

AN ABSTRACT OF THE THESIS OF

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Title: DIFFUSION COEFFICIENTS OF PROPANOL AND METHANOL  
IN MIXTURES OF AIR AND ARGON

Abstract approved: Redacted for privacy  
Dr. C. E. Wicks

By an Arnold cell technique, the diffusion coefficients of propanol and methanol in mixtures of air and argon system have been determined. The carbon tetrachloride-air system was also studied to verify the reproducibility of the experimental method.

The diffusion coefficients were compared with experimental values when available and with values evaluated from empirical equations. Comparison between the empirical and experimental data was found to be reasonably good. The diffusion coefficients were measured at 760 mm and 25° C except for the propanol-air-argon system which was measured at 45° C.

Diffusion Coefficients of Propanol and  
Methanol in Mixtures of Air and Argon

by

Dong Suk Kim

A THESIS

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Professor of Chemical Engineering

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Head of Department of Chemical Engineering

Redacted for privacy

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Dean of Graduate School

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## TABLE OF CONTENTS

INTRODUCTION	1
THEORETICAL APPROACH TO STEADY STATE MOLECULAR DIFFUSION	3
A. Development of Equation	3
B. Correction for End Effect	8
C. Time Necessary to Establish Steady State	9
DESCRIPTION OF APPARATUS	12
EXPERIMENTAL METHOD	17
DISCUSSION OF RESULTS	19
A. Experimental Data	19
B. Comparison of Results	19
C. Possible Sources of Experimental Error	29
BIBLIOGRAPHY	31
APPENDIX I. Determination of Gas Flow Rate	33
APPENDIX II. Sample Calculations	36
APPENDIX III. Physical Properties of Substances	41
APPENDIX IV. List of Experimental Data	43
APPENDIX V. Nomenclature	46

## LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Arnold diffusion cell.	4
2	Apparent diffusion path.	8
3	Time required for steady state.	11
4	Flow diagram of experimental apparatus.	13
5	Cross section of diffusion cell.	14
6	Plot for carbon tetrachloride in air (A).	20
7	Plot for carbon tetrachloride in air (B).	21
8	Plots for carbon tetrachloride in air (A and B).	22
9	Plot for propanol in air.	23
10	Plot for propanol in argon.	24
11	Plot for propanol in mixtures of air and argon.	25
12	Plot for methanol in mixtures of air and argon.	26
13	Calibration curves (A).	34
14	Calibration curves (B).	35
15	Vapor pressure data.	42

## LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Comparison of experimental data.	27
2	Physical properties of substances.	41
3	List of experimental data.	43

# DIFFUSION COEFFICIENTS OF PROPANOL AND METHANOL IN MIXTURES OF AIR AND ARGON

## INTRODUCTION

The importance of diffusion of gases in chemical engineering is well known. With growing demands for the description of these process and with current advances in diffusional operations, there has been an increasing need for accurate gas-phase diffusion coefficients. In view of the scarcity of reliable information, one must rely upon empirical correlations or else obtain additional experimental values. This investigation, therefore, presents the experimental method and results for gas-phase diffusivities. A study of diffusion coefficient measurements is essential in order to predict and understand the phenomena which occur in the system.

Measurements were made for the following systems:

- (1)  $\text{CCl}_4$  - air
- (2) propanol - air
- (3) propanol - argon
- (4) propanol - mixture of air and argon (1:2)
- (5) methanol - mixture of air and argon (1:1)

From the theoretical view points, the diffusion coefficient is defined as the proportionality constant in the Fick's rate equation. It is known that in general the mass diffusivity is a function of temperature,

pressure and composition of the system. But the diffusion coefficients of gases at low pressure are essentially independent of composition. On the other hand liquid and solid diffusivities are strongly concentration dependent. For a gas system the diffusion coefficient is a function of temperature, pressure, molecular weight of each substance, intermolecular forces and concentration of the system (16). Since the literature values on the diffusion coefficients are limited in range and accuracy, an effort to measure the diffusivities experimentally has been made by many other investigators (1, 7, 10, 11, 12, 13, 18).

The diffusion cell used in this work was described by Wilke and Lee (12) and modified by Larson (11). Many previous workers had used this Arnold-type cell for the measurement of the mass diffusivities of gases. The cell contains a tube of constant diameter which is partially filled with liquid. Vapors from the liquid diffuses toward the gas stream through the open end of the tube.

In this work weight measurements were used. By measuring the rate of evaporation, diffusion coefficients were easily determined. The experiments were carried out with a constant gas flow rate and at 25° C and 1 atmosphere pressure. The results were compared with values evaluated by empirical equations since the values had not been previously measured.

## THEORETICAL APPROACH TO STEADY-STATE MOLECULAR DIFFUSION

### A. Development of Equation

In a binary system, the governing phenomena of molecular diffusion may be described by Fick's first law

$$N_{Az} = -CD_{AB} \nabla X_A + X_A (N_{Az} + N_{Bz}) \quad (1)$$

The symbols used in all of the developed equations are defined in the nomenclature section. The above equation relates the molar flux relative to stationary coordinate in space to the concentration gradient.

Considering the diffusion system in Figure (1), liquid A is evaporating into gas B. Consider the control volume  $S\Delta z$ , where  $S$  is the uniform cross-sectional area of the tube. A mass balance for component A yields

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

Dividing through by the volume  $S\Delta z$  and letting  $\Delta z$  approach zero gives

$$\frac{d}{dz} N_{Az} = 0 \quad (3)$$

For component B the result should be the same. Equation (3) shows that molar flux of A must be constant for all values of diffusion path from  $z_1$  to  $z_2$ .

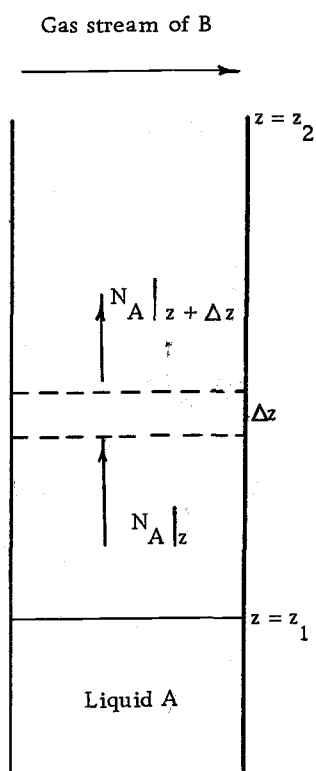


Figure 1. Arnold diffusion cell.

That is,

$$N_{Az} \Big|_z = \text{constant}$$

Accordingly,  $N_{Bz}$  is also constant.

At this stage two restrictions will be employed. Gas B will have a negligible solubility in liquid A. Therefore, at the gas-liquid interface ( $z=z_1$ ), the molar flux of the component B is zero, and  $N_{Bz}$  is zero throughout the diffusion path. Using the expression for  $N_{Az}$  given in Equation (1) with  $N_{Bz} = 0$  gives

$$N_{Az} = -\frac{CD_{AB}}{1-X_A} \frac{dX_A}{dz} \quad (5)$$

If the gases are ideal and the system is held at constant temperature and pressure, the concentration is constant, and  $D_{AB}$  is nearly independent of concentration.

$$\frac{P}{RT} = \frac{n}{V} = C \text{ (constant)} \quad (6)$$

where C is the gas phase concentration of component A.

Equation (5) can be integrated between the two boundary conditions:

$$\text{B. C. 1:} \quad \text{at } z=z_1 \quad X_A = X_{A1}$$

$$\text{B. C. 2:} \quad \text{at } z=z_2 \quad X_A = X_{A2}$$

By integrating Equation (5)

$$N_{Az} \int_{z_1}^{z_2} dz = - CD_{AB} \int_{X_{A1}}^{X_{A2}} \frac{dX_A}{1-X_A} \quad (7)$$

Solving for  $N_{Az}$

$$N_{Az} = \frac{CD_{AB}}{z_2 - z_1} \ln \frac{(1-X_{A2})}{(1-X_{A1})} \quad (8)$$

By Equation (6)

$$N_{Az} = \frac{PD_{AB}}{RT(z_2 - z_1)} \ln \frac{(1-X_{A2})}{(1-X_{A1})} \quad (9)$$

Assumptions employed in derivation of Equation (9) are as follows:

1. Negligible solubility of carrier gas
2. Gases are ideal
3. The system is held at isobaric and isothermal condition
4.  $D_{AB}$  is nearly independent of concentration
5. The liquid level remains constant during evaporation
6. Steady state conditions.

Actually the diffusion path length is not constant during the period of diffusion, since vaporization occurs. According to Wilke and Lee (12), the diffusion path length may be taken as the arithmetic average between the initial and final values under the quasi-steady state condition.

Hence:

$$N_A = \frac{W_A}{M_A \theta S} \quad (10)$$

$$z = \frac{z_0 + z_\theta}{2} \quad (11)$$

The assumption of quasi-steady state condition involves negligible error at atmospheric pressure if the change in liquid level with time is very small (12).

Rearrangement of Equation (9) gives

$$D_{AB} = \frac{W_A RT z}{M_A \theta SP \ln \frac{(1-X_{A2})}{(1-X_{A1})}} \quad (12)$$

Recalling that the gas flow rate should be large enough to keep the partial pressure of the vapor to be zero and low enough to prevent turbulence at the mouth of the tube give the following restrictions:

1.  $X_{A2} = 0$
2. viscous flow, i. e., the velocity distribution must be parabolic.

Accordingly, Equation (12) becomes

$$D_{AB} = \frac{W_A RT z}{M_A \theta SP \ln \frac{P}{P-P_{AS}}} \quad (13)$$

The expression for diffusion coefficient can be derived in terms of physically measurable quantities.

## B. Correction for End Effects

The end effects at the mouth of the tube and at the interface must be examined. Turbulence at the top of the tube and surface tension of the liquid affect the effective diffusion path length. There must be a small difference between the diffusion path lengths, since the liquid surface in the tube is curved downward. Eddies also reduce the effective diffusion path length by extending the region of vapor-free gas into the tube.

Considering the physical situation of the tube, two different lengths should be defined, the ideal and actual. Figure (2) shows the two cases.

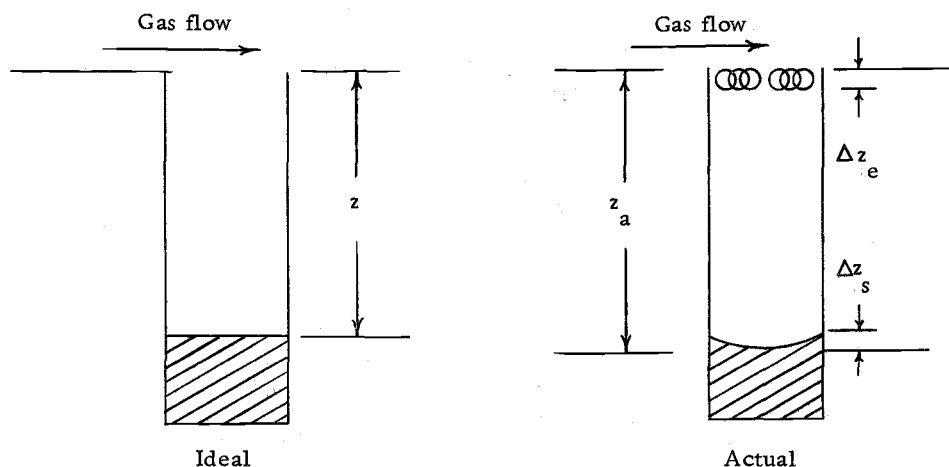


Figure 2. Apparent diffusion path.

In the above figure, the effective average diffusion length is given by (12).

$$z = z_a - \Delta z_s - \Delta z_e = z_a - \Delta z \quad (14)$$

The rate of evaporation of A may then be expressed as:

$$N_{Az} = \frac{PD_a}{RTz_a} \ln \frac{(1-X_{A2})}{(1-X_{A1})} = \frac{PD_{AB}}{RT(z_a - \Delta z)} \ln \frac{(1-X_{A2})}{(1-X_{A1})} \quad (15)$$

Eliminating common factors from Equation (15) gives

$$\frac{D_a}{z_a} = \frac{D_{AB}}{z_a - \Delta z} \quad (16)$$

Rearranging Equation (16) yields

$$\frac{1}{D_a} = -\frac{\Delta z}{D_{AB}} \frac{1}{z_a} + \frac{1}{D_{AB}} \quad (17)$$

Equation (17) can be interpreted as a linear equation with respect to  $1/z_a$ , and indicates that a plot of  $1/D_a$  versus  $1/z_a$  should be a straight line with a slope of  $-\Delta z/D_{AB}$  and an intercept of  $1/D_{AB}$ .

The correction for the end effects,  $\Delta z$ , may be calculated from the slope of the line.

### C. Time Necessary to Establish Steady State

If the diffusion tube is stoppered, the gas phase in the tube is initially saturated with the liquid vapor at partial pressure  $P'_A$ . To

deal with this kind of unsteady state system, one can select Fick's second law which describes unsteady state diffusion process.

$$\frac{\partial P_A}{\partial \theta} = D_{AB} \frac{\partial^2 P_A}{\partial z^2} \quad (18)$$

This equation must satisfy the boundary conditions:

$$\begin{aligned} \text{I. C.:} \quad & P_A = P'_A \quad \text{at } \theta=0 \quad \text{for all } z \\ \text{B. C. (1):} \quad & P_A = P'_A \quad \text{at } z=z_1 \quad \text{for all } \theta \\ \text{B. C. (2):} \quad & P_A = 0 \quad \text{at } z=z_2 \quad \text{for all } \theta > 0 \end{aligned}$$

The solution of Equation (18) is shown by Carslaw (6).

Wilke and Lee (12) have arrived at the following expression which describes the ratio of evaporation rate at any time  $\theta$  to that at steady state, i. e.,  $\theta = \infty$ .

$$\frac{(N_A)_{\theta=\theta}}{(N_A)_{\theta=\infty}} = 1 - 2e^{\frac{-D\pi^2\theta}{z^2}} + 2e^{\frac{-4D\pi^2\theta}{z^2}} - 2e^{\frac{-9D\pi^2\theta}{z^2}} + \dots \quad (19)$$

By the application of Equation (19), one can draw a curve for propanol-air system with  $z=10\text{cm}$ , and  $D_{AB}=0.10704 \text{ cm}^2/\text{sec}$ . The plot shows that the time required for steady state is less than 15 minutes. Fifteen minutes is only 3% of the total running period of ten hours. It may therefore be concluded that the assumption of steady state for the entire operation is a reasonable one.

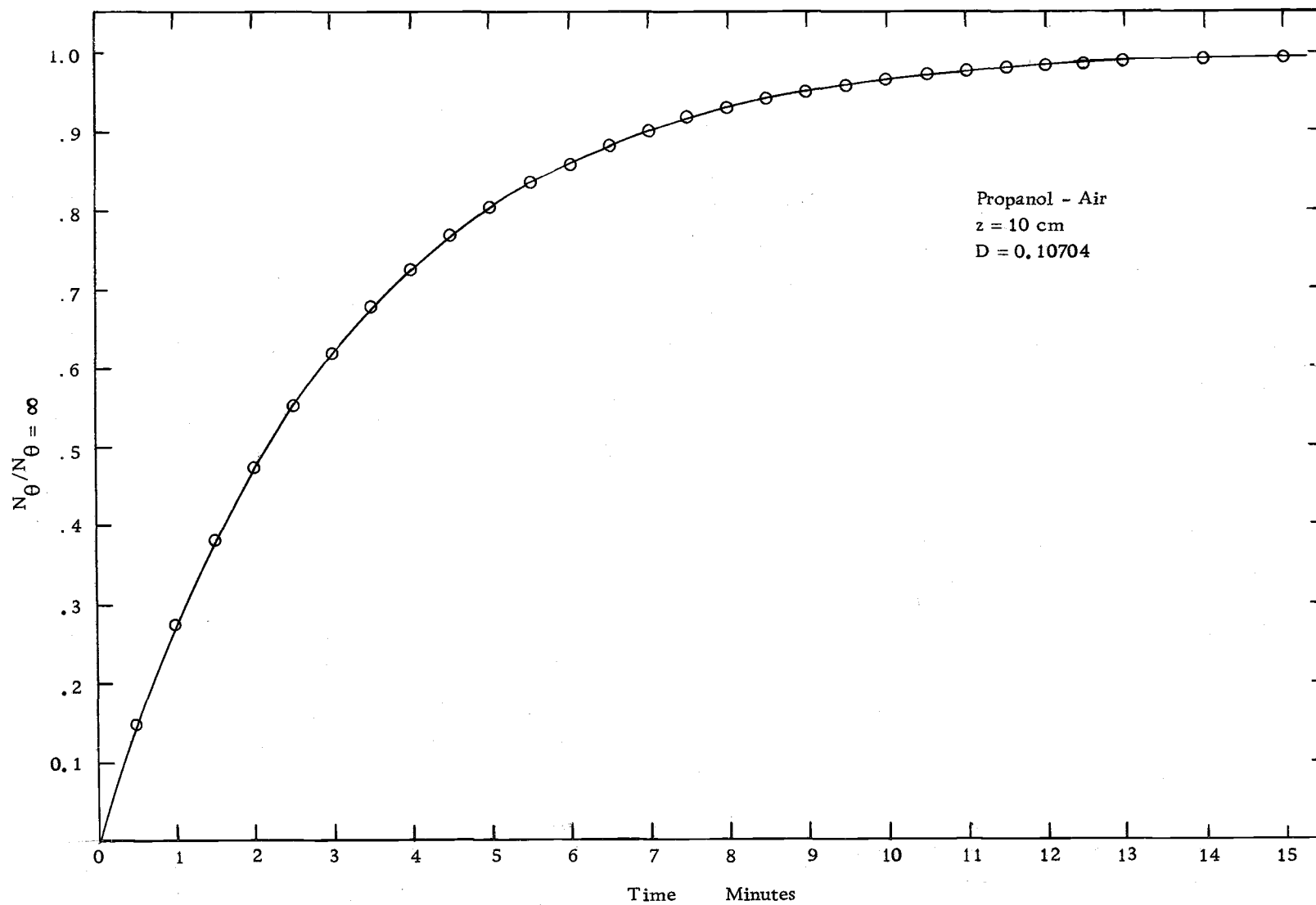


Figure 3. Time required for steady state.

## DESCRIPTION OF APPARATUS

The apparatus used in this work was essentially the same apparatus constructed by Larson (11). It consisted of a diffusion cell, a constant temperature bath in which the diffusion cell was placed, a refrigeration unit, a gas drying tower, a manometer, three pressure regulators, three rotameters and a stirrer. A flow diagram of the apparatus is shown in Figure (4) and a sketch of the diffusion cell is presented in Figure (5).

The removable diffusion assembly except for the diffusion tube, was constructed out of brass. The stainless steel diffusion tube was 14.28 centimeters in length, and 0.94 centimeters in diameter. The cross-sectional area was evaluated by measuring the volume of water at room temperature which was needed to fill the tube. This volume divided by the measured length gave the cross-sectional area. In general, it should be noted that one must have a large enough diameter to obtain a conveniently weighable evaporation rate. In order to obtain good heat transfer into the system from the constant temperature bath, the stainless steel tube was constructed so that it fitted tightly against the diffusion assembly. A bundle of 1/8-inch copper tubes was placed in the 3/4-inch inlet pipe of the diffusion cell to reduce disturbance of the gas stream due to the sudden enlargement of the flow path. A forty-foot length of 1/8-inch copper tubing was connected

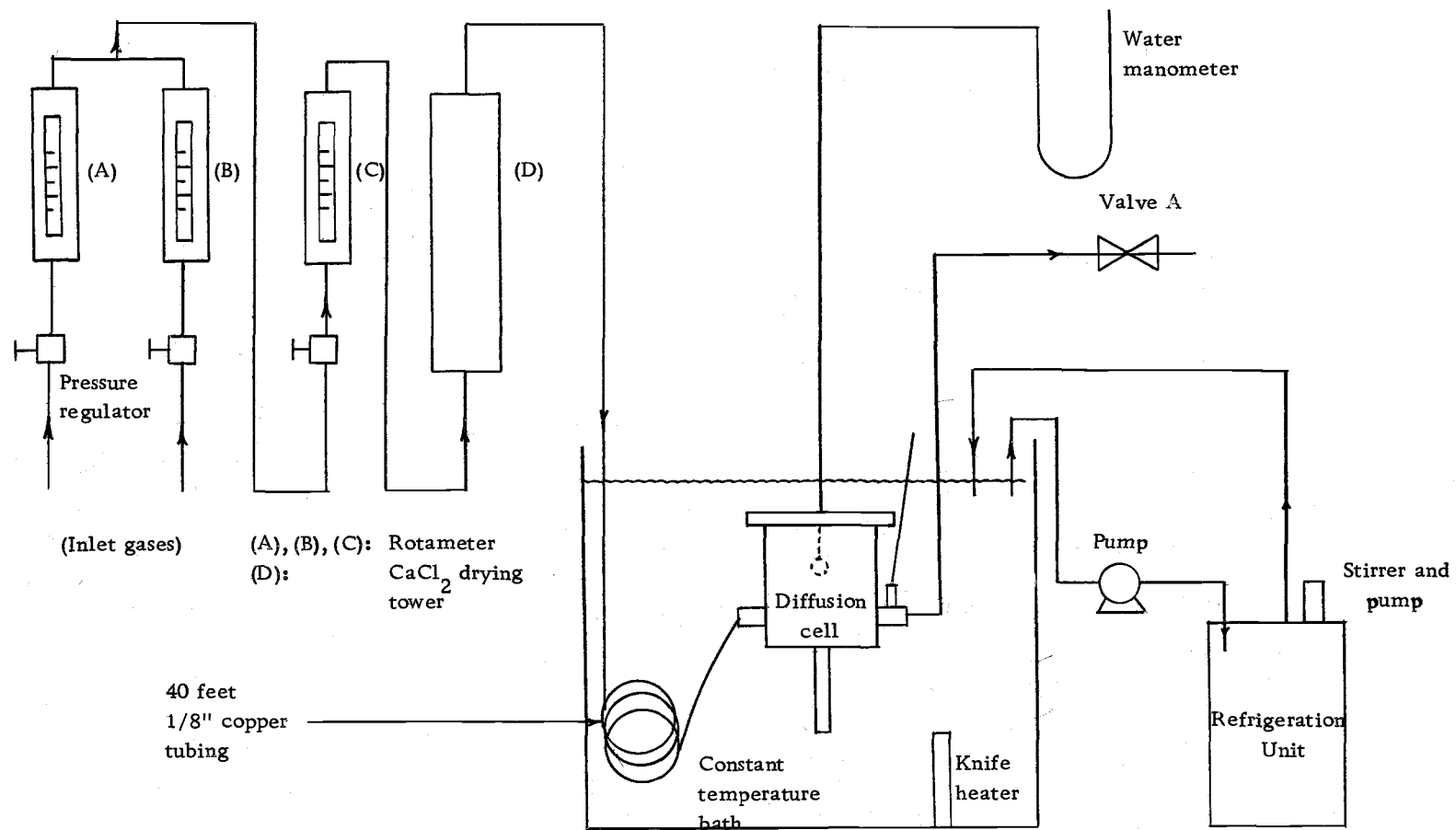


Figure 4. Schematic flow diagram of experimental apparatus.

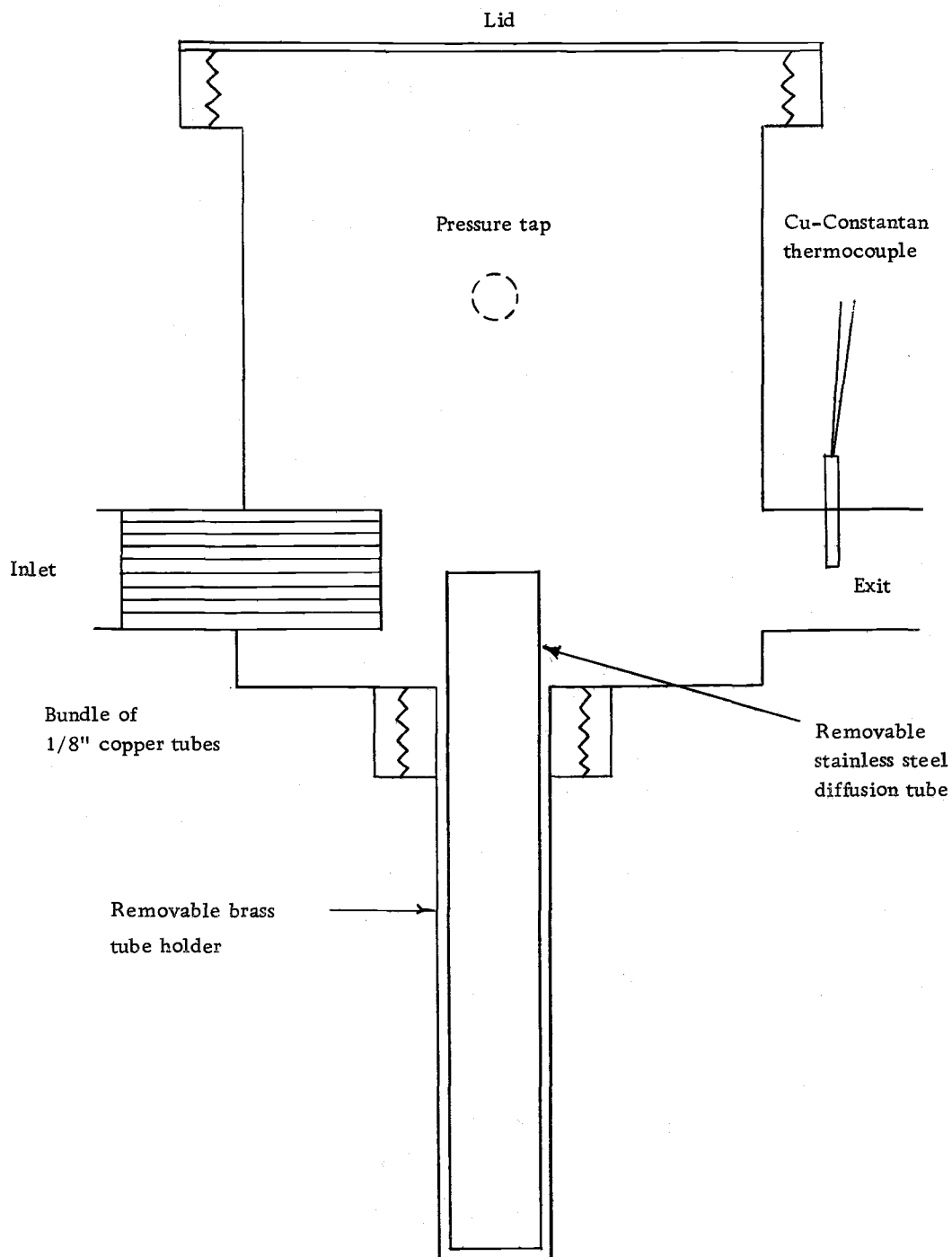


Figure 5. Cross section of diffusion cell.

to the entrance of the diffusion cell. The tubing immersed in the constant temperature bath brought the entering gas to the bath temperature. On the exit of the cell, a copper-constantan thermocouple was provided to indicate the temperature of the gases. A pressure tap was constructed in the top of the diffusion cell and a water manometer was connected to the pressure tap for measuring the pressure within the cell.

The moisture from the gases that might enter the cell was dried by virtue of the drying tower. This tower was made of  $1\frac{1}{2}$ -inch standard pipe, 16 inches long. It was filled three-quarters full with eight-mesh anhydrous calcium chloride and one-quarter full with glass wool. The glass wool was used to remove any oil drops that might come into the system.

Three rotameters were employed for determining the accurate flow rate of the gases. The rotameters were calibrated by using a wet-test meter.

The constant temperature bath, a stainless steel tank, was 18 inches in diameter and 22 inches deep. The tank was insulated with glass wool. A knife heater was used to heat the water in the tank. The temperature of the bath was controlled by a thermotrol unit. The temperature controller used was a Thermotrol Model 1053 A. The controller was reported to be accurate to  $\pm 0.002^{\circ}\text{C}$ .

The refrigerating unit was to be employed when considerable heat was transferred into the bath from the atmosphere. The low room temperatures made the use of the refrigerating unit unnecessary.

The pressure in the cell could be controlled by valve A.

To remove vibration of the diffusion cell, the stirrer for the water bath was mounted independently on the concrete floor.

An insulation box, in which the diffusion tube fitted tightly, was prepared to prevent heat transfer to the system from the atmosphere while moving the tube. The small box was constructed out of plastic and contained glass wool in it.

## EXPERIMENTAL METHOD

Diffusion coefficient were determined by measuring the rate of evaporation of a liquid into a gas stream. The experimental procedure fell into four basic parts:

1. weighing the empty diffusion tube
2. weighing the diffusion tube while containing the liquid before and after a run
3. keeping a constant gas flow rate and temperature
4. preparation of gas mixtures

Initially, the tube was rinsed with acetone several times and then dried in the room temperature. It was also rinsed with the liquid which was to be used and then partially filled with the liquid. Any unwanted liquid drops on the wall could be removed by a vacuum line from the laboratory. The vacuum line was put into the tube to about one centimeter from the liquid surface.

The diffusion tube was then stoppered and weighed on a balance. The balance was accurate to  $\pm 0.01$  milligrams. The time was recorded just after the stopper was removed. The tube was inserted into the tube holder and then the lid was replaced.

Gas flow rate, atmospheric pressure, pressure in the cell, the temperature of the bath, room temperature and pressure at the entrance of the rotameter were all recorded immediately after

immersing the diffusion cell into the constant temperature bath. The length of the time for each run varied between 10 and 12 hours. All readings were continually checked during the run.

For the following run, the tube was rinsed with acetone and dried. The tube was then filled to a different desired liquid level.

For the propanol-mixtures of air and argon system the temperature of the diffusion cell was raised to  $45^{\circ}\text{C}$  because propanol has too low vapor pressure at  $25^{\circ}\text{C}$  to get a good evaporation rate. By raising the temperature of the system or reducing the pressure of the diffusion cell one would expect an increase in the evaporation rate. The result was scaled to the same temperature,  $25^{\circ}\text{C}$ , by applying a  $3/2$  power temperature dependency as expressed in the Hirschfelder equation (9).

The method adopted for preparation of gas mixtures and calibration of rotameters are presented in the Appendix.

## DISCUSSION OF RESULTS

### A. Experimental Data

Equation (17),  $1/D_A = - \Delta z/D_{AB} z_a + 1/D_{AB}$ , gives a straight line when  $1/D_a$  versus  $1/z_a$  are plotted for various lengths of apparent diffusion path. The plots are shown in Figure (6) through Figure (12). The true diffusion coefficients were obtained from the intersection of these curves with the  $1/D_a$  axis. These curves were drawn by applying the least squares analysis to the experimental data. The values of the diffusion coefficients determined experimentally are listed in Table (1). Table (1) also gives the corrections to the diffusion path length, which can be calculated from the curves.

### B. Comparison of Results

The experimental results were compared with the values calculated from empirical equations. It is well known that the empirical calculation depends on the method used to compute the force constants between molecules. These force constants can be computed from experimental gas viscosity data and also from the critical properties. The equation of Hirshfelder, Bird and Spotz and Wilke and Lee (22) use the force constants, collision diameter and collision integral. Reid and Sherwood (17) compared experimental values with values obtained from empirical equations. The comparison showed that the

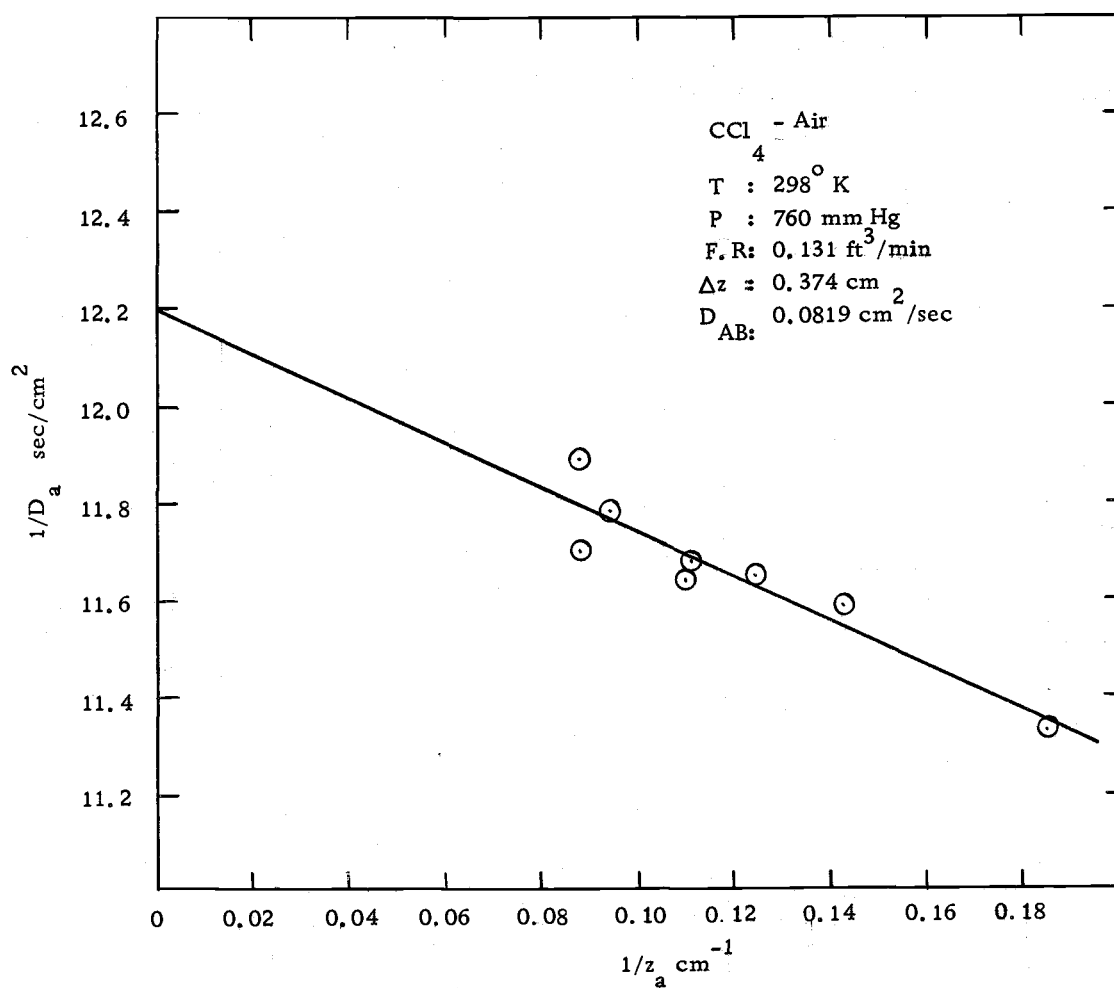


Figure 6. Plot for carbon tetrachloride in air.

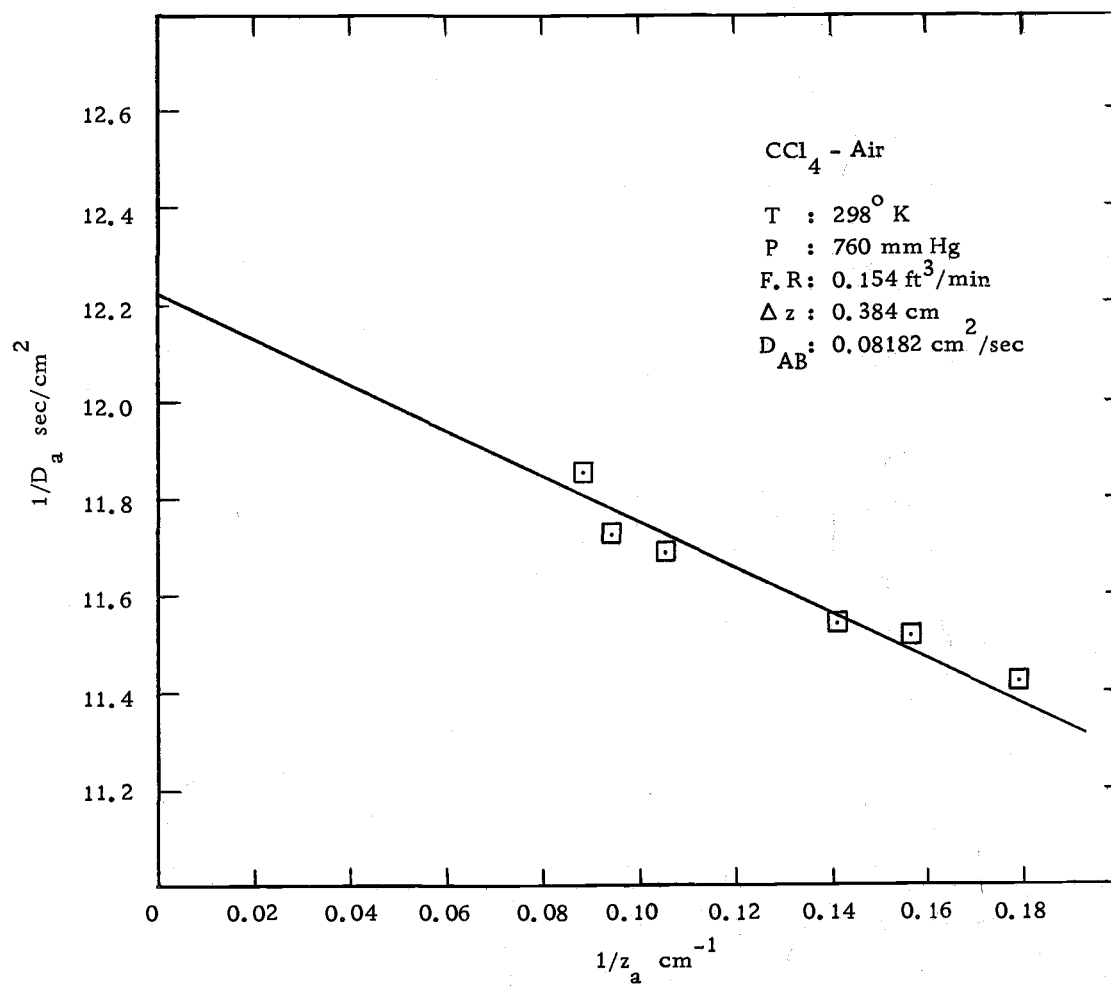


Figure 7. Plot for carbon tetrachloride in air.

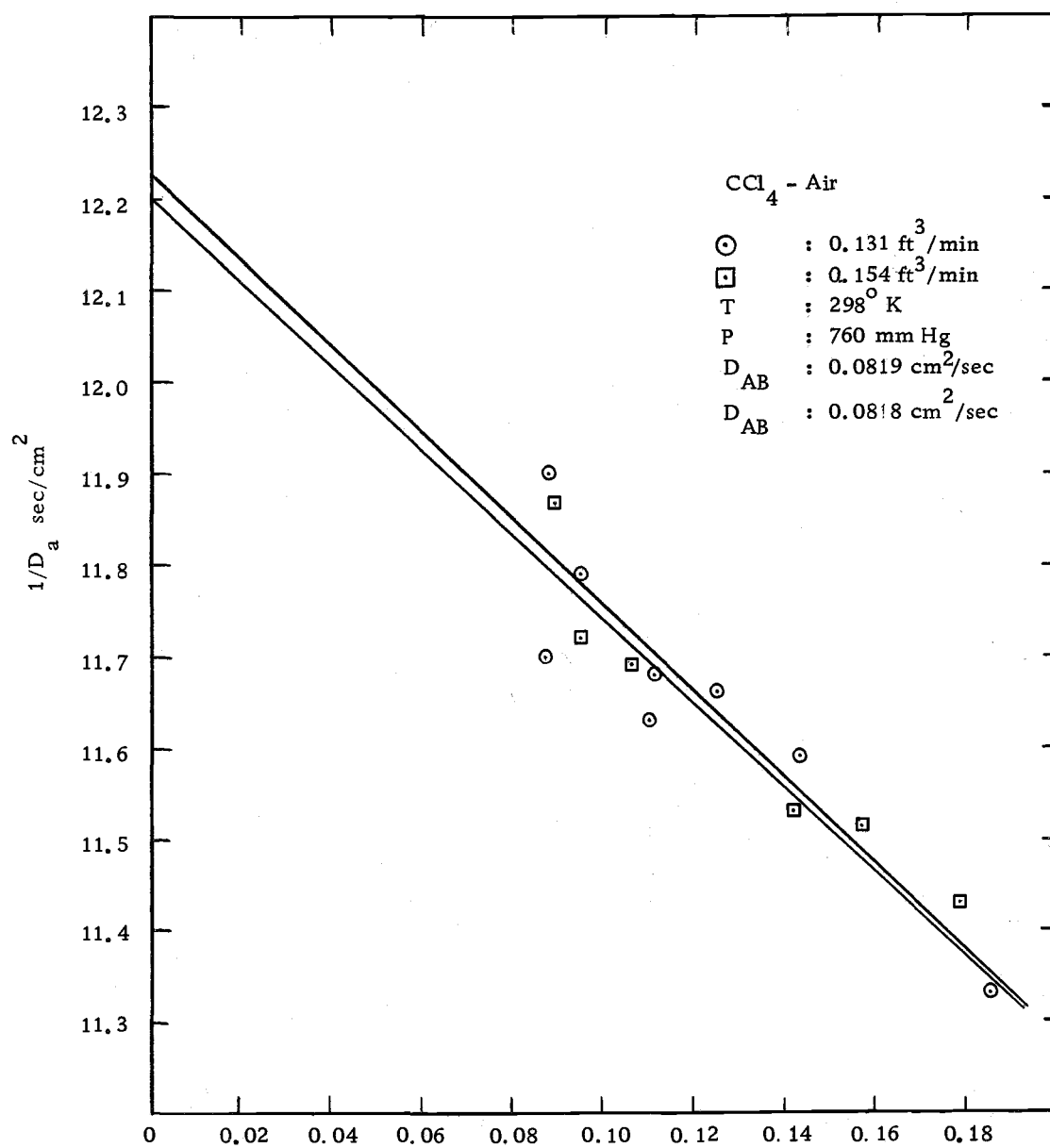


Figure 8. Plots for carbon tetrachloride in air.

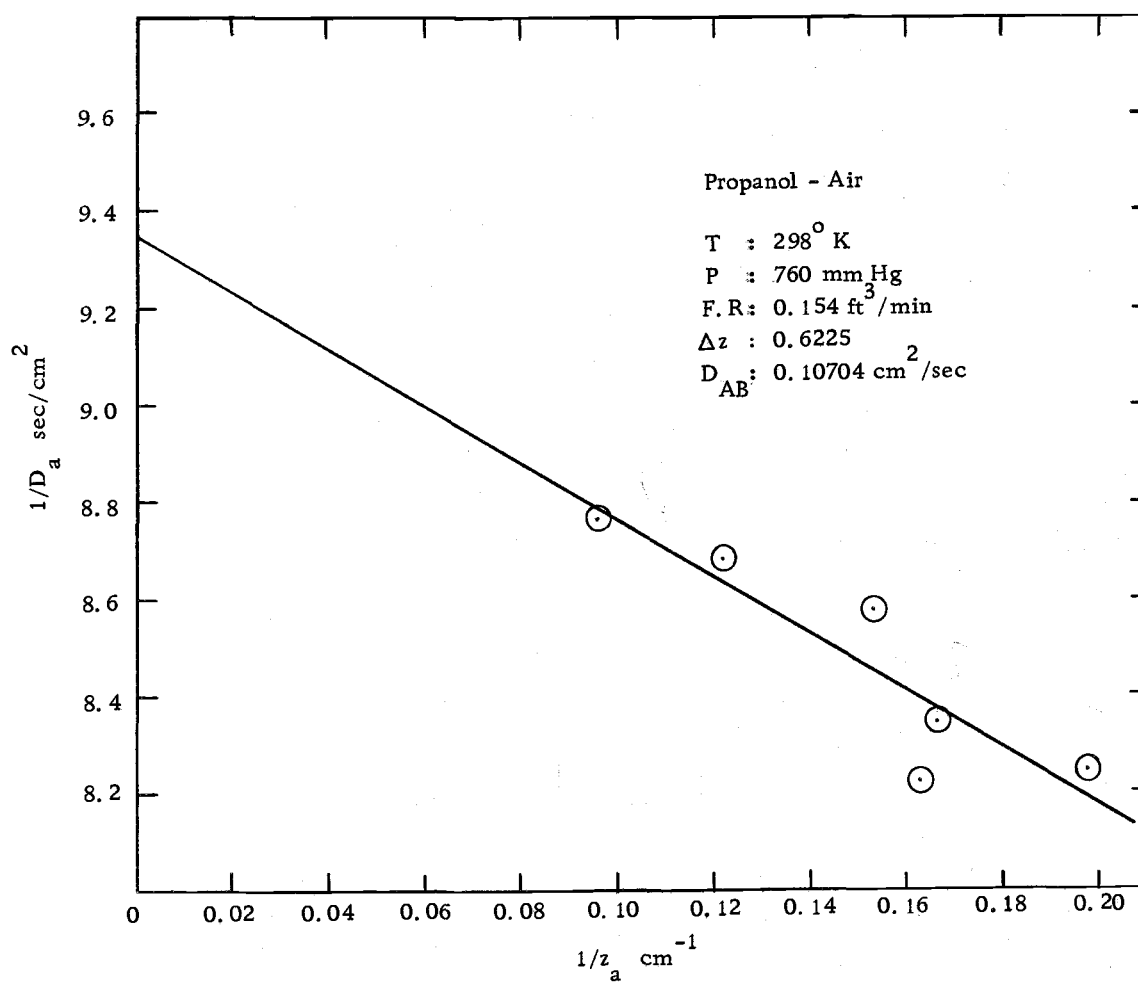


Figure 9. Plot for propanol in air.

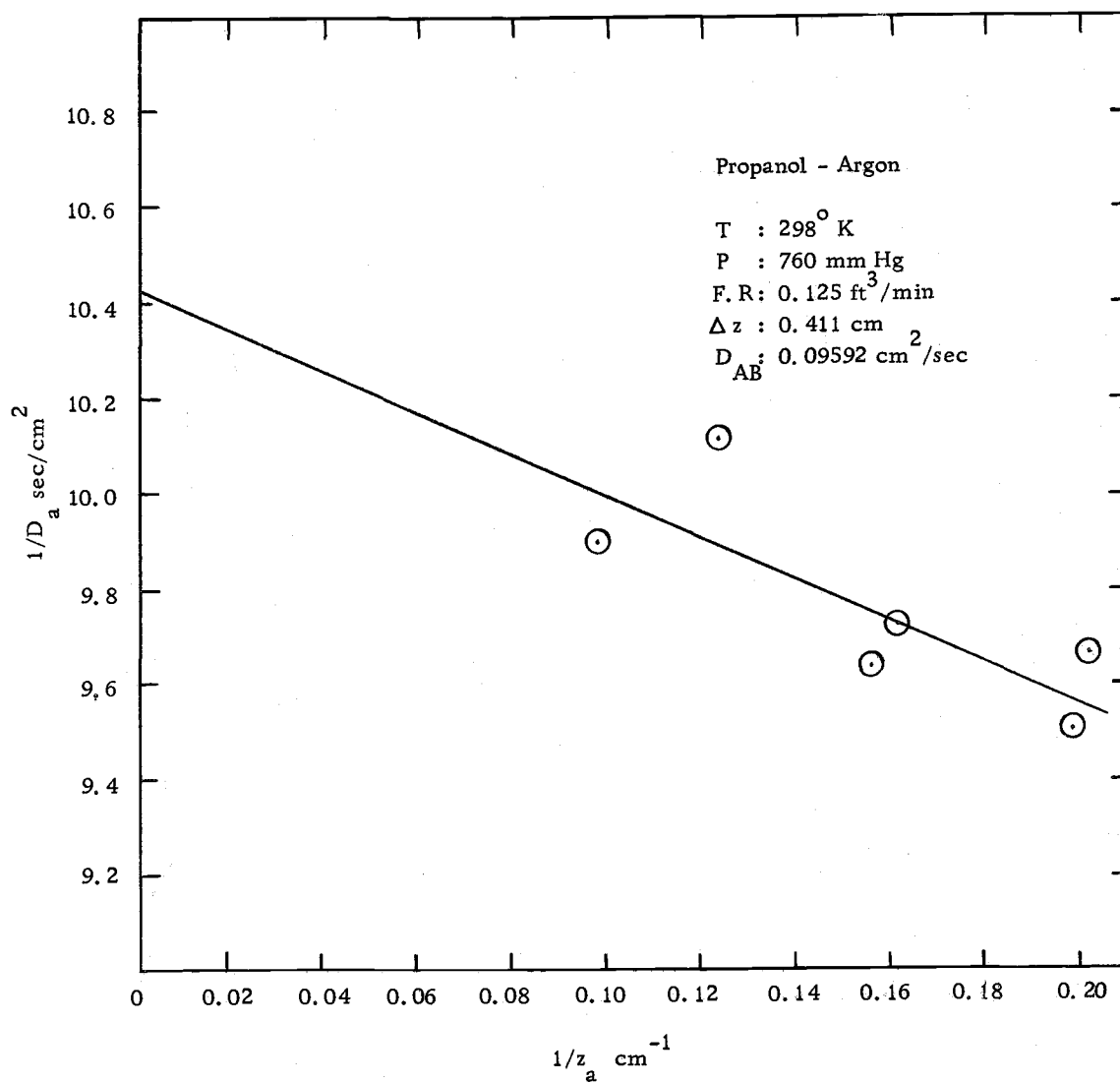


Figure 10. Plot for propanol in argon.

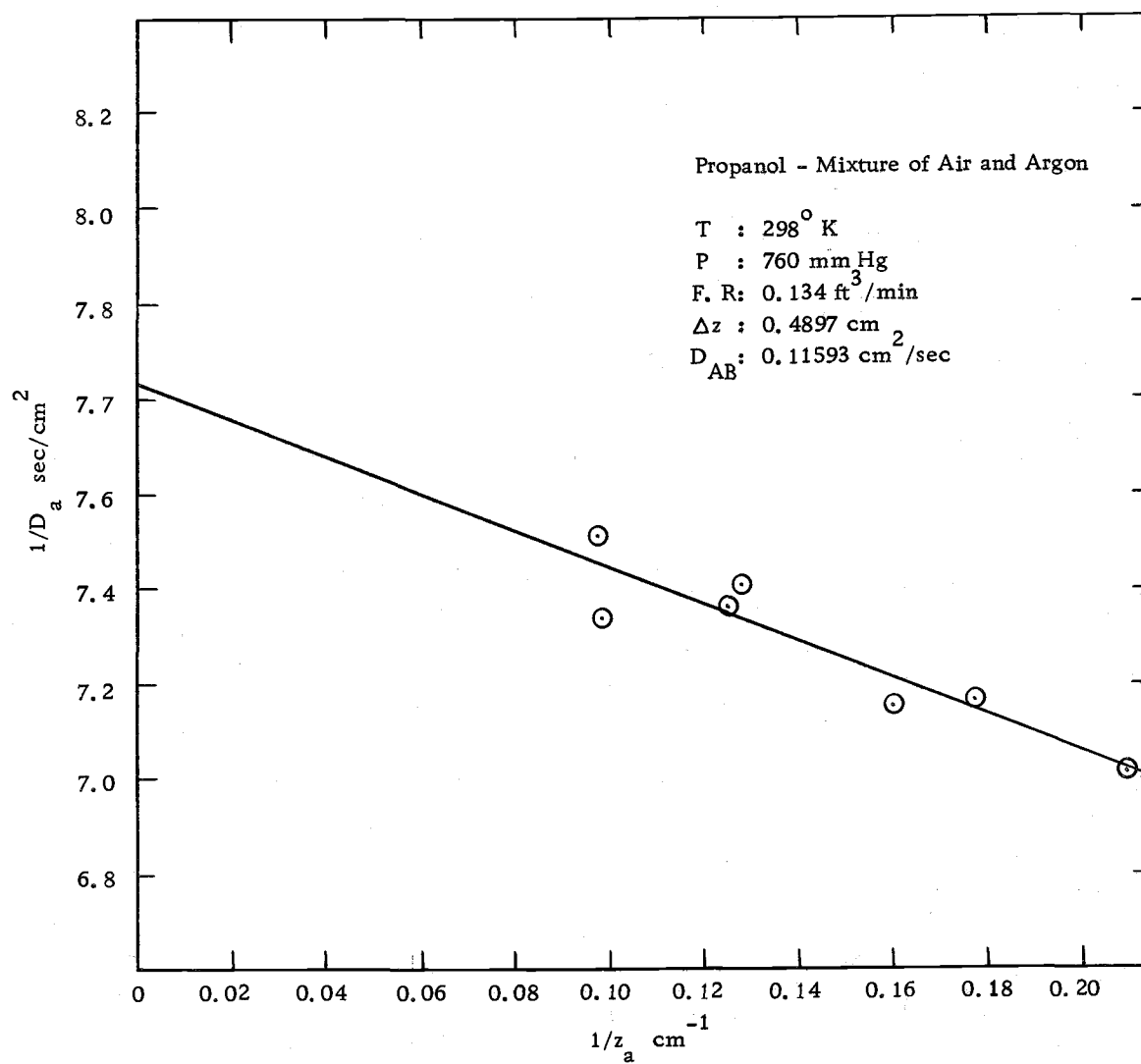


Figure 11. Plot for propanol in mixtures of air and argon.

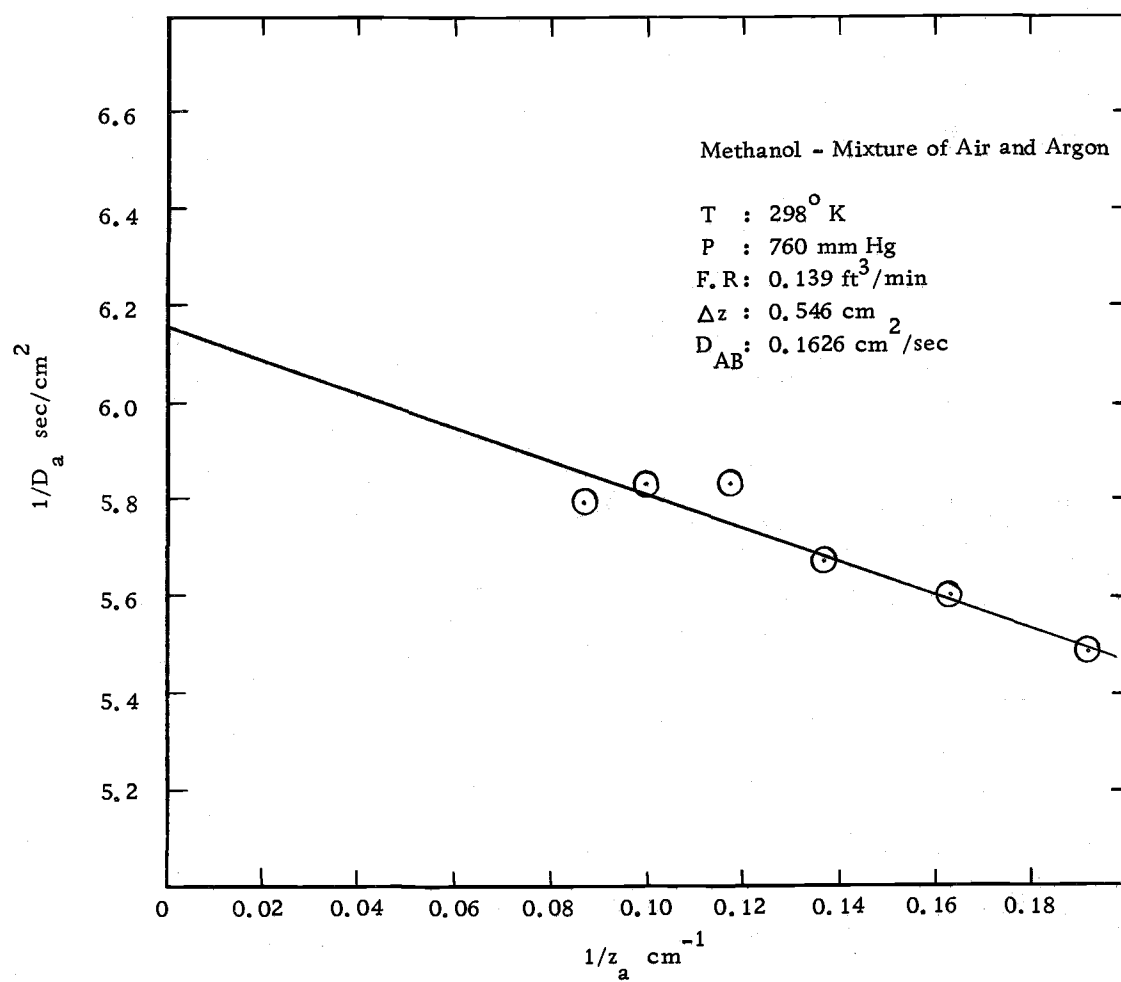


Figure 12. Plot for methanol in mixtures of air and argon.

Table 1. Comparison of experimental data.

Experimental $D_{AB}$ , (cm <sup>2</sup> /sec)	Hirshfelder Bird & Spotz $D_{AB}$ , (cm <sup>2</sup> /sec)	Equations by others $D_{AB}$ , (cm <sup>2</sup> /sec)	Temperature (° K)	$\Delta z$ (cm)	% Deviation
<u>System: CCl<sub>4</sub>-Air</u>					
0.0819			298	0.374	
0.08182			298	0.384	
	0.0755		298		-7.8
		0.0909(1)	298		-1.32
		0.0787(2)	298		-4.0
		0.083 (3)	298.5		+1.32
<u>System: Propanol-Air</u>					
0.10704			298	0.623	
	0.08909		298		-16.76
		0.0971(1)	298		-9.286
		0.0989(2)	298		-7.604
<u>System: Propanol-Argon</u>					
0.09592			298	0.411	
	0.07971		298		-16.89
<u>System: Methanol-Mixture of Air and Argon (1:1)</u>					
0.1626			298	0.546	
	0.1445(4)		298		-11.16
<u>System: Propanol-Mixture of Air and Argon (2:1)</u>					
0.11593			298	0.489	
	0.103057(4)		298		-11.1

% deviation = (calculated-experimental)/(experimental) x 100

(1): Wilke and Lee (calculated)

(2): Chen and Othmer (calculated)

(3): Larson (observed)

(4): An expression derived by Wilke (calculated)

range of error varied from zero to 40 percent. Comparison of the prediction methods based on the theory with established values indicates that the Hirschfelder equation is the best whenever experimental values are not available (21). Therefore, the diffusion coefficient for each system was calculated from the Hirschfelder, Bird and Spotz equation. Lennard-Jones parameters for the equation were obtained from the reference by Hirschfelder, Curtiss and Bird (9). For some systems, the critical temperature and pressure were used to calculate the collision integrals. An expression derived by Wilke (7) was employed to determine the diffusion coefficients of gas mixtures. The values obtained from the equations as well as the experimental results are listed in Table (1).

In the present work the diffusion coefficient for the carbon tetrachloride-air system was determined in order to test the accuracy of the results and the reliability of the apparatus. As a further check of the experimental technique and results, measurements for  $\text{CCl}_4$ -air system were made at different flow rates. The data obtained with different flow rate are shown in Figure (8) and shows a small difference of 0.2 percent.

For the  $\text{CCl}_4$ -air system the value obtained in this work is 1.32% lower than that reported by Larson (11), and 7.8% higher than that calculated by the Hirschfelder equation. The close agreement of the value of the present work with the value reported by Larson indicates the

validity of the experimental technique used in this investigation.

It is of importance to note that propanol is a polar compound and that the Hirschfelder equation is recommended for non-polar molecular compounds. It is also readily seen from Reid and Sherwood study that poor agreements are probable when the Hirschfelder equation is applied to polar compounds, where the force constants had to be estimated from critical data. Consequently, one could make the conclusion that the Hirschfelder equation appears to be an approximation for polar compounds. Table (1) shows that comparison of values from the present study and empirical equations is in good agreement within range of accuracy predicted by Reid and Sherwood and that the new observed values are the best now available.

Since no experimental data were available, except for the  $\text{CCl}_4$ -air system, the results were compared with the values calculated from the empirical equations.

As listed in Table (1), the end effect corrections were increased with higher gas flow rate.

### C. Possible Sources of Experimental Error

There are several effects which might introduce the experimental errors. They are:

1. Temperature and pressure fluctuation of the system
2. Corresponding vapor pressure variation of the liquid due to

temperature change

3. Surface tension forces
4. Turbulent effect
5. Cross-sectional area of the tube
6. Gas-liquid interface cooling
7. Steady-state approach

The temperature of the interface was not investigated. As liquid evaporates, the heat of vaporization must be supplied to the interface from the constant temperature bath. In case that heat supply is not sufficient, it is evident that the temperature of the interface must drop, and thus convective current will result. By measuring the magnitude of the cooling effect, Wilke (12) and Altshuller (1) have found that the effect can be neglected, that is, the temperature of the interface may be assumed equal to the constant bath temperature. The other effects were discussed in the other sections.

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## APPENDICES

## APPENDIX I

## DETERMINATION OF GAS FLOW RATE

Three rotameters were installed in order to measure the exact amount of gas flow rate of three streams. These rotameters were calibrated, using a wet-test meter. Calibration curves have been obtained when the gas flow rates were plotted against the rotameter readings. The calibration curves are shown in Figure (13) and Figure (14). For a given float level of a rotameter, each gas showed different flow rates because of the influence of the viscosity and density of the gases.

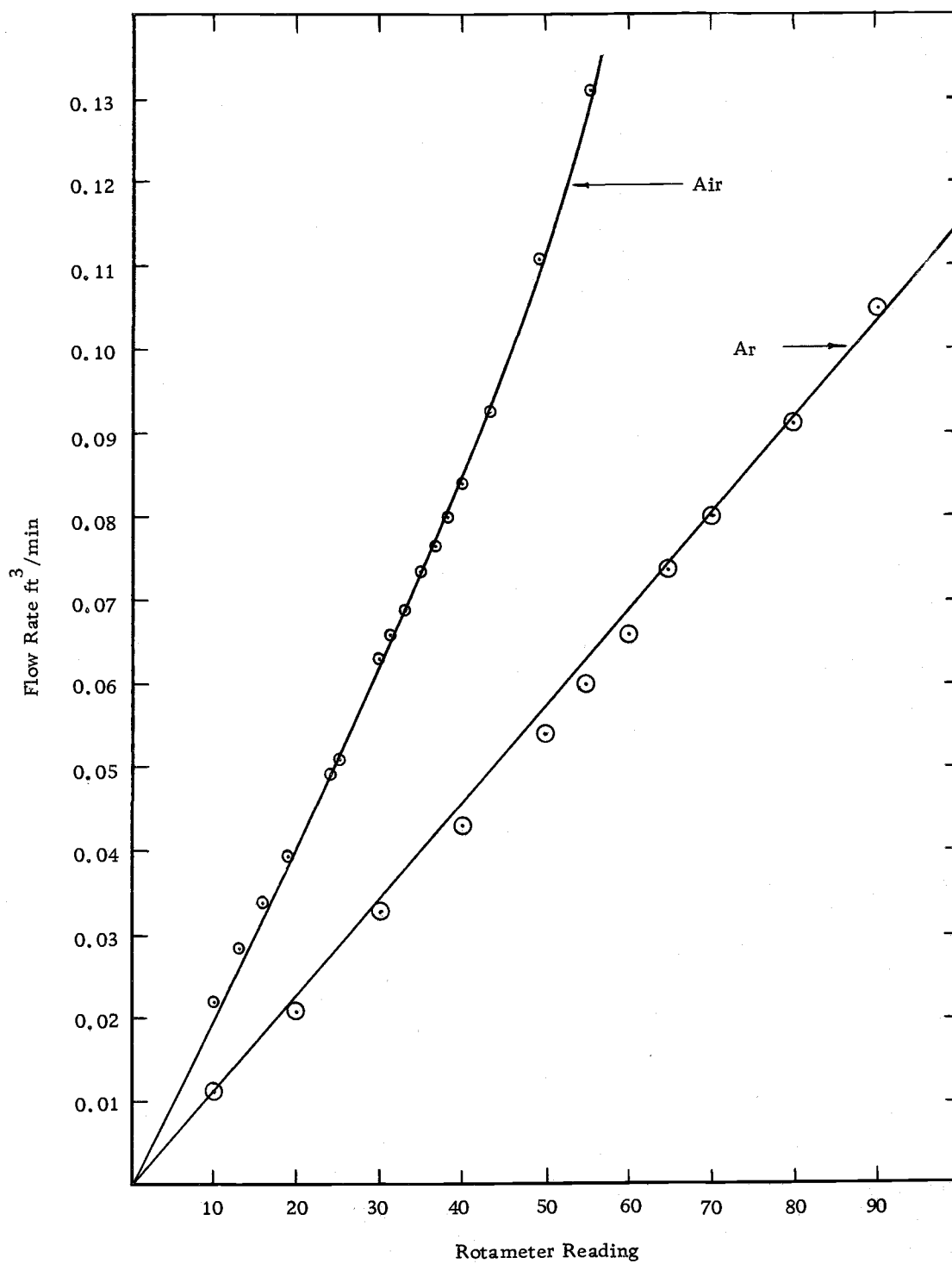


Figure 13. Calibration curves.

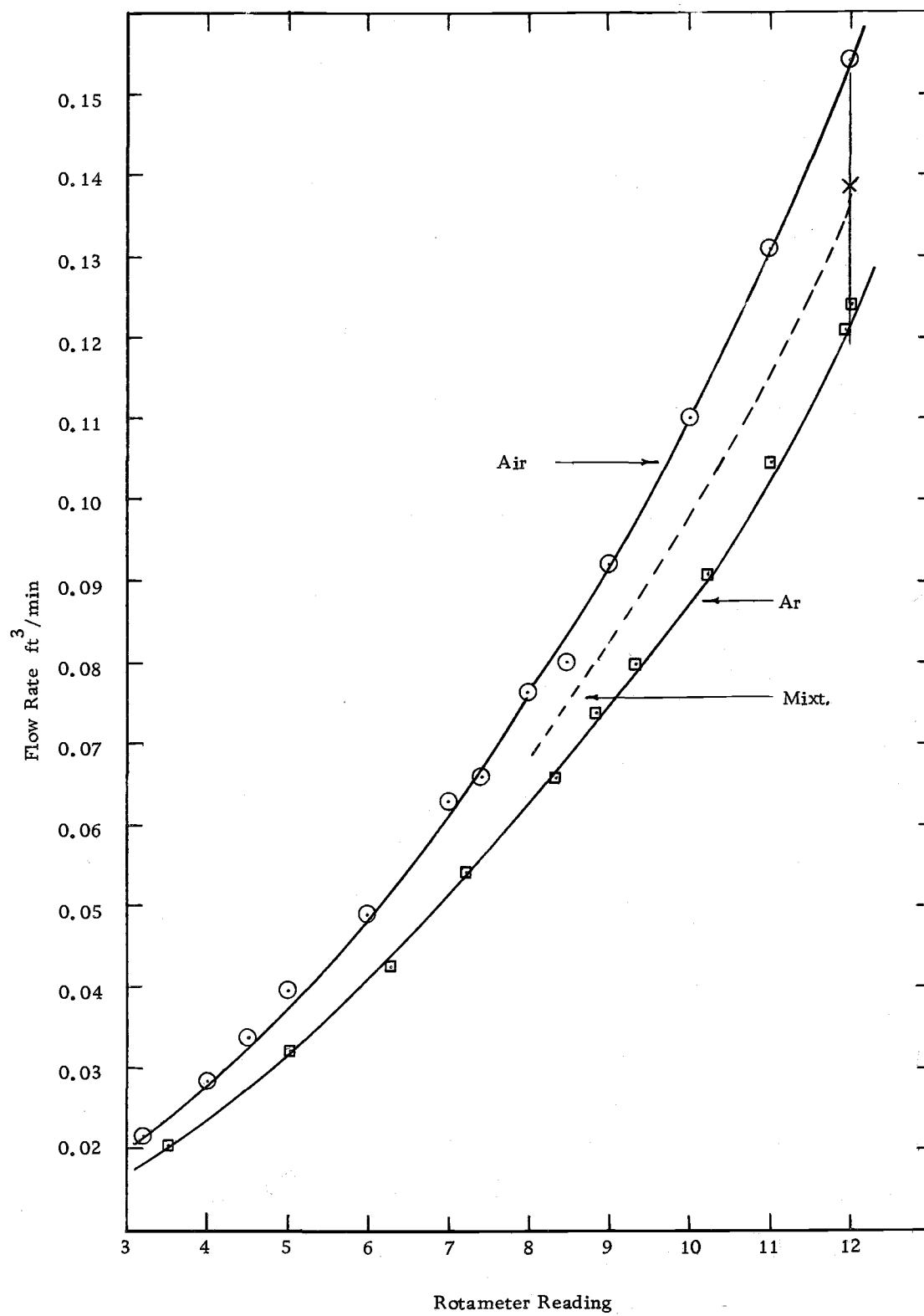


Figure 14. Calibration curves (Rotameter C).

## APPENDIX II

## SAMPLE CALCULATIONS

The expression for  $D_{AB}$  was derived in a previous section:

$$D_{AB} = \frac{W_A RTz}{M_A \theta SP \ln \frac{P}{P-P_{AS}}} \quad (A-1)$$

Substituting constant quantities into the above equation, the equation becomes

$$D_{AB} = \frac{(62.37 \frac{\text{mmHg-lit}}{\text{mole}^\circ\text{K}})(10^3 \frac{\text{cm}^3}{\text{l}}) TW_A z}{(0.71312 \text{ cm}^2)(2.3026) M_A \theta P \log \frac{P}{P-P_{AS}}} \quad (A-2)$$

$$= (3.79835 \times 10^4) \frac{TW_A z}{M_A \theta P \log \frac{P}{P-P_{AS}}}$$

The cross-sectional area of the diffusion tube was determined by weighing the total amount of water in the tube and dividing this weight by the density of the water at room temperature. This volume was then divided by the length of the diffusion tube. In this method the area was  $0.71312 \text{ cm}^2$ . The diffusion path length was evaluated from the dimensions of the tube and the density of the liquid by the formula

$$\begin{aligned}
 z &= 14.28 - \frac{W_L}{S\rho_L} \\
 &= 14.28 - \frac{W_L}{0.71312 \rho_L}
 \end{aligned}
 \tag{A-3}$$

From Equation (17), the slope of the curve is equal to

$$m = - \frac{\Delta z}{D_{AB}} \tag{A-4}$$

#### 1. Evaluation of $D_{AB}$ for the $\text{CCl}_4$ -air system

Before run: Total weight including tube assembly - 52.9322 gm

After run : Total weight including tube assembly - 52.6739 gm

$$W_A = 0.2534$$

$$W_L = 6.0004$$

The average weight of the liquid in the tube was taken as the arithmetic average of the liquid quantities before and after a run.

$$\theta = 38205 \text{ sec.}$$

$$z = 8.9877 \text{ cm}$$

$$P = 762.65 \text{ mm Hg}$$

$$P_{AS} = 110 \text{ mm Hg}$$

$$M_A = 153.84$$

$$T = 298^\circ \text{ K}$$

From the Equation (A-2)

$$D_a = \frac{(3.79835 \times 10^4)(298)(0.2543)(8.98755)}{(153.84)(38205)(762.6) \log (762.6/652.65)}$$

$$= 0.08534 \text{ cm}^2/\text{sec}$$

The corrected value for the diffusion coefficient at 760 mm Hg, 298° K is

$$D_a = 0.08534(762.6/760) = 0.08564 \text{ cm}^2/\text{sec}$$

$$1/D_a = 1/0.08564 = 11.6768 \text{ sec/cm}^2$$

$$1/z_a = 1/8.9877 = 0.1113 \text{ cm}^{-1}$$

From Figure (6), the true diffusion coefficient can be found.

$$D_{AB} = 0.0819 \text{ cm}^2/\text{sec}$$

## 2. Evaluation of $D_{AB}$ for the $\text{CCl}_4$ -air system by the Hirshfelder equation

	$\epsilon_{A/k} \text{ in } ^\circ \text{K}$	$\sigma \text{ in } \text{\AA}$
Carbon tetrachloride	327	5.88
Air	97	3.617

$$M_A = 153.84$$

$$M_B = 29$$

$$P = 1 \text{ atm.}$$

$$T = 298^\circ \text{K}$$

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} = \frac{5.88 + 3.617}{2} = 4.749 \text{ \AA}$$

$$\epsilon_{AB}/k = \sqrt{(\epsilon_A/k)(\epsilon_B/k)} = \sqrt{(327)(97)} = 178.1$$

$$\epsilon_{AB}/kT = 0.5977$$

$$kT/\epsilon_{AB} = 1.6732$$

$$\Omega(9) = 1.147$$

Substituting these values into the equation

$$D_{AB} = \frac{0.001858 T^{3/2} (1/M_A + 1/M_B)^{1/2}}{P \sigma_{AB}^2 \Omega} \quad (A-5)$$

$$= \frac{0.001858 (298)^{3/2} (1/153.84 + 1/29)^{1/2}}{(1) (4.749)^2 (1.147)}$$

$$= 0.0758 \text{ cm}^2/\text{sec}$$

### 3. Evaluation of $D_{AB}$ for propanol-mixtures of air and argon system.

In multicomponent system the mass diffusivities are dependent on the composition of gases. An expression proposed by Wilke (7) may be used for the diffusion coefficient of gas mixtures.

$$D_{A\text{-mixture}} = \frac{1}{y'_B/D_{AB} + y'_C/D_{AC} + y'_D/D_{AD} + \dots} \quad (A-6)$$

where  $D_{A\text{-mixture}}$  is the diffusion coefficient for component A in the gas mixture;  $D_{AB}$  is the binary diffusion coefficient; and  $y'_B, y'_C,$

etc., are the mole fraction of the components in the mixture.

$$y_B' = 0.6666$$

$$y_C' = 0.3333$$

$$D_{\text{prop-air}} = 0.10704 \text{ at } 25^\circ \text{ C, } 1 \text{ atm.}$$

$$D_{\text{prop-air}} = 0.09592 \text{ at } 25^\circ \text{ C, } 1 \text{ atm.}$$

When substituting these values in Equation (A-6)

$$D_{\text{prop-air, Ar}} = \frac{1}{0.6666/0.1074 + 0.3333/0.09592} = 0.103157$$

$$D_{\text{prop-air, Ar}} = 0.103057 \text{ cm}^2/\text{sec}$$

## APPENDIX III

## PHYSICAL PROPERTIES OF SUBSTANCES

It is seen that the diffusion coefficients determined by experiment have values which are dependent upon the physical properties used. Vapor pressure data were obtained from Chemical Engineer's Handbook (15) and the Handbook of Chemistry and Physics (20).

Table 2. Physical properties of substances used.

Substance	Molecular weight	Density (gm/cm <sup>3</sup> )	Boiling point (° C)	Vapor pressure at 298° K (mm Hg)
CCl <sub>4</sub>	153.84	1.594	76.8	110
Propanol	60.1	0.801 <sup>*</sup>	67.8	20
Methanol	32.04	0.7866 <sup>*</sup>	64.7	122

\* Values obtained from the following references:

Technical Data Book - Petroleum Refining (P 6.47) (2)

International Critical Table (V3, P27)

Chemical Engineer's Handbook 4th ed. (P3-85) (15)

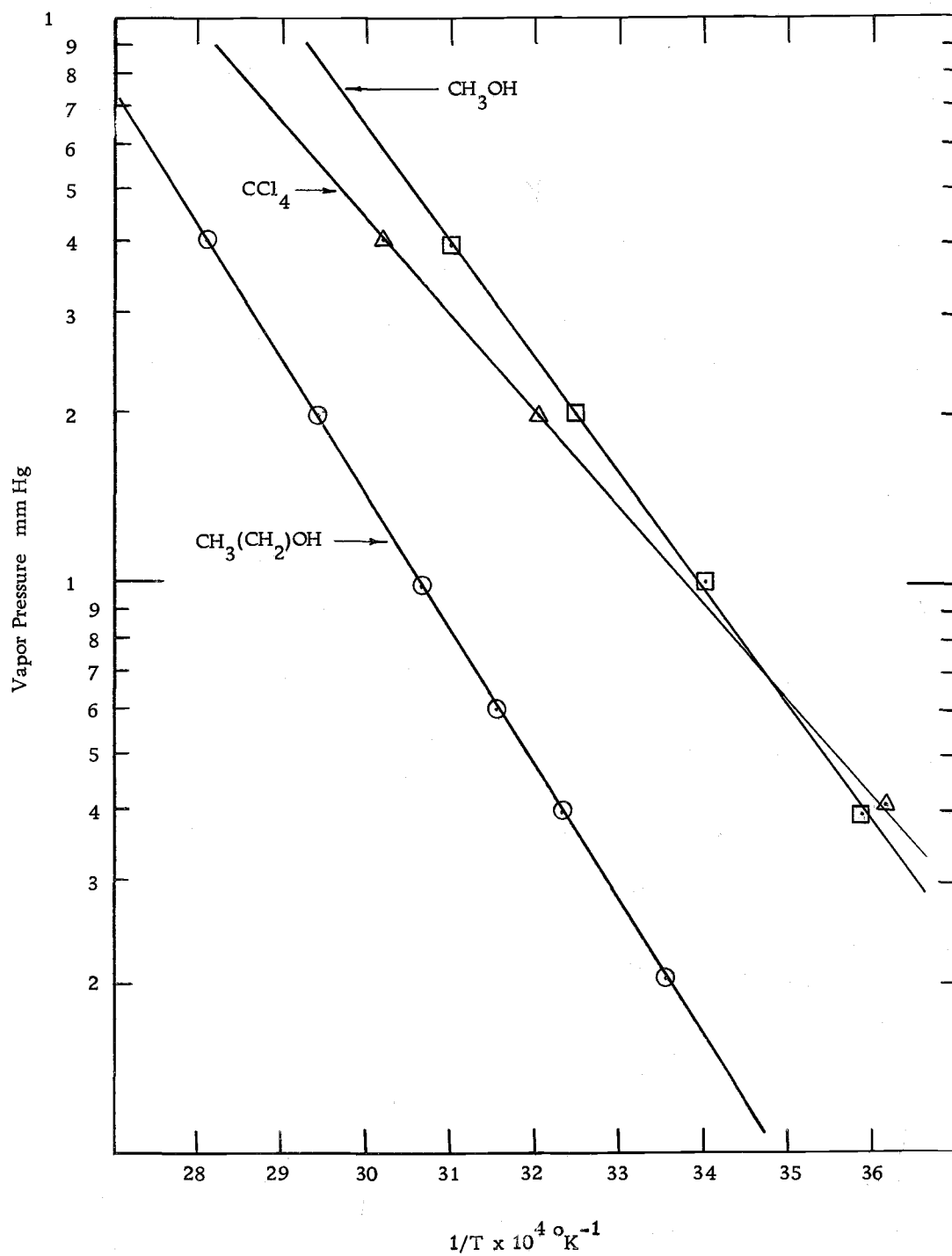


Figure 15. Vapor pressure data.

# APPENDIX IV

Table 3. Experimental data and related conditions.

Run No.	W <sub>A</sub> (gm)	z <sub>a</sub> (cm)	θ (sec)	D <sub>a</sub> <sup>2</sup> (cm /sec)	Atmospheric pressure (mmHg)	Cell pressure (mmHg)
System : CCl <sub>4</sub> -Air Flow Rate : 0.131 ft <sup>3</sup> /min Temperature: 298° K						
1	0.19320	11.436	36,800	0.08547	757.0	758.92
2	0.25020	9.078	37,545	0.08599	756.1	757.99
3	0.42320	5.390	36,915	0.08826	759.2	761.09
4	0.25430	8.988	38,205	0.08564	760.7	762.65
5	0.32060	6.978	37,125	0.08625	761.0	762.92
6	0.20720	10.594	37,055	0.08485	761.2	763.12
7	0.29120	8.031	38,730	0.08578	755.7	757.62
8	0.21990	11.326	42,205	0.08401	757.2	759.15
System : CCl <sub>4</sub> -Air Flow Rate : 0.154 ft <sup>3</sup> /min Temperature: 298° K						
9	0.4043	5.572	36,855	0.08745	760.0	762.29
10	0.3379	7.050	39,400	0.08670	761.6	763.84
11	0.2593	9.361	40,495	0.08553	758.1	760.34
12	0.2040	11.217	38,695	0.08419	756.5	758.79
13	0.3652	6.380	38,437	0.08684	759.5	761.82
14	0.2189	10.532	38,690	0.08530	760.6	762.84

Table 3 continued.

Run	$W_A$ (gm)	$z_a$ (cm)	$\theta$ (sec)	$D_a$ $(cm^2/sec)$	Atmospheric pressure (mmHg)	Cell pressure (mmHg)
System : Propanol-Air Flow Rate : $0.154 \text{ ft}^3/\text{min}$ Temperature: $298^\circ \text{ K}$						
15	0.0480	5.062	42,950	0.12116	759.1	761.39
16	0.0334	6.554	40,225	0.11655	758.4	760.69
17	0.0211	10.410	41,220	0.11413	758.5	760.76
18	0.0297	7.822	39,975	0.12446	758.4	760.64
19	0.0384	6.152	41,570	0.12172	758.0	760.29
20	0.0377	6.014	40,490	0.11993	757.8	760.04
21	0.0263	8.208	40,165	0.11512	759.2	761.44
System : Propanol-Argon Flow Rate : $0.154 \text{ ft}^3/\text{min}$ Temperature: $298^\circ \text{ K}$						
22	0.03770	4.956	38,700	0.10341	757.3	759.64
23	0.02812	6.436	37,480	0.10380	760.2	762.56
24	0.02187	8.120	38,830	0.09867	761.9	764.23
25	0.01805	10.341	39,570	0.10103	759.9	762.26
26	0.03785	5.054	38,855	0.10545	759.0	761.36
27	0.02978	6.225	38,760	0.10281	760.75	763.11

Table 3 continued.

Run No.	W <sub>A</sub> (gm)	z <sub>a</sub> (cm)	θ (sec)	D <sub>a</sub> (cm <sup>2</sup> /sec)	Atmospheric pressure (mmHg)	Cell pressure (mmHg)
System : Propanol-Mixture of Air and Argon (2:1) Flow Rate : 0.134 ft <sup>3</sup> /min Temperature: 318° K						
28	0.16311	4.754	37,680	0.14226	758.5	760.94
29	0.12710	6.227	39,395	0.13987	761.3	763.79
30	0.09218	7.951	37,625	0.13576	762.5	764.94
31	0.06970	10.284	37,577	0.13312	763.0	765.44
32	0.08445	7.812	34,150	0.13492	763.8	766.24
33	0.07103	10.164	37,092	0.13637	766.0	768.44
34	0.13000	5.634	36,750	0.13948	765.5	767.94
System : Methanol-Mixture of Air and Argon (1:1) Flow Rate : 0.139 ft <sup>3</sup> /min Temperature: 298° K						
35	0.21825	5.214	38,415	0.18244	762.6	764.84
36	0.14277	7.286	36,282	0.17633	761.5	763.79
37	0.12377	8.555	37,780	0.17138	757.2	759.49
38	0.10857	10.067	39,067	0.17156	759.4	761.69
39	0.09530	11.505	39,030	0.17268	761.3	763.59
40	0.17625	6.108	37,260	0.17845	764.5	766.79

## APPENDIX V

## NOMENCLATURE

<u>Symbols</u>	<u>Meanings</u>	<u>Units</u>
C	concentration of gas mixture	moles/liter
$D_a$	apparent diffusion coefficient	$\text{cm}^2/\text{sec}$
$D_{AB}$	diffusion coefficient of A through B	$\text{cm}^2/\text{sec}$
L	total length of diffusion tube	cm
m	slope of experimental curves	
$M_A$	molecular weight of A	
$N_A$	molar flux of A	$\text{moles}/\text{sec. cm}^2$
$N_B$	molar flux of B	$\text{moles}/\text{sec. cm}^2$
P	total pressure of cell	mm Hg
$P_A$	partial pressure of diffusing vapor	mm Hg
$P'_A$	vapor pressure of liquid A	
$P_{AS}$	vapor pressure of liquid A at surface temperature	mm Hg
R	gas constant	$\frac{(\text{mmHg})(\text{lit})}{(\text{mole})(^\circ \text{K})}$
S	cross-sectional area of diffusion tube	$\text{cm}^2$
T	temperature	$^\circ \text{K}$
$W_A$	weight of A evaporated in time $\theta$	gm
$W_L$	average weight of the liquid in the tube	gm
$X_A$	mole fraction of A	

<u>Symbols</u>	<u>Meanings</u>	<u>Units</u>
$X_B$	mole fraction of B	
$z$	effective diffusion path length	cm
$z_a$	apparent diffusion path length	cm
$z_1$	length at bottom of diffusion tube	cm
$z_2$	length at top of diffusion tube	cm
$\Delta z$	end effects correction	cm
$\Delta z_e$	change in $z$ due to eddies	cm
$\Delta z_s$	change in $z$ due to surface tension	cm
$z_0$	value of $z$ at time $\theta = 0$	cm
$z_\theta$	value of $z$ at time $\theta = \theta$	cm
$\rho_L$	density of liquid	gm/cm <sup>3</sup>
$\theta$	total diffusion time	sec
$\sigma_{AB}$	collision diameter, a Lennard-Jones parameter	Å
$\Omega$	collision integral, a function of $kT/\epsilon_{AB}$	
$\epsilon_{AB}$	energy of molecular interaction for the binary system AB, a Lennard-Jones parameter	ergs
$k$	Boltzmann constant, $1.38 \times 10^{-16}$	ergs/°K