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Title DIFFUSION COEFFICIENTS OF CHLORINATED
HYDROCARBONS IN AIR

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The diffusion coefficients of several chlorinated hydrocarbons in air were determined by using an Arnold cell. The chlorinated hydrocarbons used were carbon tetrachloride, chloroform, 1, 2-dichloroethane and dichloromethane. To determine the reliability of the experimental method, diffusion coefficients were obtained for benzene and ethanol. These were compared with diffusion coefficients measured by other investigators.

An Arnold cell was used to determine the diffusion coefficients. The diffusion tube was 0.373 inches in diameter, and the diffusion path length varied between 4 and 13 centimeters.

The air flow rate across the top of the tube was maintained at 0.14 ft³/min. for all runs except one series of runs with benzene. For this one series of runs the flow rate was 0.095 ft³/min.

End effects due to turbulent eddies at the mouth of the tube and the surface tension of the liquid were accounted for in the determination of the diffusion coefficients.

DIFFUSION COEFFICIENTS OF CHLORINATED
HYDROCARBONS IN AIR

by

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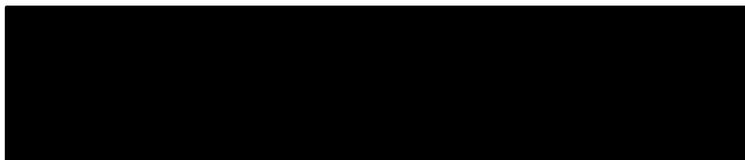


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DIFFUSION COEFFICIENTS OF CHLORINATED HYDROCARBONS IN AIR

INTRODUCTION

The process of diffusion is an important and fundamental process in Chemical Engineering. Such basic operations as absorption, extraction and dissolving depend upon the transport or diffusion of mass between phases or within one phase.

The diffusion coefficient is the proportionality constant between the rate of mass transfer and the concentration gradient. Its function in mass transfer is similar to that of thermal conductivity in heat transfer and viscosity in momentum transfer. Before the rate of diffusion of one substance through another can be calculated it is necessary to determine the diffusion coefficient. The diffusion coefficient is a function of temperature, pressure, molecular weight of each substance, the interaction between the molecules, the size of the individual molecules and in some cases, the concentration of the substances. The coefficient is best determined by experimental measurement although empirical equations have been developed (8, 10, 12, 18).

Through the years various types of experimental apparatus have been developed for the measurement of diffusion coefficients (2, 3, 4, 15, 16, 17). The Arnold cell is probably the most widely used cell for the measurement of diffusion coefficients. Basically

the cell consists of a tube of constant diameter which is partially filled with liquid. Gas, through which the vapor of the liquid diffuses, is passed over the top of the tube. The cell is designed so that the liquid level changes very slowly with time and therefore, the pseudo-steady state solution of the diffusion equation can be assumed with negligible error. Several investigators (1, 6, 13, 14, 15, 17) have used this type of cell.

The equations for an unsteady state Arnold cell were solved by Arnold (3). Arnold also constructed an unsteady state Arnold cell and measured diffusion coefficients with it. Wilke and Fairbanks (16) also used the unsteady state Arnold cell for measuring diffusion coefficients. Barry and Koeller (4) have used a Lös Schmidt cell to measure diffusion coefficients at pressures up to 15,000 psi. Andrew (2) has used an apparatus which consisted of a tube of known length and bore, which connected two reservoirs of gases at different concentrations, to measure diffusion coefficients.

This research project consisted of the measurement of diffusion coefficients at one temperature and pressure of several chlorinated hydrocarbons in air. The diffusion cell used in this study was designed after that of Wilke and Lee (17) and was basically an Arnold cell. End effects, due to eddies at the mouth of the diffusion tube and the meniscus at the liquid-air interphase, were taken into account in the calculation of the diffusion coefficients.

THEORETICAL CONSIDERATIONS

A. Diffusion Equation

The general equation describing the diffusion of one substance through another is given by Fick's first law. Written in terms of the diffusion flux, N_A , relative to stationary coordinates Fick's first law is:

$$N_A = x_A (N_A + N_B) - C D_{AB} \nabla x_A \quad (1)$$

Considering the system shown in Figure 1., a mass balance for each component yields the following equations. For component A:

$$S N_A|_z - S N_A|_{z+\Delta z} = 0 \quad (2)$$

which upon dividing by Δz and upon passing to the limit as $\Delta z \rightarrow 0$ yields the differential equation

$$\frac{d N_A}{d z} = 0. \quad (3)$$

Similarly, the mass balance on component B gives the differential equation

$$\frac{d N_B}{d z} = 0. \quad (4)$$

If substance B is insoluble in liquid A then $N_B|_{z=0}$ is zero.

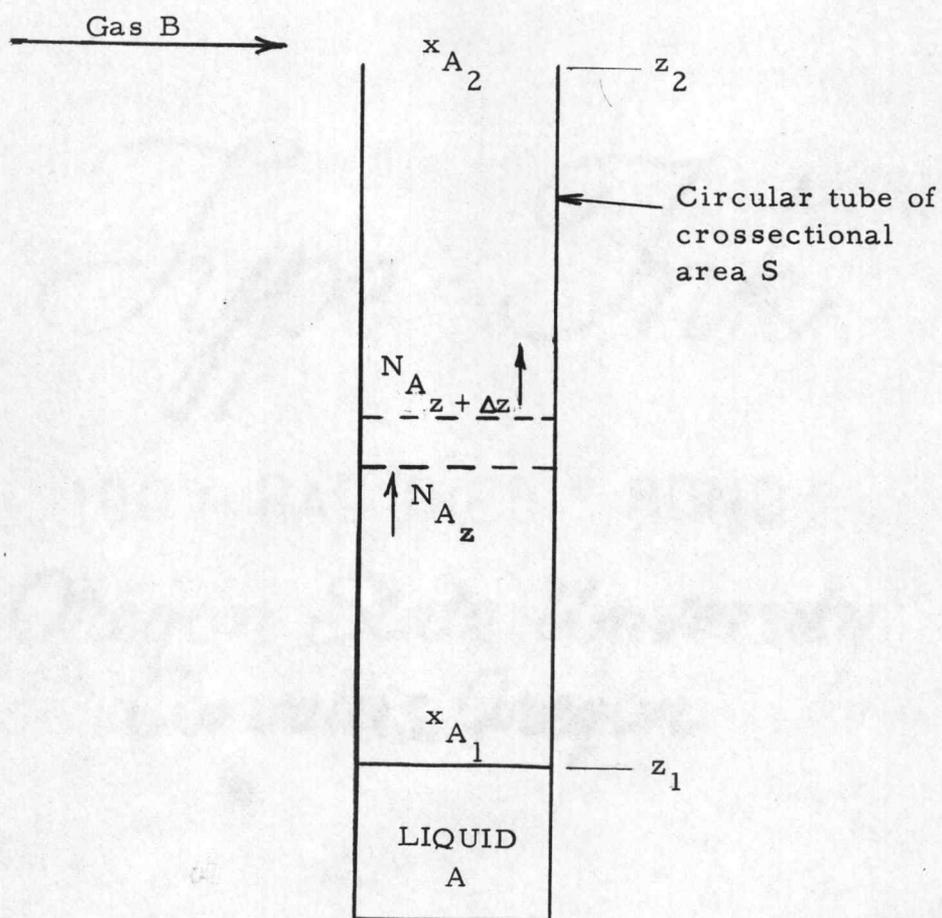


FIGURE 1. DIFFUSION MODEL

Equation (3) describes N_B as a constant for all values of z including z equal to zero. Accordingly, N_B must be zero for all values of z .

If the mole fraction of component A is only a function of z , equation (1) simplifies to

$$N_A = - \frac{C D_{AB}}{(1-x_A)} \frac{d x_A}{d z} \quad (5)$$

Since equation (3),

$$\frac{d N_A}{d z} = 0, \quad (3)$$

stipulates that

$$N_A \Big|_z = \text{constant}, \quad (6)$$

equation (5) becomes

$$\frac{1}{(1-x_A)} \frac{d x_A}{d z} = C_1 \quad (7)$$

Upon separating the variables and integrating one obtains

$$- \ln (1-x_A) = C_1 z + C_2 \quad (8)$$

Applying the boundary conditions

$$z = z_1 \quad x_A = x_{A_1} \quad (9)$$

$$z = z_2 \quad x_A = x_{A_2} \quad (10)$$

one can evaluate the constants C_1 and C_2 .

$$C_1 = \frac{\ln(x_{B_1}/x_{B_2})}{(z_2 - z_1)} \quad (11)$$

and

$$C_2 = \frac{z_1 \ln(x_{B_2}) - z_2 \ln(x_{B_1})}{(z_2 - z_1)} \quad (12)$$

The diffusion flux, N_A , in the case of A diffusing through the nondiffusing B was described by equation (5):

$$N_A = -\frac{C D_{AB}}{(1-x_A)} \frac{dx_A}{dz} \quad (5)$$

Equations (7) and (11) may be used to define the concentration gradient

$$\frac{dx_A}{dz} = -C_1(1-x_A) = -\frac{(1-x_A) \ln(x_{B_2}/x_{B_1})}{z_2 - z_1} \quad (13)$$

Substitution of the concentration gradient into equation (5) yields

$$N_A = -\frac{C D_{AB} \ln(x_{B_1}/x_{B_2})}{z_2 - z_1} \quad (14)$$

or

$$N_A = \frac{C D_{AB} \ln(x_{B_2}/x_{B_1})}{z_2 - z_1} \quad (15)$$

If the gases are ideal

$$C = P/RT \quad (16)$$

Equation (15) then becomes

$$N_A = \frac{P D_{AB}}{RT (z_2 - z_1)} \ln(x_{B_2}/x_{B_1}) \quad (17)$$

or in terms of the mole fraction of A

$$N_A = \frac{P D_{AB}}{RT (z_2 - z_1)} \ln \left[\frac{1 - x_{A_2}}{1 - x_{A_1}} \right] \quad (18)$$

Assumptions included in the above derivation are listed below:

1. The gases are ideal.
2. D_{AB} is independent of concentration.
3. The liquid level remains constant during evaporation.
4. The system is at steady state.

If the change in the liquid level with time is not very large then the average between the initial height and the final height can be used as the diffusion path length. Also if the change in liquid level with time is small the assumption of quasisteady state conditions may be used, i. e. the results derived above.

B. Start Up and Approach to Steady State.

Initially the vapor space above the liquid will be saturated with the vapor of the liquid. It is of interest to determine the time necessary for the concentration profile above the liquid to reach that predicted by equation (13).

If one assumes that Fick's second law without the bulk motion term applies, which is a good assumption if the vapor pressure of the liquid is small, then the following equation is obtained:

$$\frac{\partial a}{\partial \theta} = D \frac{\partial^2 a}{\partial z^2} \quad (19)$$

The boundary conditions that must be satisfied are:

$$\alpha = 1 \text{ at } z = z_1 \text{ for all } \theta \quad (20)$$

$$\alpha = 1 \text{ at } \theta = 0 \text{ for all } z \quad (21)$$

$$\alpha = 0 \text{ at } z = z_2 \text{ for all } \theta > 0 \quad (22)$$

The above equation has been solved by Carslaw (5) and the ratio of the diffusion rate at anytime θ to that at steady state, i. e. $\theta = \infty$, is

$$\frac{(N_A)_{\theta=\theta}}{(N_A)_{\theta=\infty}} = 1 - 2e^{-\frac{D\pi^2\theta}{z^2}} + 2e^{-\frac{4D\pi^2\theta}{z^2}} - 2e^{-\frac{9D\pi^2\theta}{z^2}} \dots \quad (23)$$

Figure 2 is a plot of the above equation for the diffusion of carbon-tetrachloride in air with a diffusion path length of ten centimeters.

C. End Effect Corrections

Due to end effects both at the top of the tube and at the liquid surface, the effective diffusion path is shorter than the distance from the liquid surface to the top of the tube. Due to turbulence at the top of the tube, eddies extend down into the tube a short distance. These eddies tend to decrease the diffusion path by moving the point of zero concentration closer to the liquid. The meniscus also effects the diffusion length. Molecules evaporating near the wall have a shorter diffusion length than those evaporating from the center of the tube.

Figure 3 shows the ideal case and the actual case.

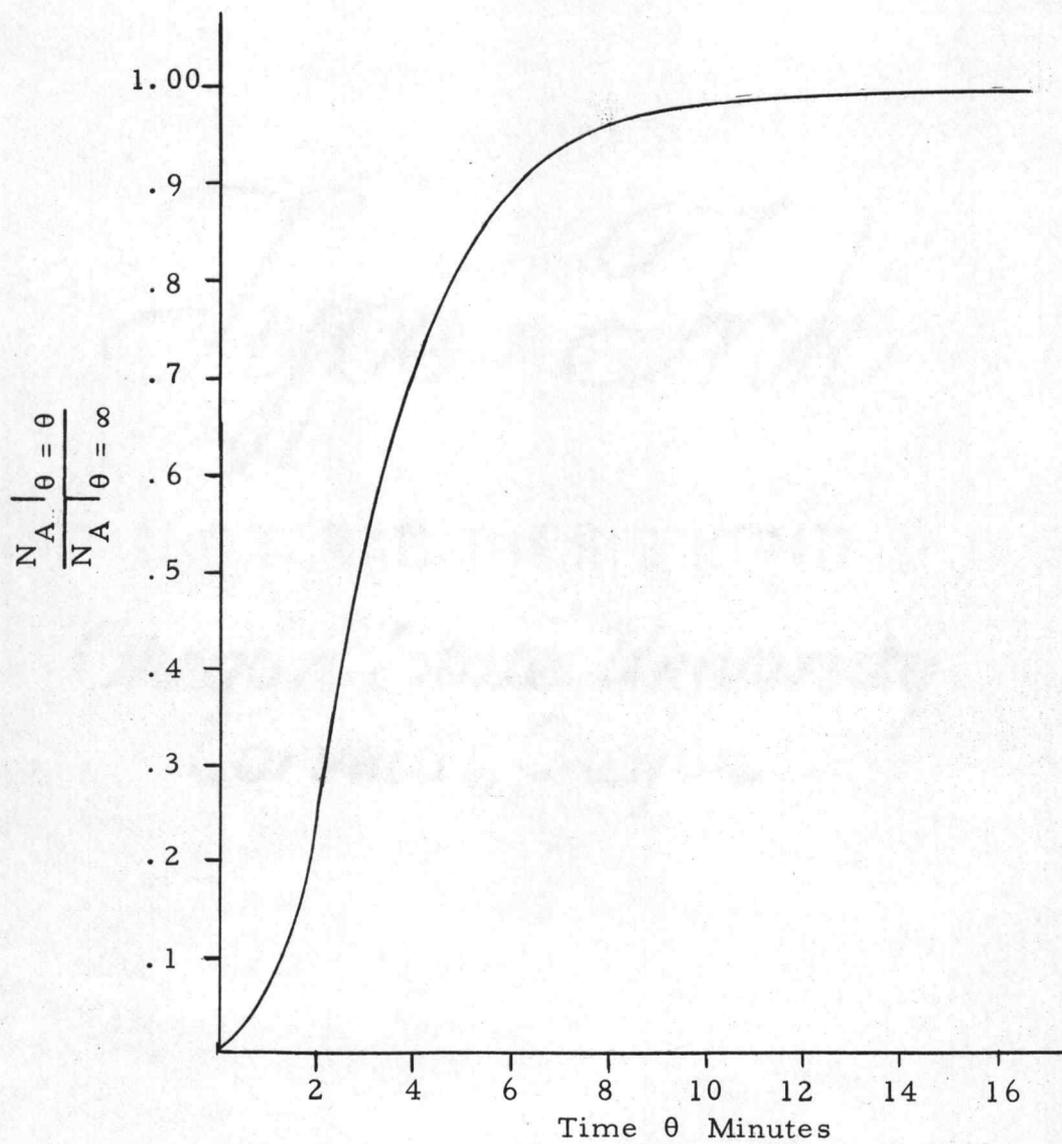


FIGURE 2. APPROACH TO STEADY STATE

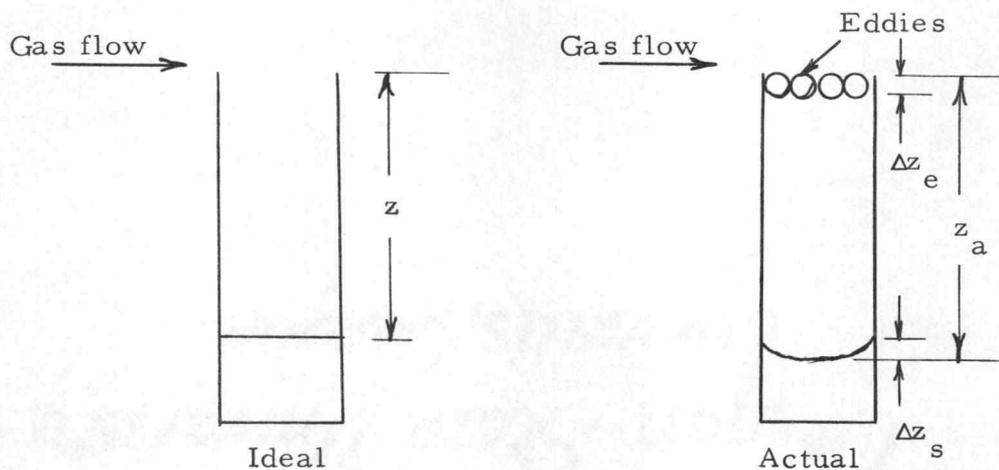


FIGURE 3. APPARENT PATH LENGTH

If the effective average diffusion length is given by (17)

$$z = z_a - \Delta z_s - \Delta z_e = z_a - \Delta z, \quad (24)$$

then two equations can be set up:

$$N_A = \frac{P D_a \ln \frac{(1-x_{A_2})}{(1-x_{A_1})}}{RT z_a} = \frac{P D_{AB}}{RT(z_a - \Delta z)} \ln \frac{(1-x_{A_2})}{(1-x_{A_1})}. \quad (25)$$

Eliminating factors common to both expressions and rearranging one obtains:

$$\frac{1}{D_a} = -\frac{\Delta z}{D_{AB}} \frac{1}{z_a} + \frac{1}{D_{AB}}. \quad (26)$$

This shows that a plot of $1/D_a$ vs. $1/z_a$ should give a straight line whose intersection with the $1/D_a$ axis is $1/D_{AB}$. The

correction to the diffusion path length, Δz , can also be determined from the slope of the plot.

EXPERIMENTAL APPARATUS

The apparatus used in this project consisted of a drying tower packed with calcium chloride, a rotameter, a pressure regulator, a manometer, a diffusion cell and a constant temperature bath. Figure 4 illustrates the flow diagram of the assembled apparatus.

Figure 5 shows the diffusion cell. The diffusion cell was constructed out of brass and copper except for the tube in which the liquid was placed; this tube was made of 304 stainless steel. The removable diffusion assembly consisted of a brass tube six inches long into which the six and a half inch long stainless steel tube fit. The stainless steel tube was machined to a diameter that would just provide a slip fit between it and the brass tube. This tight fit was designed to insure good heat transfer from the constant temperature bath to the diffusing liquid. The stainless steel diffusion tube had a diameter of 0.373 inches.

A bundle of 1/8" copper tubes was placed in the 3/4" inlet pipe of the diffusion cell to provide a flow of air perpendicular to the diffusion tube. A forty foot coil of 1/8" copper tubing was connected to the entrance of the diffusion cell and was placed in the constant temperature bath. The coil of tubing heated the incoming air to the temperature of the bath before it entered the cell.

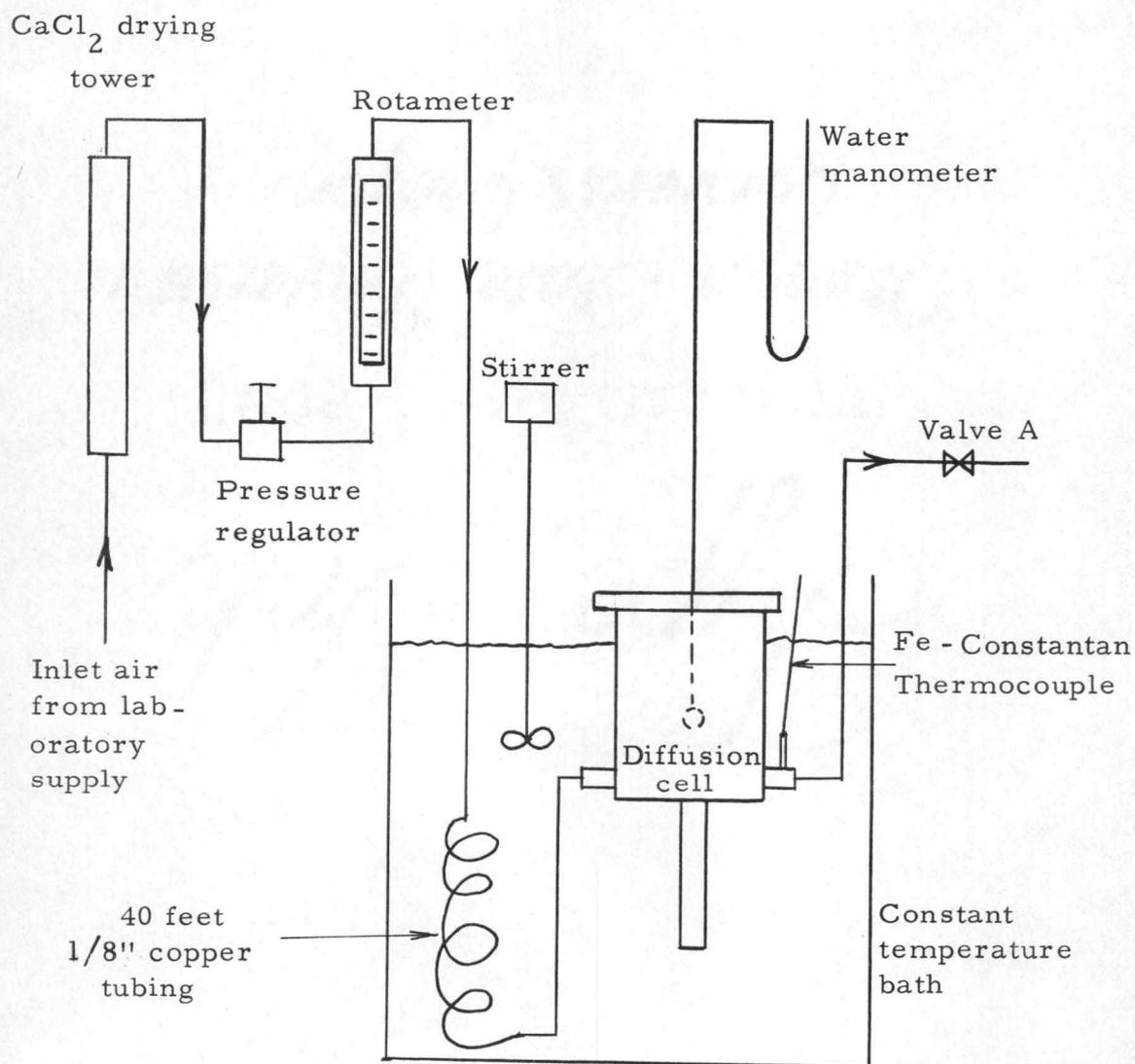


FIGURE 4. FLOW DIAGRAM OF APPARATUS

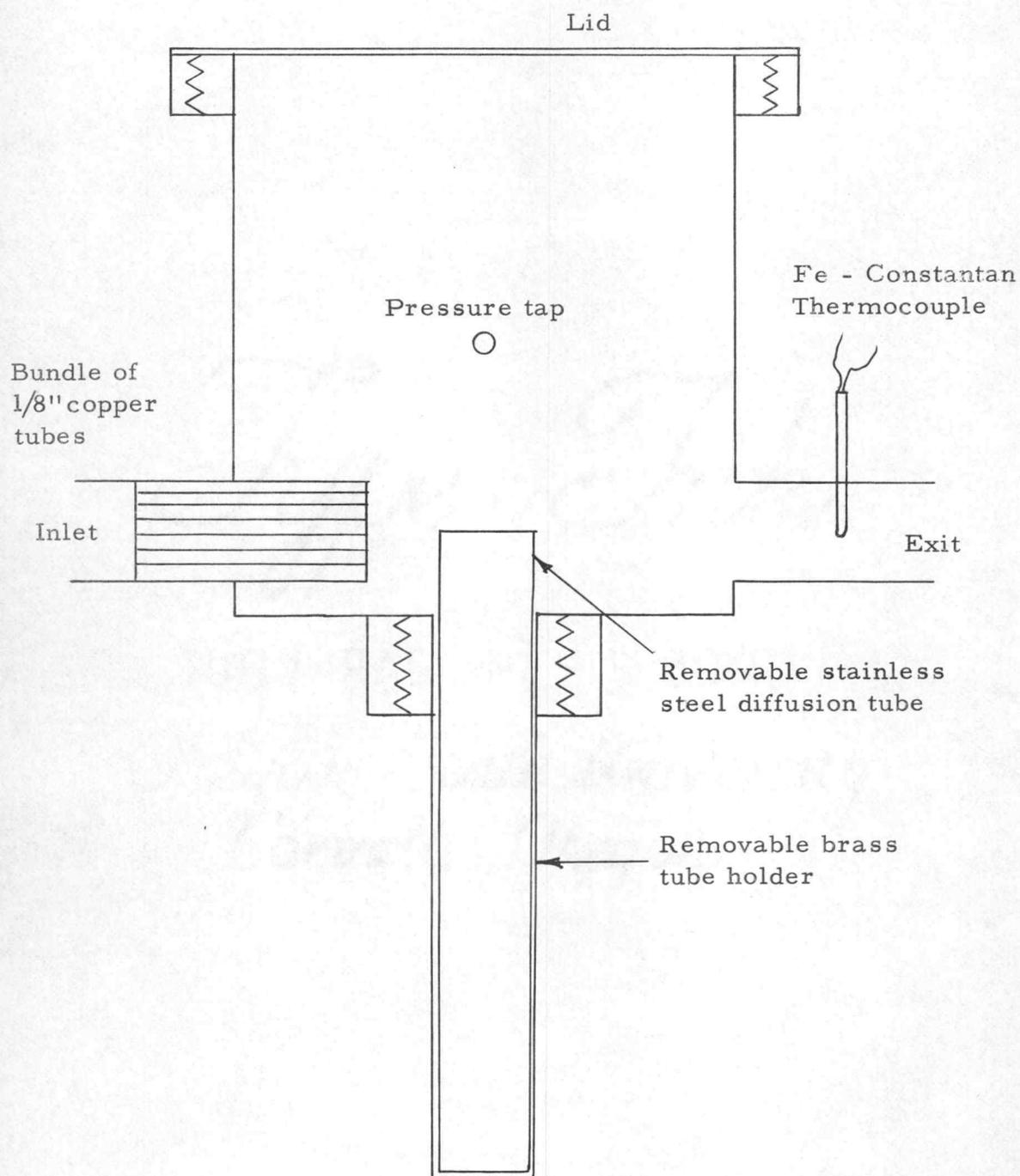


FIGURE 5. CROSS SECTION OF DIFFUSION CELL

A pressure tap was connected to the side of the diffusion cell and an iron-constantan thermocouple was installed in the exit stream of the cell. A water manometer was connected to the pressure tap on the cell.

Compressed air from the building was used. A drying tower was used to remove the moisture from the air supply. The tower consisted of a 1-1/2 inch standard pipe, 16 inches long. It was packed three-quarters full of eight mesh anhydrous calcium chloride and one-quarter full of glass wool. The glass wool was used to remove any drops of oil that may have gotten into the air supply from the compressor.

A rotameter supplied by the Brooks Rotameter Company was used to measure the air flow rate to the diffusion cell. The rotameter was calibrated using a wet-test meter.

A pressure regulator was installed just before the rotameter to provide constant pressure at the entrance to the rotameter. Due to the large resistance to the flow of air produced by the 40 foot coil of 1/8" copper tubing the flow rate through the cell was only slightly affected by the position of valve A. Valve A was used to control the pressure in the cell.

The constant temperature bath was contained in a stainless steel tank, 18 inches in diameter and 22 inches deep. The tank was enclosed in

a wood box, 22" x 22" x 25", and was insulated with glass wool.

Two knife blade heaters were used to heat the bath. The temperature controller used was a Thermotrol Model 1053A made by Hallekainen Instruments, Berkeley, California. The controller was capable of controlling the temperature of a water bath to $\pm 0.002^{\circ}\text{C}$.

A stirrer was used in the temperature bath. The stirrer was suspended independently of the constant temperature bath to prevent vibration of the diffusion cell.

The device used to measure the height of the liquid in the diffusion tube is shown in Figure 6. The device consisted of a piece of plastic 1-1/2" x 1/2" x 1/4" fitted with a 1/16" diameter brass rod and a set screw.

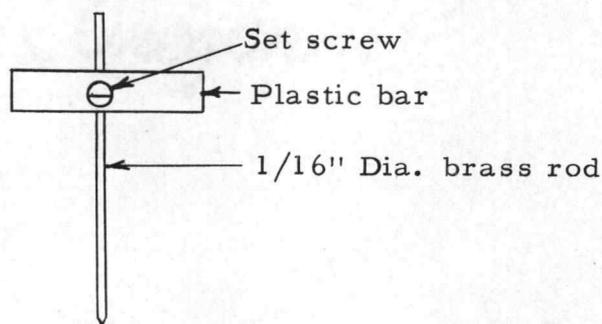


FIGURE 6. DEPTH GAGE

EXPERIMENTAL PROCEDURE

In general the experimental procedure consisted of weighing the diffusion tube and measuring the liquid level before and after each run.

In preparing the diffusion tube for a run, the tube was rinsed several times with acetone and then dried. The tube was then rinsed a few times with the liquid to be used and filled to the desired level with the liquid. A rubber tube connected to a vacuum line was inserted into the tube to a height about one centimeter from the liquid surface. The air drawn into the tube by the vacuum line evaporated any drops of liquid that may have splashed onto the walls while the tube was being filled.

The liquid level was then measured with the device described in the apparatus section. The plastic bar was placed on the top of the diffusion tube and the brass rod was lowered until it just touched the surface of the liquid. Just when the point of the rod touched the surface of the liquid, a change in the pattern of the light reflected from the surface of the liquid was observed. The set screw was then tightened. The length of the rod was measured with a ruler marked in millimeters. The ruler could be read to ± 0.15 millimeters.

The diffusion tube was then stoppered and weighed on a balance capable of weighting to ± 0.01 milligrams. The lid to the diffusion cell was removed and the tube was placed in the tube holder. The stopper was then removed and the time was recorded. The lid was replaced on the diffusion cell. The temperature of the water bath, the temperature at the cell exit, the temperature at the rotameter, the pressure at the entrance of the rotameter, the rotameter float level, the pressure in the cell, and the atmospheric pressure were read and recorded immediately after placing the diffusion tube in the cell. Valve A was used to adjust the pressure in the diffusion cell. The cell pressure was usually three inches of water.

The readings mentioned above were recorded periodically throughout the run. The length of the runs varied between 10 and 13 hours. At the end of the run the lid on the diffusion cell was removed and the diffusion tube was stoppered. The diffusion tube was then removed from the cell and was weighed immediately. After weighing, the stopper was removed and the liquid level was remeasured.

If the same liquid was to be used in the following run a new liquid level was established by adding or removing liquid. The above procedure was then repeated. In the case where a new liquid was used the diffusion tube was prepared as described at the beginning of this section.

RESULTS

Figures 7 through 12 show the curves that were obtained when the reciprocal of the apparent diffusion coefficient was plotted against the reciprocal of the apparent diffusion path length. Diffusion coefficients for benzene, ethanol, carbon tetrachloride, chloroform, dichloromethane and 1, 2 dichloroethane in air were obtained for various diffusion path lengths. A least squares analysis of the experimental data was used to determine the curves in the figures. The diffusion coefficients were determined from the intersection of these curves with the $1/D_a$ axis and are shown on the figures as well as in Table 1. The corrections to the diffusion path length were calculated from the slope of the lines and are given in Table 1.

TABLE 1. EXPERIMENTAL RESULTS

Compound	Experimental D(cm ² /sec.) 298.5 °k 760 mm Hg	Hirshfelder equation D(cm ² /sec.)	Other investigators	Δz (cm)
CCl ₄	0.08306	0.0758		0.471
1-2C ₂ H ₄ Cl ₂	0.08937	---		0.616
CHCl ₃	0.09042	0.1075		0.551
Benzene	0.09833	0.0873	0.0962 (17) 0.0926 (1)	0.367
Benzene	0.09852	0.0873	0.0915 (15)	0.457
CH ₂ Cl ₂	0.1130	0.0972		0.574
C ₂ H ₅ OH	0.1295	0.117	0.125 (15) 0.135 (17) 0.119 (7)	0.769

T = 25.3°C P = 760 mm Hg

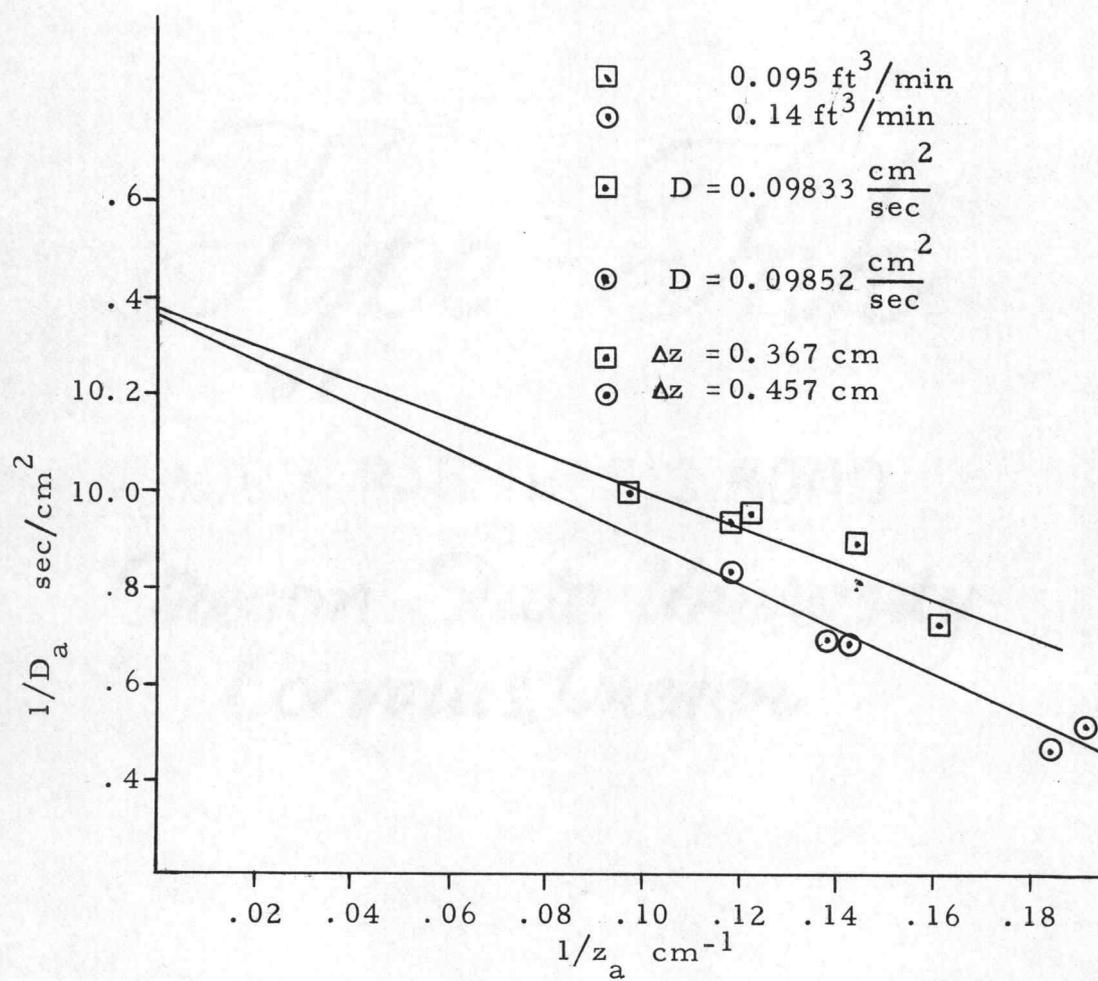


FIGURE 7. RESULTS FOR BENZENE IN AIR

T = 25.3°C P = 760 mm Hg

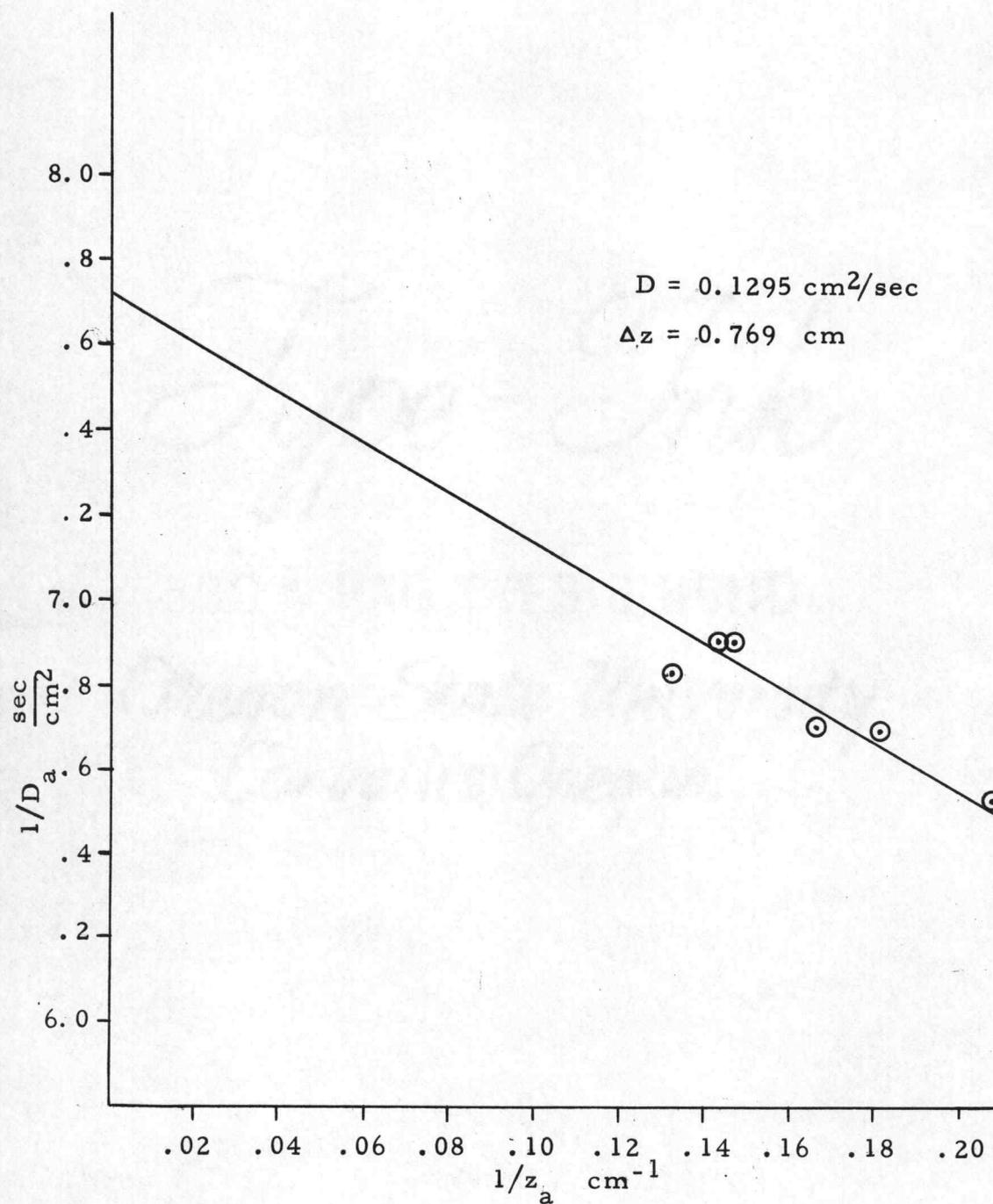


FIGURE 8. RESULTS FOR ETHANOL IN AIR

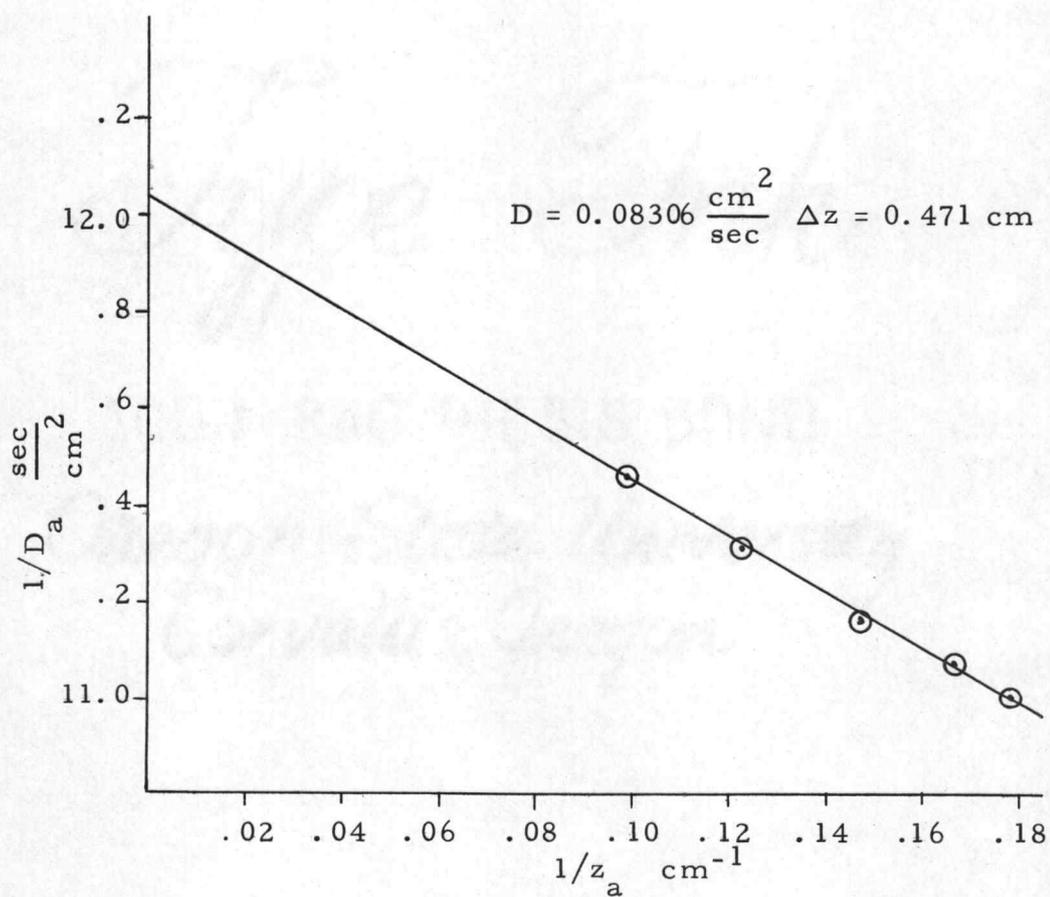
$T = 25.3^{\circ}\text{C}$ $P = 760\text{ mm Hg}$ 

FIGURE 9. RESULTS FOR CARBON TETRACHLORIDE IN AIR

T - 25.3°C P = 760 mm Hg

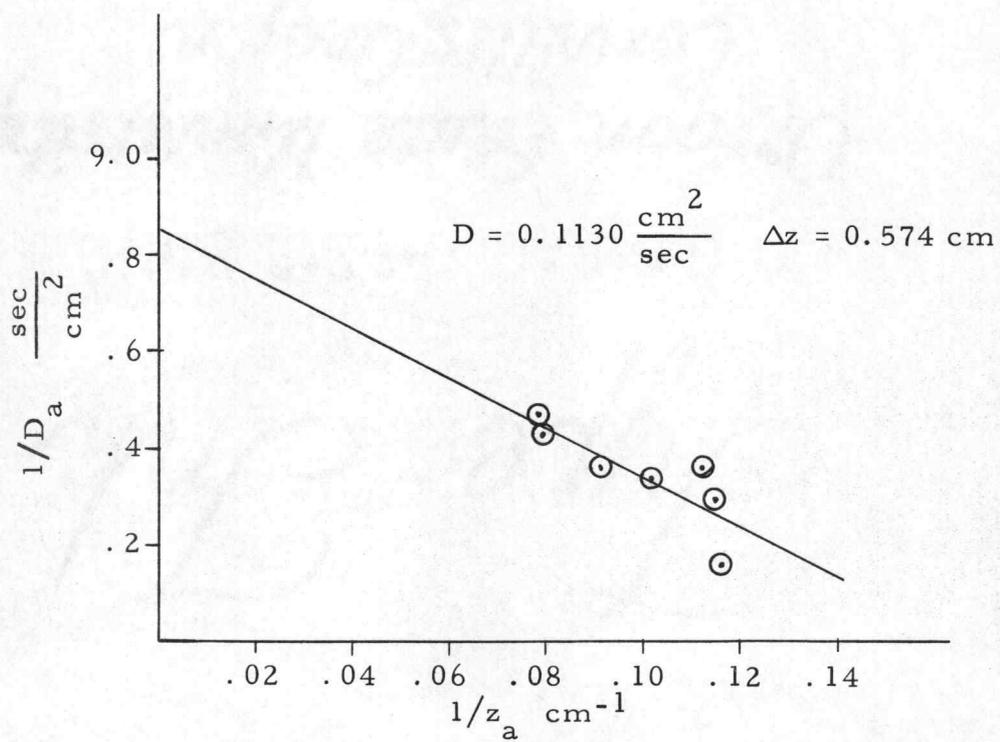


FIGURE 10. RESULTS FOR DICHLOROMETHANE IN AIR

T = 25.3°C P = 760 mm Hg

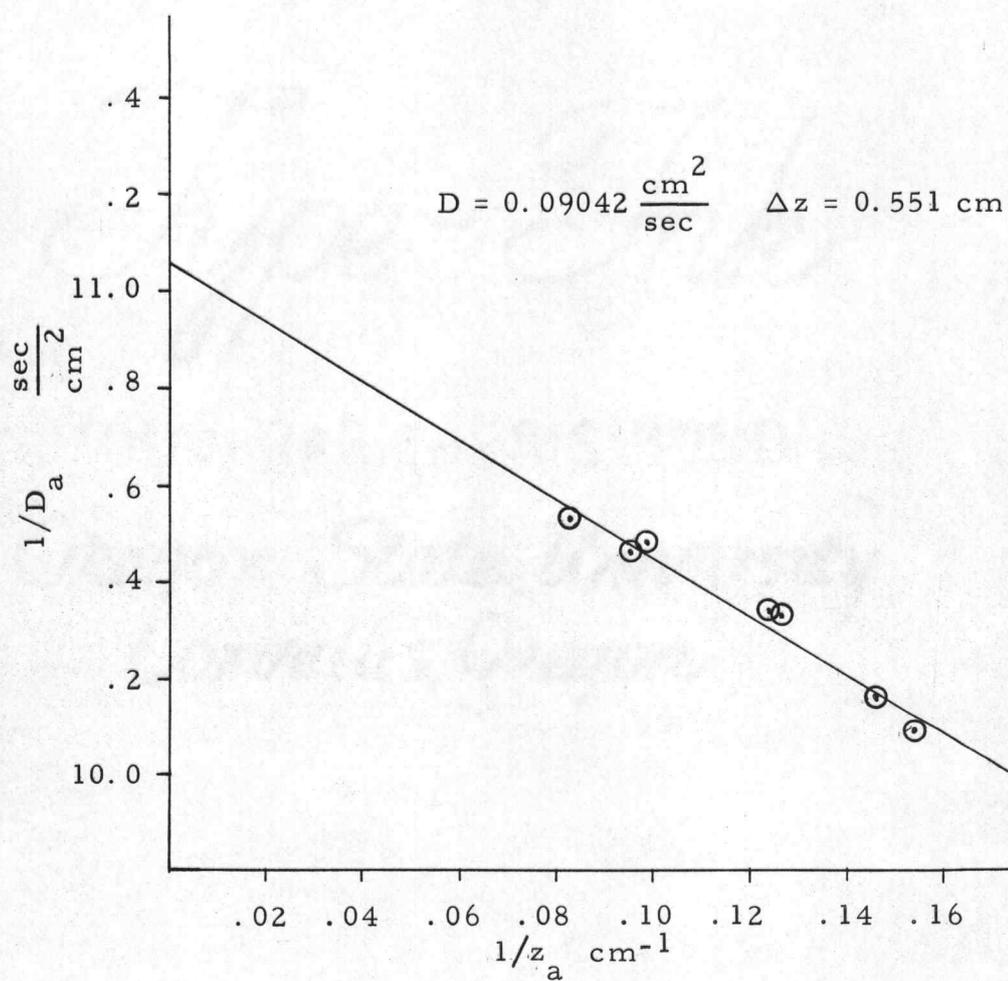


FIGURE 11. RESULTS OF CHLOROFORM IN AIR

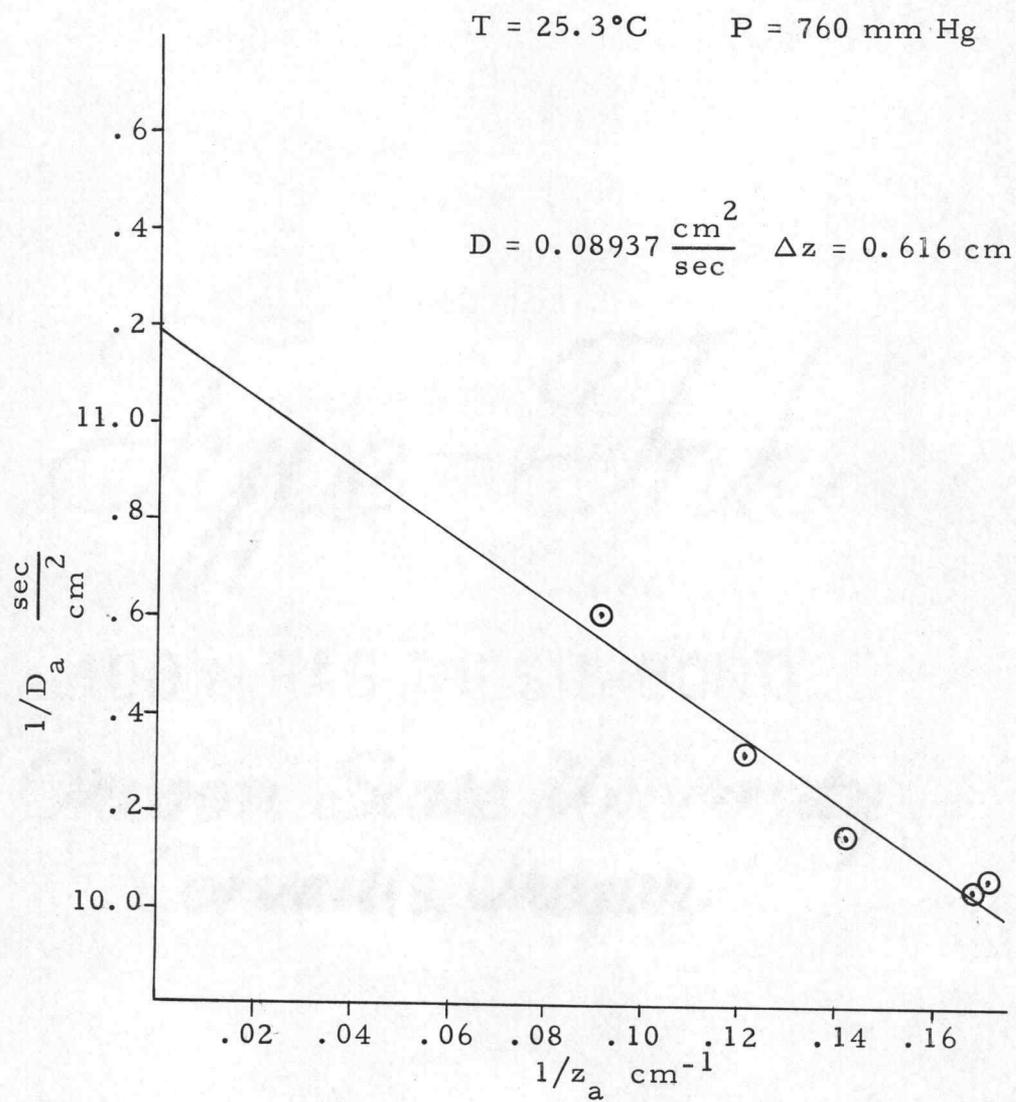


FIGURE 12. RESULTS FOR 1,2-DICHLOROETHANE IN AIR

The diffusion coefficient for each substance was calculated from the Hirshfelder, Bird and Spotz (10) equation and was compared with the experimental results. Collision integrals for the equation were obtained from Foust (7). The values obtained from the equation are listed in Table 1.

DISCUSSION OF RESULTS

To determine the reliability of the experimental apparatus and the experimental procedure, the diffusion coefficients of benzene and ethanol were determined. Several investigators have experimentally measured the diffusion coefficients of these substances. Wilke (17), Winkelmann (15) and Altshuller (1) have determined the diffusion coefficient of benzene in air and obtained $0.0962 \text{ cm}^2/\text{sec}$, $0.0915 \text{ cm}^2/\text{sec}$ and $0.0926 \text{ cm}^2/\text{sec}$, respectively. Winkelmann (15), Wilke (17) and Foust (7) have determined the diffusion coefficients for ethanol in air. They obtained $0.125 \text{ cm}^2/\text{sec}$, $0.135 \text{ cm}^2/\text{sec}$ and $0.119 \text{ cm}^2/\text{sec}$, respectively. The results that were obtained in this work were $0.0984 \text{ cm}^2/\text{sec}$ and $0.129 \text{ cm}^2/\text{sec}$ for benzene and ethanol, respectively.

The diffusion coefficient obtained for ethanol was 7.7 percent higher and 3.9 percent lower than the values obtained by Foust and Wilke, respectively. The average of the reported values for ethanol is $0.126 \text{ cm}^2/\text{sec}$ which is 2.3 percent lower than the results obtained in this work.

The diffusion coefficient of benzene was higher than those obtained by the other investigators. The diffusion coefficient was 2.2 percent higher than that obtained by Wilke (17) and 8.1 percent higher than that obtained by Winkelmann (15). The

experimental value was 5.0 percent higher than the average of the reported values. However, the results that were obtained for the two different flow rates agreed within 0.2 percent. The close precision of the results of this work and the disagreement of the diffusion coefficient with other investigators would indicate possibly that this particular cell gives results which are in error by a constant factor.

Errors in such measurements as the area of the diffusion tube or the determination of the vapor pressure would cause the results to be off by a constant factor. If the error was in the measurement of the area of the diffusion tube, one would expect the result that was obtained for ethanol to also be higher than the other experimental values. However, the diffusion coefficient for ethanol was between those of the other investigators and was only 2.3 percent higher than the average of the reported values. This would tend to discount the possibility that an error was made in determining the area of the tube. If one investigator used a different vapor pressure than did another, the two diffusion coefficients would not be in agreement. The vapor pressure of benzene used in this work was identical to that used by Wilke (17), and the diffusion coefficient obtained in this work was within 2.2 percent of Wilke's value. The vapor pressure used by Winkelmann (15) could not be determined.

Due to the fact that the diffusion coefficient of ethanol fell between the results of the other investigators, and the fact that Wilke's result for benzene was only 2.2 percent lower than the diffusion coefficient obtained in this work, it is felt that the other experimental results reported in this work should be within about three percent of the actual value.

The corrections to the diffusion path length were calculated and are shown in Table 1. There seems to be no correlation between these corrections and the vapor pressure of the liquid as was indicated by Wilke (17). Similarly, Altshuller (1) could find no relation between these corrections and the vapor pressure of the liquid. For benzene, where two different air flow rates were used, the correction was larger at the higher flow rate. This would be expected due to the increase in the size of the eddies caused by the higher air flow rate.

The apparent diffusion path length can be obtained by two methods. The liquid level can be measured as described in the experimental procedure, or knowing the amount of liquid in the tube, it can be calculated. It was decided that the calculation method would give more consistent values for the diffusion coefficient because it eliminated the measurement of one experimental variable. The weight of the tube and its contents was needed in the determination of the evaporation rate, and it was the only experimentally measured

quantity required to calculate the height of the liquid level. The differences between the measured value and the calculated value were less than 0.06 cm in most cases. Due to the extrapolation method used in determining the diffusion coefficients, any error in using the measured value in place of the calculated value would be small.

The area of the tube was needed in the calculation of the diffusion coefficients. The area was determined by two different methods. In one method the volume of the tube was found by weighing the amount of water required to fill the tube and dividing this weight by the density of the water. This volume was then divided by the length of the diffusion tube to obtain the area of the tube. This method gave an area of 0.7073 cm^2 . In the second method the diameter of the tube was measured with a pair of vernier calipers and was found to be 0.373 inches. This gives an area of 0.705 cm^2 . It was decided to use the area obtained by method one because this area would be the average area for the length of the tube, whereas the second method would give the area only at the top of the tube.

It was of interest to investigate the possibility that the evaporation of the liquid lowers the surface temperature of the liquid.

When the liquid evaporates the heat of vaporization must be supplied by the liquid, and if the rate of heat transfer to the liquid from the constant temperature bath is not sufficient to supply this heat, the

liquid temperature will drop. A temperature gradient at the surface of the liquid could cause convection currents which would introduce an error in the diffusion coefficient measurement. Wilke (17) and Altshuller (1) have investigated the temperature lowering due to evaporation and have found that the effects are negligible. The cell that was used by Wilke was made of brass, and that used by Altshuller was made of glass. It is assumed that the cell used in this work, which was designed similar to the cell used by Wilke (17), would cause a negligible lowering of the temperature at the liquid surface.

The approach to steady state was developed in the section on theoretical considerations. Figure 2 shows the results obtained for the diffusion of carbon tetrachloride in air. Since carbon tetrachloride's diffusion coefficient is the lowest coefficient measured, its time to come to steady state would be the longest. The path length that was used in this calculation was ten centimeters. From Figure 2 it is seen that the cell reaches steady state rapidly, and that the evaporation rate is 96 percent of the steady state evaporation rate in eight minutes. Most of the experimental runs lasted between 11 and 12 hours, so it was a valid assumption to neglect the unsteady state portion of the run.

RECOMMENDATIONS FOR FUTURE WORK

An obvious extension of the present work would be to investigate the temperature dependence of the diffusion coefficient. The present apparatus could be used without any alteration except changing the setting on the temperature controller.

The effect of concentration on the diffusion coefficient could be studied if the concentration of the constituent being studied was different than zero at the top of the tube. If the inlet air was saturated at a temperature different than that of the diffusion cell with the vapor of the liquid being evaporated, the composition of the air passing across the top of the tube would be different than that at the liquid surface. By controlling the temperature at which the inlet air was saturated, the composition of the inlet air could be adjusted to any desired value.

As a further check of the reliability of the results of this work, the same substances could be run but with a different air flow rate. The results should agree with those obtained in this work. It would also be of interest to determine if there is an air flow rate at which the end effect correction would be negligible but still the concentration of the diffusing vapor at the top of the tube could be taken as zero.

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NOMENCLATURE

C	- concentration of gas mixture	moles/liter
C_1, C_2	- constants of integration	
D_{AB}	- diffusion coefficient of A through B	cm^2/sec
D_a	- apparent diffusion coefficient	cm^2/sec
L	- length of diffusion tube	cm
M_A	- molecular weight of A	
m	- slope of experimental curves	sec /cm
N_A	- diffusion flux of A	moles/sec. cm^2
N_B	- diffusion flux of B	moles/sec cm^2
P	- cell pressure	mm, Hg
P_{ATM}	- atmospheric pressure	mm, Hg
P_s	- vapor pressure of liquid	mm, Hg
p	- partial pressure of diffusing substance	mm, Hg
R	- gas constant	(mm Hg)(liter)/(mole)(°K)
S	- crosssectional area of diffusion tube	cm^2
T	- temperature	°K
W	- weight of empty diffusion tube	gm
W_A	- weight of A evaporated	gm
W_L	- weight of diffusion tube and liquid	gm
x_A	- mole fraction of A	

x_B	-	mole fraction of B	
z	-	distance along diffusion path length	cm
z_a	-	apparent diffusion path length	cm
z_1	-	z at bottom of diffusion tube	cm
z_2	-	z at top of diffusion tube	cm
Δz	-	correction due to the end effects	cm
α	-	p/P_s	
θ	-	diffusion time	sec
ρ_L	-	density of liquid	g/cm^3

APPENDIX

A. Calculations

Rearrangement of equation (18) gives

$$D_{AB} = \frac{N_A RT (z_2 - z_1)}{P \ln \frac{1 - x_{A2}}{1 - x_{A1}}} \quad (1a)$$

For the case where $x_{A2} = 0$ and expressing N_A in terms of the weight of liquid evaporated and the time of evaporation, equation (18) becomes

$$D_{AB} = \frac{W_A RT (z_2 - z_1)}{\theta SP M_A \ln \frac{P}{P - P_s}} \quad (2a)$$

Substituting for quantities that remain constant for all runs equation (2a) reduces to

$$\begin{aligned} D_{AB} &= \frac{(62.37 \frac{\text{mmHg} \cdot \ell}{\text{mole} \cdot \text{K}})(298.5 \text{K})(10^3 \frac{\text{cm}^3}{\ell}) W_A (z_2 - z_1)}{(.70713 \text{ cm}^2)(2.3026) M_A \theta P \log \frac{P}{P - P_s}} \\ &= (1.14340 \times 10^7) \frac{W_A (z_2 - z_1)}{M_A \theta P \log \frac{P}{P - P_s}} \quad (3a) \end{aligned}$$

The height of the liquid from the top of the tube can be calculated if the dimensions of the tube and the density of the liquid are known. The height of the liquid in the tube can be calculated from the following formula.

$$z = L - \frac{W_L - W}{S \rho_L} = 14.17 - \frac{(W_L - 33.41037)}{.70713 \rho_L} \quad (4a)$$

From equation (26) it is seen that the magnitude of the end effect correction can be calculated from the slope of the curves in Figures 7 through 12. The end effect correction equals

$$\Delta z = D_{AB} m \quad (5a)$$

Sample Calculation

Start: weight of tube + CCl_4 41.85933 gm

Finish: weight of tube + CCl_4 41.50039 gm

$W_A = 0.35894$ gm

$\theta = 38,520$ sec.

$(z_2 - z_1)_{\text{ave}}$ calculated 6.81 cm

$(z_2 - z_1)_{\text{ave}}$ measured 6.83 cm

$P = 767.2$ mm Hg

$M_A = 78.11$ gr/mole

$P_s = 96.5$ mm Hg

$$D_{AB} = \frac{(1.14340 \times 10^7)(0.34894)(6.81)}{(78.11)(38,520)(767.2) \log(767.2/654.2)}$$

$$D_{AB} = 0.08884 \text{ cm}^2/\text{sec}$$

Correcting D_{AB} to 760 mm Hg

$$D_{AB} @ 760 \text{ mm Hg, } 298.5^\circ\text{C} = \frac{(767.2)}{(760)}(0.08884) = 0.08964 \text{ cm}^2/\text{sec}$$

$$1/D_{AB} = 1/0.08964 = 11.156 \text{ sec}/\text{cm}^2$$

$$1/z_a = 1/6.81 = 0.1468 \text{ cm}^{-1}$$

TABLE 2. PHYSICAL PROPERTIES OF LIQUIDS

Compound	Molecular weight	Density 298 °k (gm/cm ³)	Vapor pressure at 298.5 °k (mm Hg)
Benzene	78.11	0.8715	96.5
CCl ₄	153.84	1.590	113
CHCl ₃	119.39	1.485	200
CH ₂ Cl ₂	84.94	1.330	420
1,2C ₂ H ₄ Cl ₂	98.97	1.250	84.0
C ₂ H ₅ OH	46.07	0.7840	57.7

The vapor pressure data were obtained from Jordan (11) and the Handbook of Chemistry and Physics (9) and are shown in Figure 13. The vapor pressure of benzene was calculated from a formula given in the Handbook of Chemistry and Physics (9, p. 2423).

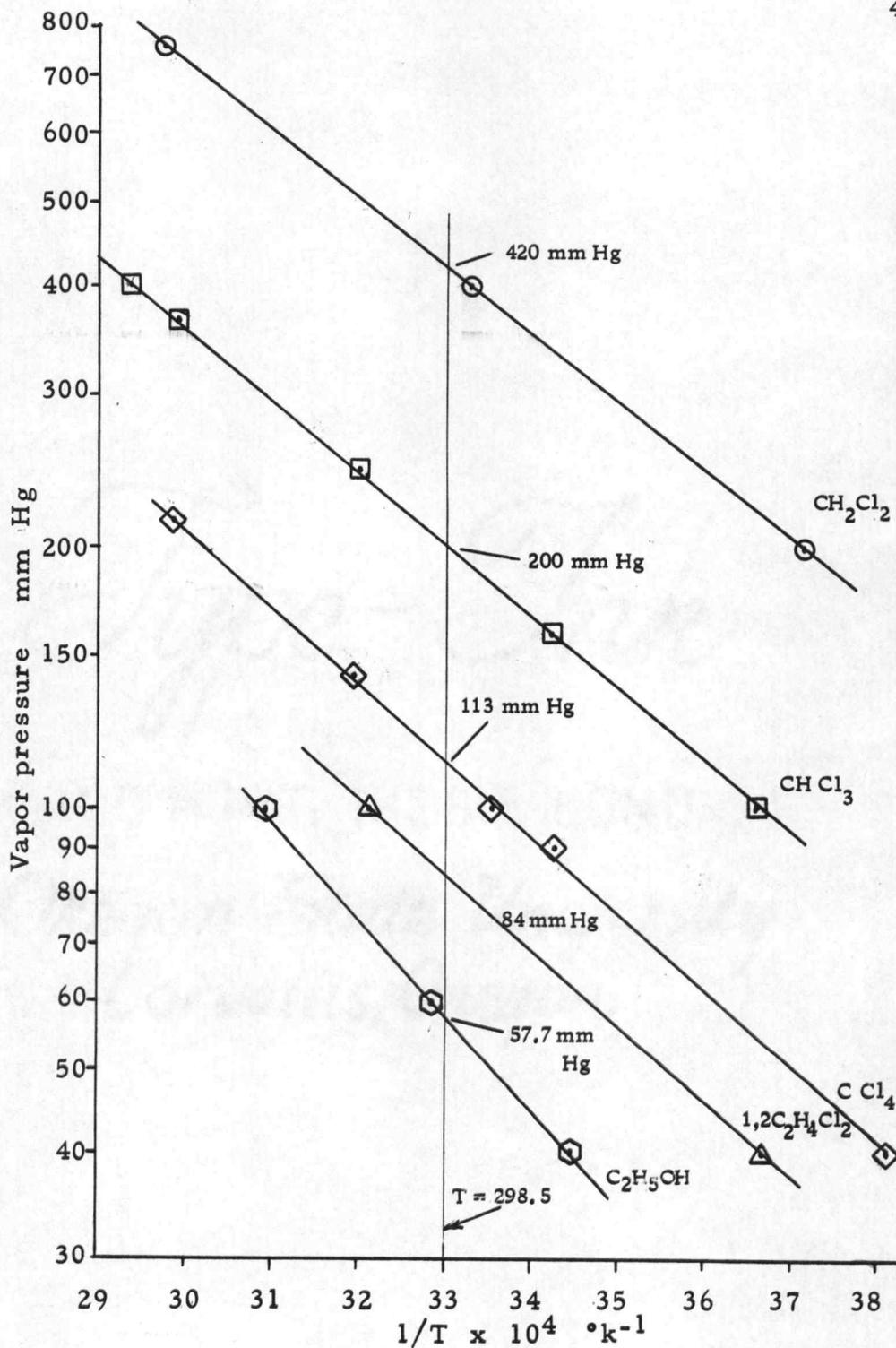


FIGURE 13. VAPOR PRESSURE DATA

TABLE 3. EXPERIMENTAL DATA

Run Number	Weight lost by diffusion tube gm.	Diffusion time sec.	Average path diffusion length		Cell pressure in. H ₂ O gage	Atmospheric pressure mm Hg	Apparent diffusion coefficient cm ² /sec.
			Calculated cm.	Measured cm.			
BENZENE AIR FLOW RATE 0.14 ft ³ /min. T = 298.5°K							
1	0.16255	25,980	5.22	5.28	3.80	754.0	0.1074
2	0.19807	33,345	5.45	5.56	2.80	766.8	0.1080
3	0.18330	40,440	7.02	7.12	2.80	764.5	0.1055
4	0.14862	40,110	8.57	8.47	2.90	761.0	0.1038
5	0.19069	43,500	7.26	7.33	2.80	762.2	0.1054
BENZENE AIR FLOW RATE 0.095 ft ³ /min. T = 298.5°K							
6	0.14046	45,960	10.31	10.38	3.10	746.9	0.1022
7	0.18516	36,000	6.22	6.32	3.00	754.9	0.1050
8	0.17715	46,440	8.22	8.27	3.00	751.6	0.1026
9	0.12872	34,440	8.46	8.55	3.00	748.4	0.1028
10	0.18098	39,600	6.92	6.99	3.00	750.8	0.1032
C ₂ H ₅ OH AIR FLOW RATE 0.14 ft ³ /min. T = 298.5°K							
11	0.09000	41,280	6.97	7.00	3.10	754.8	0.1449
12	0.15595	46,800	4.84	4.89	3.00	752.9	0.1532
13	0.09971	38,400	6.03	6.09	3.10	756.1	0.1493
14	0.12202	43,350	5.52	5.55	3.10	762.1	0.1495
15	0.07549	37,740	7.56	7.61	3.00	766.4	0.1464
16	0.09804	43,920	6.80	6.83	3.05	766.5	0.1449
C Cl ₄ AIR FLOW RATE 0.14 ft ³ /min. T = 298.5°K							
17	0.38564	36,240	6.01	6.04	2.90	761.6	0.09035
18	0.35705	46,380	8.15	8.16	2.90	759.7	0.08841
19	0.26011	42,540	10.09	10.10	2.85	762.2	0.08724
20	0.35894	38,520	6.81	6.83	3.00	761.7	0.08964
21	0.46144	40,140	5.61	5.63	2.90	766.2	0.09101
CH ₂ Cl ₂ AIR FLOW RATE 0.14 ft ³ /min. T = 298.5°K							
22	1.09484	41,820	8.93	8.93	2.90	759.0	0.1196
23	0.90505	43,440	11.23	11.27	2.90	758.4	0.1196
24	0.74377	40,440	12.66	12.68	3.00	757.5	0.1186
25	0.74330	40,500	12.69	12.68	2.90	754.5	0.1181
26	0.92105	37,860	9.83	--	2.90	749.3	0.1199
27	1.20333	42,240	8.60	8.60	3.00	747.7	0.1225
28	0.99143	36,600	8.73	8.73	2.85	758.0	0.1207

CHCl₃ AIR FLOW RATE 0.14 ft³/min. T = 298.5° K

29	0.36439	44,040	12.01	12.03	2.85	758.2	0.09496
30	0.38310	40,080	10.54	10.62	2.80	754.7	0.09564
31	0.62602	41,820	6.87	6.88	2.80	759.6	0.09840
32	0.59057	46,680	7.96	7.97	2.80	762.3	0.09680
33	0.58594	36,780	6.48	6.45	2.80	761.4	0.09824
34	0.53999	43,200	8.09	8.09	2.80	759.3	0.09675
35	0.37950	38,610	10.15	10.17	2.80	759.5	0.09852

1,2 C₂H₄Cl₂ AIR FLOW RATE 0.14 ft³/min T = 298.5° K

36	0.15879	40,350	8.26	8.30	2.90	752.9	0.09692
37	0.17725	38,160	7.06	7.09	2.90	758.7	0.09852
38	0.22944	41,100	5.94	5.97	2.90	758.2	0.09965
39	0.12260	42,150	10.94	10.95	2.85	748.2	0.09422
40	0.23795	41,640	5.84	5.86	2.85	752.5	0.09942
