the range of concentrations given was only about 1% for the methanol-air system, and on the order of 9% for the chloroform-air system. This agrees qualitatively with the results of Schäfer, Corte, and Moesta (*9*), who found that the concentration dependency increases as the difference in the molecular weights or atomic volumes between the two species increases.

The diffusion coefficients given in Table II are not the values at a given concentration, but rather an average over a concentration range. The significance of this can be seen by returning to the basic differential equation for diffusion of a gas through a second stagnant gas:

$$N_A = \frac{-PD_{AB}}{RT(1-x_A)}\frac{dx_A}{dz} \tag{2}$$

If one assumes that a suitable average value of the diffusion coefficient can be used for the concentration range of interest, integration of Equation 2 will yield the precursor to Equation 1.

$$N_A = \frac{P\bar{D}_{AB}}{RTz}\ln\left(\frac{1-x_{A2}}{1-x_{A1}}\right) \tag{3}$$

However, if one notes that the diffusion coefficient is a function of concentration—i.e., $D_{AB} = f(x_A)$—integration of Equation 2 will yield

$$N_A = \frac{-P}{RTz}\int_{x_{A1}}^{x_{A2}}\frac{f(x_A)dx_A}{(1-x_A)} \tag{4}$$

Comparison of Equations 3 and 4 shows that the concentration-average diffusion coefficient, $\bar{D}_{AB}$, given in Table II is defined by

Table II. Concentration Average Diffusion Coefficients

Concentration		Concn. Average Diffusion Coefficient, $\bar{D}_{AB}$, Sq. Cm./Sec.
At liquid surface, x_{A1}	In air stream, x_{A2}	
Chloroform-Air System at 50° C. and 1 Atm.		
0.681	0.000	0.106
0.682	0.174	0.107
0.682	0.257	0.108
0.682	0.364	0.110
0.683	0.435	0.111
0.683	0.566	0.115
Methanol-Air System at 55° C. and 1 Atm.		
0.666	0.000	0.195
0.665	0.148	0.196
0.666	0.242	0.196
0.666	0.473	0.197

Table III. Comparison of Diffusion Coefficients

	$\bar{D}_{AB}$, Sq. Cm./Sec.	
	This Work	Literature
Chloroform-air at 25° C. and 1 atm.	0.091	0.0904 (*4*)[a]
Methanol-air at 25° C. and 1 atm.	0.162	0.1620 (*8*)

[a] Same apparatus. Measured at 25° C.

$$\bar{D}_{AB} = \frac{-\int_{x_{A1}}^{x_{A2}} \frac{f(x_A)dx_A}{(1 - x_A)}}{\ln\left(\frac{1 - x_{A2}}{1 - x_{A1}}\right)} \qquad (5)$$

If a point value of the diffusion coefficient is desired, the function $f(x_A)$ must be determined. This was done by assuming a functional form for substitution into Equation 5, integrating the expression, and fitting the resulting equation to the experimental data. The best values of the constants in the assumed equation were determined by the method of regression on a digital computer.

Several functional relationships between diffusivity and composition, including a linear relationship and that of Amdur and Schatzki (*1*), were investigated for the chloroform-air system at 50° C. However, the lowest order equation which would give good reproduction of the data was

$$D_{AB} = f(x_A) = a + bx_A + cx_A^2 \qquad (6)$$

Integration of Equation 5 then yields

$$\bar{D}_{AB} = (a + b + c) + \frac{(b + c)\ (x_{A2} - x_{A1}) + c(x_{A2}^2 - x_{A1}^2)/2}{\ln\left(\frac{1 - x_{A2}}{1 - x_{A1}}\right)} \qquad (7)$$

The constants in the assumed quadratic function were then determined, and it was found that the following equation will reproduce the experimental data for the chloroform-air system at 50° C. to better than 0.3%:

$$D_{AB} = 0.10296 - 0.0349x_A + 0.0853x_A^2 \qquad (8)$$

The number of significant figures in Equation 8 is not an indication of the accuracy of the data, but rather the number of figures required to reproduce the values given in Table II.

Although the procedure used to define a concentration-average diffusivity according to Equation 5 is general, the experimental data for the chloroform-air system place a limitation on the use of Equation 8. Table II shows that all of the data for the chloroform-air system at 50° C. correspond to a mole fraction at the liquid interface of $x_{A1} = 0.682$. Therefore, in obtaining Equation 8, it was not possible to account for variation in x_{A1}, and until data are available for a range in values of both x_{A1} and x_{A2}, Equation 8 should be taken to represent only the diffusivity at 50° C. For these conditions, x_{A1} will always equal 0.682 at a total pressure of 1 atm. for this type of apparatus. It is hoped that a more general expression will result from future investigations for this system in which x_{A1} is varied, probably by measuring the diffusion coefficient at different total pressures.

The above fitting procedure was not carried out for the methanol-air system. As can be seen from Table II, the variation in the diffusion coefficient for this system over the range of experimental measurement was only about 1%. Thus, no attempt was made to represent this small variation analytically.

NOMENCLATURE

a, b, c = constants
D_a = apparent concentration-average diffusion coefficient, sq. cm./sec.
D_{AB} = true diffusion coefficient, sq. cm./sec.
$\bar{D}_{AB}$ = true concentration-average diffusion coefficient, sq. cm./sec.
f = function
M_A = molecular weight of diffusing species
N_A = molar flux of diffusing species, gram mole/sq. cm. -sec.
P = absolute pressure, atm.
R = gas constant, cc. -atm./gram mole-° K.
S = cross-sectional area of diffusion tube, sq. cm.
T = absolute temperature, ° K.
W_A = weight of liquid evaporated, grams
x_A = mole fraction of diffusing species
x_{A1} = mole fraction of diffusing species in equilibrium with liquid at interface
x_{A2} = mole fraction of diffusing species at mouth of diffusion cell
z = length of diffusion path, cm.
z_a = apparent length of diffusion path, cm.
θ = time, sec.

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