


AN ABSTRACT OF THE THESIS OF

Kumbla Narasimha Srinivas Prabhu for the M.S. in Chemical Engineering  
(Name) (Degree) (Major)

Date thesis is presented May 13, 1966

Title THE EFFECT OF CONCENTRATION ON DIFFUSION COEFFICIENTS IN BINARY GASEOUS SYSTEMS

Abstract approved   
(Major professors)

Diffusion coefficients were determined for the chloroform-air system at 50°C and for the methanol-air system at 55°C by the Arnold-cell technique. The effect of concentration was studied by varying the concentration of the gas stream passing across the top of the Arnold cell.

The chloroform-air system exhibited a strong dependency on concentration; for this system the diffusion coefficient changed by approximately ten percent as the chloroform concentration in the gas stream was changed from zero to 56 percent. The variation of the diffusion coefficient in the methanol-air system was small; a total variation of one percent was observed over the concentration range of zero to 46 percent methanol.

Since the variation of diffusion coefficient for methanol-air system was of the order of one percent, assumption of constancy of diffusion coefficient with concentration would cause little error in

design calculations; hence, no correlation was attempted for the methanol-air system. However attempts were made to correlate the concentration dependency of diffusion coefficients in the chloroform-air system. It was found that a quadratic functional relationship in concentration for the diffusion coefficients was the best possible correlation. A quadratic function in weight fraction was used to account for the effect of molecular weight differences. It was concluded that the difference in molecular weight of the two diffusing species has a pronounced effect on the variation of diffusion coefficients with concentration.

THE EFFECT OF CONCENTRATION ON DIFFUSION  
COEFFICIENTS IN BINARY GASEOUS SYSTEMS

by

KUMBLA NARASIMHA SRINIVAS PRABHU

A THESIS

submitted to

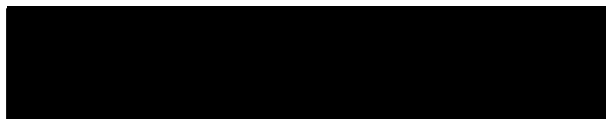
OREGON STATE UNIVERSITY

in partial fulfillment of  
the requirements for the  
degree of

MASTER OF SCIENCE

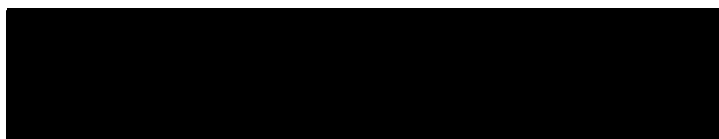
June 1966

APPROVED:



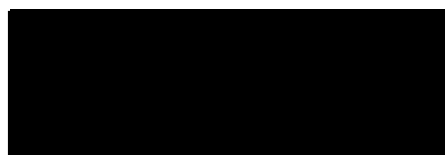
\_\_\_\_\_  
Professor of Chemical Engineering

In Charge of Major

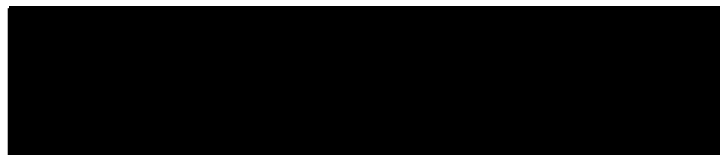


\_\_\_\_\_  
Professor of Chemical Engineering

In Charge of Major



\_\_\_\_\_  
Head of Department of Chemical Engineering



\_\_\_\_\_  
Dean of Graduate School

Date thesis is presented May 13, 1966

Typed by Carol Baker

## ACKNOWLEDGEMENT

The author wishes to express his gratitude to Dr. R. V. Mrazek for his guidance during the course of this work, and for his advice during the preparation of this manuscript. The author is also indebted to Dr. C. E. Wicks for proposing this project and for his guidance during the preliminary course of this work, and to Professor J. S. Walton for the assistantship and for the use of the facilities of the department.

Thanks are also extended to Drs. Michael Schaer and James R. Divine for their help during the experimental work.

## TABLE OF CONTENTS

	Page
INTRODUCTION	1
THEORETICAL DEVELOPMENT	4
Equations Governing Diffusion	4
End Effect Correction	8
Establishment of Steady State	9
Concentration profile	9
Transient heat transfer	12
The Effect of Temperature and Pressure on Diffusion Coefficients	12
EXPERIMENTAL METHODS OF MEASURING DIFFUSION COEFFICIENTS	14
EXPERIMENTAL APPARATUS	16
EXPERIMENTAL PROCEDURE	23
RESULTS	25
DISCUSSION OF RESULTS	29
Conclusion	38
RECOMMENDATIONS	39
BIBLIOGRAPHY	40
NOMENCLATURE	43
APPENDICES	
Appendix I - Derivation of Pertinent Mass-Transfer Equations	46
Appendix II - Correlation to End-Effects	50
Appendix III-Transient Heat-Transfer Effect	53
Appendix IV-Diffusion Path and Equilibrium Calculations	57

## TABLE OF CONTENTS (Continued)

	Page
Appendix V - Sample Calculation	62
Appendix VI - Experimental Results	66
Appendix VII- Vapor Pressure Data	70

## LIST OF FIGURES

Figure		Page
1.	Transient diffusion of the nitrobenzene-air system at 25°C and 1 atmosphere.	11
2.	Flow diagram of the experimental apparatus.	18
3.	Equilibrium cell.	19
4.	Diffusion cell.	20
5.	Experimental results for chloroform-air system at 50°C and 1 atmosphere.	26
6.	Experimental results for methanol-air system at 55°C and 1 atmosphere.	27
7.	Variation of diffusion coefficients as a linear function of mole fraction for chloroform-air system at 50°C and 1 atmosphere.	32
8.	Variation of diffusion coefficient as a quadratic function of mole fraction for chloroform-air system at 50° C and 1 atmosphere.	36
9.	Variation of diffusion coefficient as a quadratic function of weight fraction for chloroform-air system at 50°C and 1 atmosphere.	37
10.	Diffusion model for diffusion of A through stagnant B.	47
11.	Model for end effect corrections.	51
12.	Model for diffusion path.	58
13.	Vapor pressure data for chloroform and methanol.	71



## LIST OF TABLES

Table		Page
1.	Experimental results.	28
2.	Diffusion coefficients at 25.5°C and 1 atmosphere.	29
3.	Properties of chloroform and methanol.	54
4.	Equilibrium calculations.	61
5.	Experimental data - chloroform-air system at 50°C and 1 atmosphere.	67
6.	Experimental data - methanol-air system at 55°C and 1 atmosphere.	69

# THE EFFECT OF CONCENTRATION ON DIFFUSION COEFFICIENTS IN BINARY GASEOUS SYSTEMS

## INTRODUCTION

Molecular diffusion is a process whereby molecules of one substance gradually interpenetrate another substance. Sherwood (29) defined this as "the spontaneous intermingling of miscible fluids placed in mutual contact, accomplished without the aid of mechanical mixing."

After the importance of diffusion was first recognized, several methods were devised to determine diffusivities. Unfortunately diffusivities are rather difficult to measure accurately, as is indicated by the disagreement of the results given by different workers for the same system.

The kinetic theory of gases has provided two basically different theories of diffusion (17): one that of Stefan - Maxwell and the other that of Meyer, which was later modified by Jeans (19). The former assumes that there is no variation of the diffusion coefficient with concentration, while the latter allows a maximum variation of 33%. The theory put forward by Chapman and Enskog (17) predicts only a slight variation of the diffusion coefficient with concentration. Upon consideration of these various theories a question arises: "Does the diffusion coefficient depend on the relative proportion of

the gases in a binary gas system, or is it independent of composition as predicted by Maxwell's equation?"

A series of experiments were conducted at Halle, Germany, to determine the concentration dependency of diffusion coefficients, a summary of which was published by Anton Lonius (23). Experiments were conducted on the gas pairs, hydrogen-oxygen, hydrogen-nitrogen, nitrogen-oxygen, hydrogen-carbon dioxide and helium-argon. It was concluded "The gas diffusion coefficient must not be considered as a constant, but it is a function of the mixing ratio." Lonius and co-workers were unable to get very accurate results because precise experimental techniques had not been developed. However, they stated that the dependency becomes rather pronounced when the content of the heavier gas increases.

Measurement of the concentration dependency of diffusivity of argon-xenon system has been reported by Amdur and Schatzki (2). The experiments involved four separate runs in which inert argon containing a trace of radio-active xenon diffused into inert argon. The values were also calculated using an empirical relation.

$$D_{12} = (D_{12})_1 f_D \quad (1)$$

Where  $(D_{12})_1$  is the first approximation to the mutual diffusion coefficient, independent of composition, and

$$f_D = 1 + \frac{0.1}{\frac{m_1}{m_2} + 1.6 \frac{m_1}{m_2} + 1} \frac{x_2^2}{x_2 + 1} (6C_{12}^* - 5)^2 \quad (2)$$

$$0 < \frac{m_1}{m_2} < \frac{1}{2}$$

where  $X_2$  = mole fraction of the component of molecular mass  $m_2$ , and  $C_{12}^*$  is a function of the temperature and intermolecular potential. They concluded that the dependency is less than 0.7 percent.

This research project was undertaken to determine the dependency of the diffusion coefficient on concentration for the chloroform-air and methanol-air systems. Whenever diffusion is referred to in this discussion, it means diffusion due to a concentration gradient only, and not due to thermal or pressure gradients.

## THEORETICAL DEVELOPMENT

### Equations Governing Diffusion

The diffusion coefficient is the proportionality constant between the amount of material transferred across a unit surface in a unit time and the concentration gradient normal to that surface. The flux of species A into a stagnant layer of species B for a constant diffusion coefficient  $D_{AB}$ , is given by Fick's first law as

$$N_A = \frac{P}{RTZ} D_{AB} \ln \frac{1-X_{A2}}{1-X_{A1}} \quad (3)$$

where

$N_A$  = the average molar flux of A  $\frac{\text{g moles}}{(\text{sec})(\text{cm}^2)}$

$P$  = total pressure of the system, mm Hg

$R$  = gas constant,  $62.37 \frac{\text{mm Hg-liter}}{\text{mole } ^\circ \text{K}}$

$T$  = temperature,  $^\circ \text{K}$

$X_{A1}$  = mole fraction of A at gas liquid interface

$X_{A2}$  = mole fraction of A at the mouth of the diffusion tube

$Z$  = diffusion path length, cm

The derivation of this equation is given in Appendix I.

$N_A$  can be expressed in terms of the weight of the liquid evaporated as

$$N_A = \frac{W_A}{\theta S M_A} \quad (4)$$

where

$W_A$  = weight of the liquid evaporated, gm

$\theta$  = duration of diffusion, sec

$S$  = cross sectional area of the diffusion tube,  $\text{cm}^2$

$M_A$  = molecular weight of species A.

Hence we get

$$D_{AB} = \frac{W_A R T Z}{\theta S P M_A} \ln \frac{1 - X_{A1}}{1 - X_{A2}} \quad (5)$$

Equation (5) is the basis of calculation of diffusion coefficients with the following assumptions:

1. The evaporation of the liquid is such that it does not affect the concentration profile, i. e. quasi-steady-state conditions prevail during the course of the experiment,
2. The gas behaves as an ideal gas under the experimental conditions,

3. The calculated diffusion coefficient between two given concentrations  $X_{A_1}$  and  $X_{A_2}$  is the concentration average diffusion coefficient,  $\bar{D}_{AB}$ , and is a constant for this range of concentration. The definition of  $\bar{D}_{AB}$  is given below:

Let the point value of diffusion coefficient,  $D_{AB}$ , be defined as

$$D_{AB} = F(X_A) \quad (6)$$

where  $F(X_A)$  = the concentration function. By Fick's law for the diffusion of species A through B, where species B is non-diffusing,

$$N_A = \frac{-CD_{AB}}{1-X_A} \frac{dX_A}{dZ} \quad (7)$$

The development of this equation is discussed in Appendix I. If the diffusion coefficient,  $D_{AB}$ , is a function of concentration, then equation (7) could be combined with equation (6) to give, with the assumption of ideal gas behavior,

$$N_A = \frac{-P}{RT} \frac{F(X_A)}{(1-X_A)} \frac{dX_A}{dZ} \quad (8)$$

Equation (8) on integration gives

$$N_A Z = \frac{-P}{RT} \int_{X_{A_1}}^{X_{A_2}} \frac{F(X_A) dX_A}{1-X_A} \quad (9)$$

If diffusion coefficient is not a function of concentration the integration could be immediately carried out to yield equation (3). However it was experimentally observed that for the air-chloroform system diffusion coefficient is a function of concentration. Hence, define a concentration average diffusion coefficient,  $\bar{D}_{AB}$ , which is the average value in the range of concentration between  $X_{A_1}$  and  $X_{A_2}$  and is a constant for fixed values of  $X_{A_1}$  and  $X_{A_2}$ . Using  $\bar{D}_{AB}$  in equation (8) and carrying out the integration analytically yields

$$N_A Z = \frac{P}{RT} \bar{D}_{AB} \ln \frac{1-X_{A_2}}{1-X_{A_1}} \quad (10)$$

Comparing (9) and (10) the defining relationship for concentration average diffusion coefficient is

$$\bar{D}_{AB} \equiv \frac{- \int_{X_{A_1}}^{X_{A_2}} \frac{F(X_A) dX_A}{1-X_A}}{\ln \left( \frac{1-X_{A_2}}{1-X_{A_1}} \right)} \quad (11)$$



### End Effect Corrections

As the gas flows across the open end of the diffusion tube, turbulent eddies are formed. These eddies decrease the diffusion path length by shifting the point of concentration  $X_{A_2}$  closer to the liquid surface. In the present work there are three main factors which affect the turbulence:

1. As the gas density increases, the turbulent eddies penetrate deeper into the mouth of the tube.
2. As the gas velocity increases, the rate of momentum transfer is increased, thereby increasing the turbulence.
3. As the viscosity of the gas increases, turbulence decreases.

No direct correlations of these three factors are available, nor has any attempt been made in the present work to give their relationship.

One other factor which might produce error in the measured diffusivities is the surface tension of the liquid. The formation of the meniscus due to surface tension affects the diffusion path. Molecules evaporating from the center of the liquid surface have to travel a longer distance than those evaporating at the wall.

Wilke (22) has shown that the effect of turbulent eddies on the diffusivity can be accounted for by taking data for several path lengths

and extrapolating to infinite path length. The mathematical treatment of the turbulent eddies is discussed in Appendix II.

### Establishment of Steady State

Concentration profile. Initially a uniform profile exists in the diffusion tube, but as soon as diffusion begins, there is no longer a uniform concentration profile. Thus, it is necessary to determine the magnitude of this transient effect, i. e. , the time required to reach steady state when an initial uniform concentration profile exists. The experiment should be run for such a period of time that the time required for this initial transient effect is negligible compared to the total time.

Lee and Wilke (33) discussed the approach to steady state as determined by Fick's law,

$$\frac{\partial C_A}{\partial \theta} = D_{AB} \frac{\partial^2 C_A}{\partial Z^2} \quad (11)$$

and arrived at the final equation

$$\frac{(N_A)_{\theta = \theta}}{(N_A)_{\theta = \infty}} = 1 - 2e^{-\frac{\pi^2 D \theta}{Z^2}} + 2e^{-\frac{4\pi^2 D \theta}{Z^2}} - 2e^{-\frac{9\pi^2 D \theta}{Z^2}} + \dots \quad (12)$$

Figure 1 represents the transient effect during diffusion of nitrobenzene vapor into air. The values are calculated mathematically. The vaporization rate reaches 99.29 percent of the steady-state value in about 15 minutes.

Altshuller and Cohen (1) have given an empirical approach for calculating the time required to reach steady-state. According to these authors steady-state conditions will be reached within one percent when

$$\theta > \frac{Z^2}{2D_{AB}} \quad (13)$$

where

$\theta$  = time, seconds

$Z$  = diffusion path length, cm

$D_{AB}$  = the actual coefficient,  $\text{cm}^2 / \text{sec}$ .

If the experimental value of diffusivity for the nitrobenzene-air system is substituted in equation (7), the time required is approximately 10 minutes for a path length of 10 cm. This is in good agreement with the value calculated mathematically (Figure 1). In the present work the duration of a run was more than 10 hours; if  $Z$  is 10 centimeters and  $D_{AB}$  is approximately  $0.1 \text{ cm}^2 / \text{sec}$ ,  $\theta$  must be greater than eight minutes. Hence in a run of over 10 hours duration, the effect of the transient period is less than three percent.

Figure from Lee and Wilke (22)

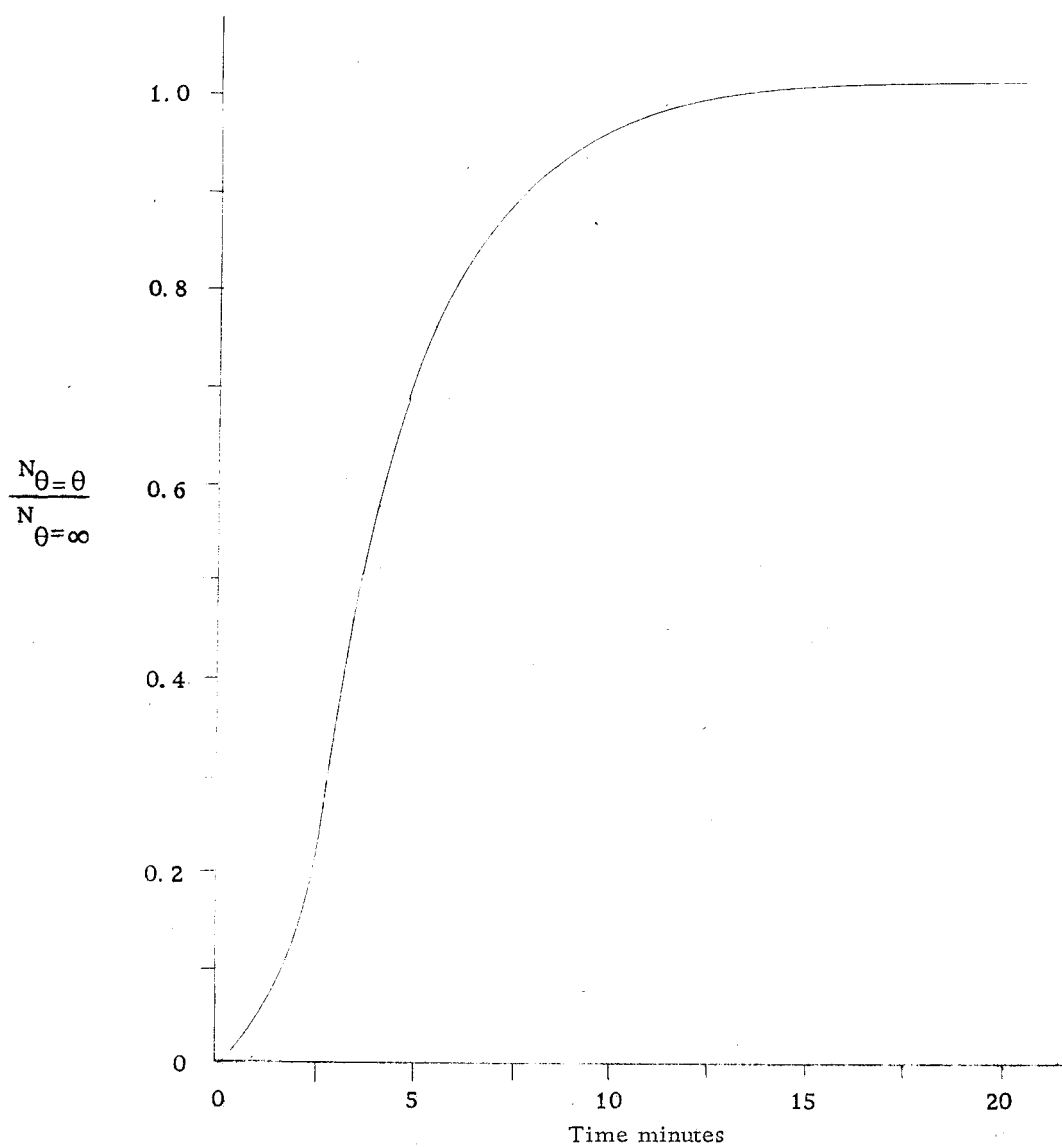


Figure 1. Transient diffusion of the nitrobenzene-air system at 25°C and 1 atmosphere.

Transient heat transfer. Sufficient time should be allowed before the cork is removed from the diffusion tube which was placed in the diffusion cell, so that the liquid in the diffusion tube will attain the bath temperature. It was observed that when the cork was left on the tube for some time, the solvent vapors from the tube condensed on the cork, thereby affecting its weight.

A calculation of the magnitude of the transient effect due to heat transfer indicated that the temperature of the liquid would be within one degree of the bath temperature in approximately two minutes. (See Appendix III.) The magnitude of the error caused by starting a run as soon as the tube was placed in the diffusion cell is less than one percent. Hence it was decided not to attempt to eliminate this small error.

### The Effect of Temperature and Pressure on Diffusion Coefficients

The dependence of the diffusivity on pressure is well established, and it is now agreed that the diffusion coefficient is inversely proportional to the pressure (1, 17, 25). The temperature dependence, on the other hand, is still not completely reconciled. The temperature dependence of diffusivities is expressed as

$$\frac{(D_{AB})_1}{(D_{AB})_2} = \left( \frac{T_1}{T_2} \right)^n \quad (14)$$

where the exponent lies between 1.5 and 2.0 (1). However there is still uncertainty as to exactly what the value of  $n$  will be for a particular system. Application of kinetic theory to a model of rigid molecules leads to the conclusion that the exponent,  $n$ , is equal to 1.5 (1). On the other hand, kinetic theory, using the Lennard-Jones potential for intermolecular forces, as done by Hirschfelder, Curtiss and Bird (17), leads to a temperature dependence of the diffusion coefficient on the quantity  $\frac{\Omega_D}{T^{3/2}}$  where  $\Omega_D$  is a weakly temperature dependent collision integral. Gilliland's equation (15) gives a value of 1.81 for the exponent.

In order to compare the results of the investigators with those measured in this investigation the values obtained at 50°C and 55°C for the air-chloroform and air-methanol systems, respectively, were converted to 25.5°C using collision integrals. The comparative values are tabulated in Discussion of Results.

## EXPERIMENTAL METHODS OF MEASURING DIFFUSION COEFFICIENTS

Various methods for the experimental determination of diffusion coefficients have been devised; the most important are listed below:

### 1. Evaporation of a liquid in a narrow tube

This is essentially an Arnold cell. One of the two components, in the liquid state, is placed in the bottom of a vertical tube. The tube and the liquid are held at a constant temperature and a gas is passed over the top of the tube. The diffusion coefficient is computed from the measured evaporation rate. This is the most widely used method (1, 3, 22), since the method is simple.

### 2. Unsteady-state inter-diffusion of two gases

The unsteady-state diffusion cell was first devised by Loschmidt. The two gaseous components are placed in separate sections of a horizontal tube, and the diffusion is allowed to take place by removing the partition separating the sections. After a known time interval the gases from the various portions of the tube are analyzed and the results compared with an integrated form of the unsteady-state diffusion equation,

$$\frac{\partial C_A}{\partial \theta} = D_{AB} \frac{\partial^2 C_A}{\partial Z^2} \quad (11)$$

in which  $D_{AB}$  is assumed to be a constant. The method involves complex mathematical calculations. This method has been used by Arnold (4), Wilke and Fairbanks (32) and Lonius (23).

### 3. Miscellaneous methods

The diffusion coefficient of iodine in air has been computed by measuring the evaporation rate of small iodine spheres suspended in still air. But this method suffers from the fact that considerable error is involved due to the convection currents set up in the air.

The Arnold method is simple, and the incoming air stream can be saturated at any known temperature by employing an equilibrium cell, thus fixing the concentration in the stream blowing across the top of the Arnold cell. Hence in this project an Arnold cell was used to determine diffusivities. The cell was built by Larson (21) and is fairly similar to the one used by Lee and Wilke (22).



## EXPERIMENTAL APPARATUS

The basic Arnold cell used in this project is the same as that used by Larson (21) with an additional apparatus for providing varying composition in the stream flowing across the top of the diffusion cell. Hence only those parts of the equipment which have been designed by the author will be described thoroughly. A brief description of the set-up designed by Larson is given for completeness.

The diffusion cell (A),<sup>\*</sup> which is made of brass, is mounted in a stainless steel constant temperature bath (B). The bath temperature is maintained to  $\pm 0.002^{\circ}\text{C}$  by a Thermotrol control unit. The diffusion tube is made of type 304 stainless steel and is machined to such a diameter that a tight fit is obtained in the removable diffusion assembly. To allow the incoming gas and vapors to equilibrate with the bath temperature, a forty foot length of 1/8-inch copper tubing (c) is connected to the 3/4-inch entrance of the diffusion cell. A pressure tap is connected to the side of the diffusion cell. A water manometer (O) is connected to this pressure tap through a liquid tap (P) to indicate the pressure in the cell. A copper-constantan thermocouple is mounted on the exit end of the diffusion cell to indicate the temperature of the exit gas. The complete set up of the diffusion cell is shown in Figure 4 .

---

\* Letters refer to designations in Figure 2.

The exit of the diffusion cell is connected to a water condenser (D) and a liquid trap (E). Thus the vapors are condensed before exhausting to the atmosphere through valve (F).

The compressed air from the supply line is passed through a drying tower (G) which is packed three quarters full with anhydrous calcium chloride and one quarter with glass wool. The entrained grease and oil droplets are removed by the glass wool, and the moisture is absorbed by the anhydrous calcium chloride.

The dried air stream is split into two streams, as shown in the flow diagram (Figure 2). One stream is taken to the pressure regulator to maintain a pressure in the reservoir (H) higher than that in the equilibrium cell (J). The other stream is connected to a glass float rotameter (K) through two pressure regulators to help maintain a constant pressure in the equilibrium cell throughout the run. The needle valve is used for finer adjustments of the pressure in the cell.

The equilibrium cell (J) is a piece of four inch brass pipe, eight inches long. The pressure in the cell is indicated by a mercury manometer (L) connected to the inlet tubing of the cell. The inlet of the equilibrium cell is connected to a gas sparger and is soldered to the lid of the equilibrium cell (Figure 3). The outlet is also soldered to the lid, and an entrainment catcher is connected from the inside. A copper-constantan thermocouple is mounted through

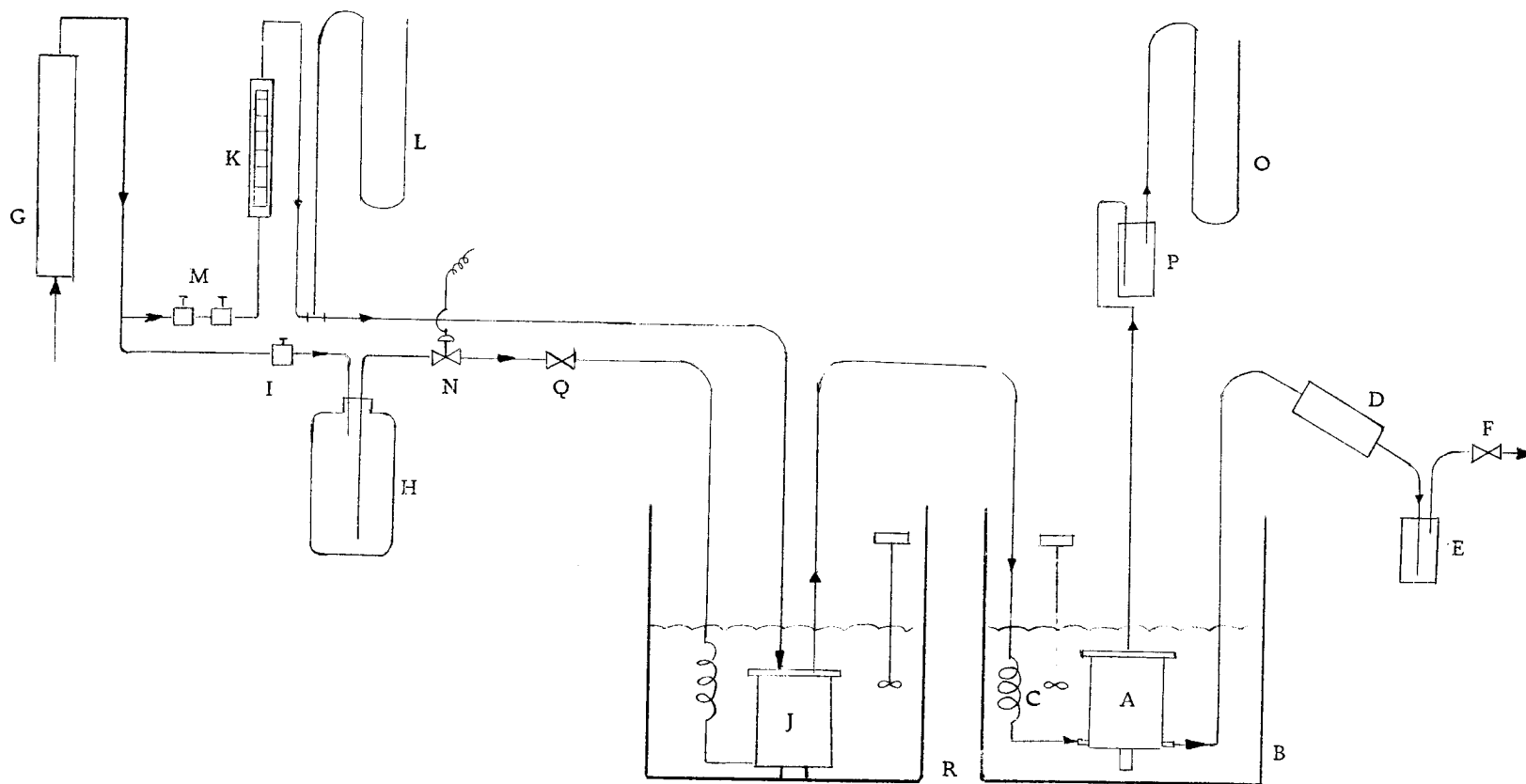


Figure 2. Flow diagram of the experimental apparatus.

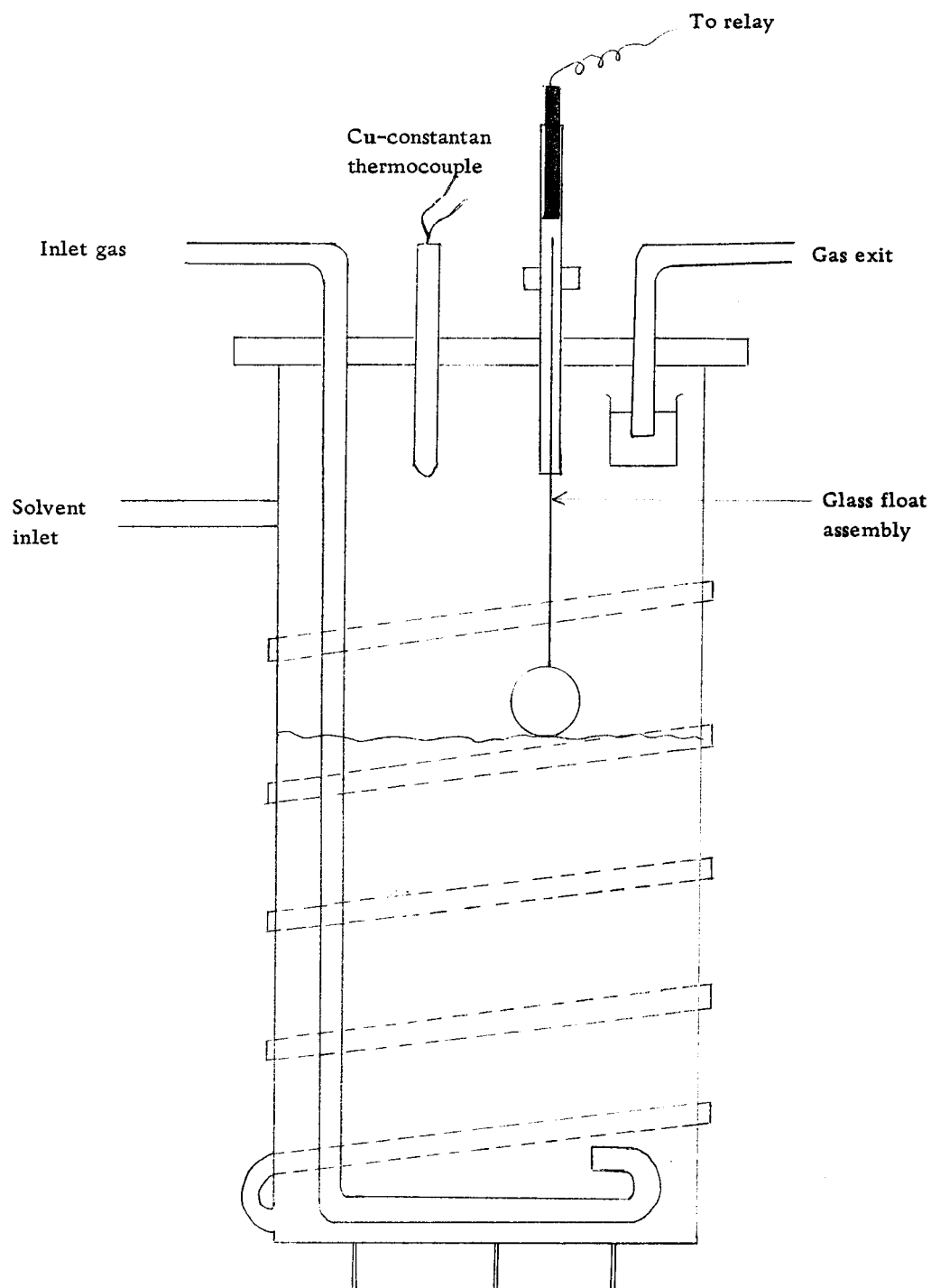


Figure 3. Equilibrium cell.

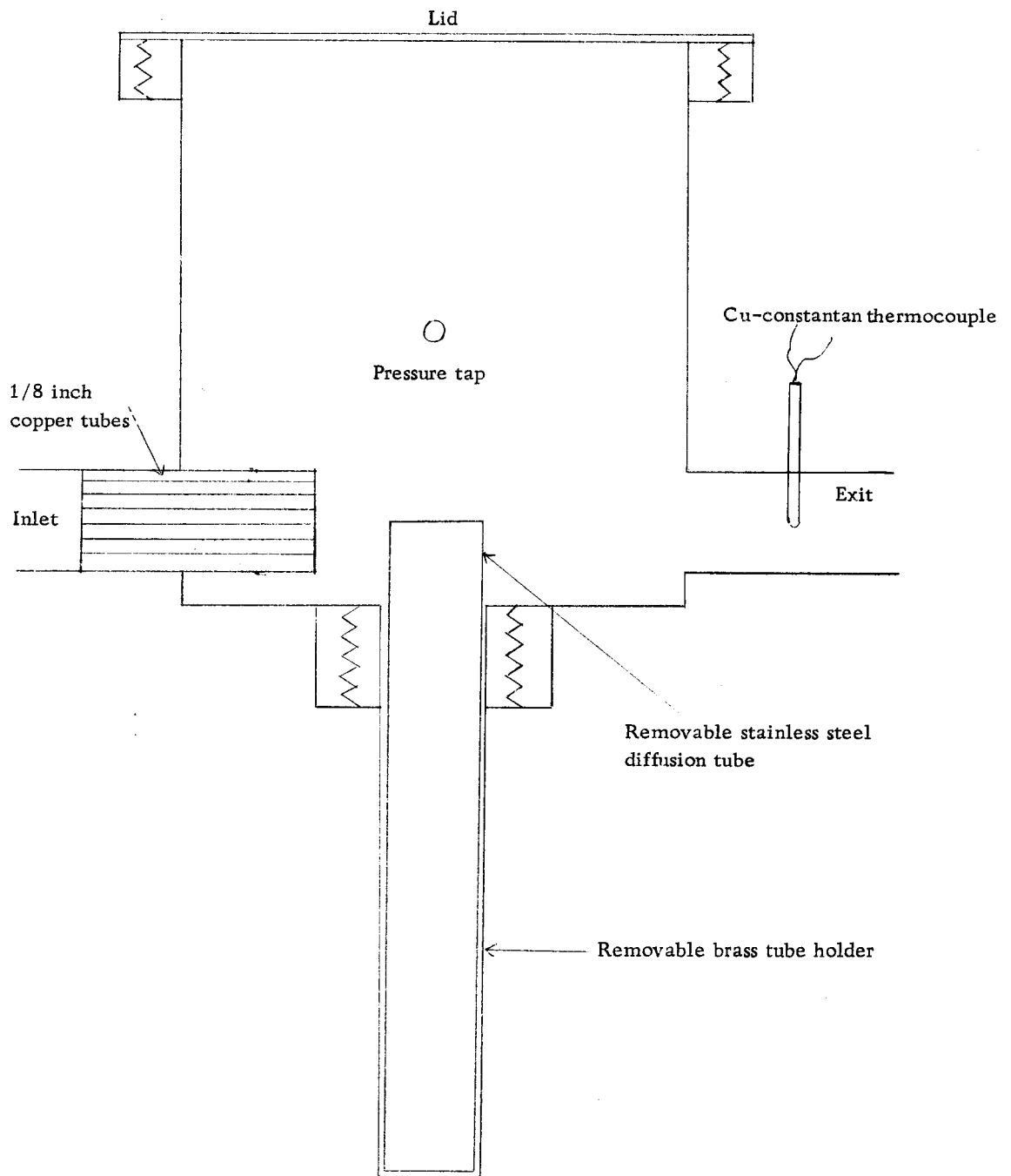


Figure 4. Diffusion cell.

the lid to indicate the temperature of the vapors inside the equilibrium cell. A piece of 1/4-inch copper tubing, one inch long is soldered on the lid and is connected to a 1/4-inch diameter glass tube by means of a Swagelock<sup>\*</sup> fitting. A 3/16-inch brass rod is glued on the top end of the glass tube. The rod serves as a liquid level controlling contact. A cork float assembly is mounted inside this tubing. The complete set-up of the equilibrium cell is shown in Figure 3.

The storage tank is connected to the equilibrium cell through a solenoid valve and a needle valve. An electronic relay system connects the solenoid valve and the liquid-level control probe of the equilibrium cell. The liquid-level control maintains a constant level in the equilibrium cell. When the level is correct, the float rod is in contact with the probe. As the liquid level falls this contact is lost, activating the relay which in turn opens the solenoid valve to allow the solvent level to rise in the equilibrium cell until the float rod touches the probe. By maintaining a constant liquid level in the equilibrium cell the major fluctuations in pressures are eliminated.

The equilibrium cell is housed in a constant temperature bath. The water bath is maintained at any desired temperature by heaters controlled by a mercury thermocontrol. The controller is

---

<sup>\*</sup> Trade name

capable of controlling the temperature of the water bath to  $\pm 0.01^{\circ}\text{C}$ . The inlet and exit copper tubing of the diffusion cell are wound with electrical heating tapes and maintained at  $60^{\circ}\text{C}$ . It was found that the air stream leaving the equilibrium cell was effectively saturated with the liquid in the equilibrium cell at the cell temperature.

At the end of each set of runs a wet test meter is connected at the exit end of valve (F) and the correct flow rate is measured with corrections made for temperature and pressure.

## EXPERIMENTAL PROCEDURE

The diffusion tube was thoroughly cleaned with distilled water and then rinsed with acetone and allowed to dry. It was then rinsed and filled with solvent to the desired level, corked and weighed accurately.

The supply air was passed through the diffusion cell via the equilibrium cell for about five minutes before the beginning of a run. The lid of the diffusion cell was opened and the diffusion tube was inserted. The cork was removed, and the lid was replaced on the diffusion cell. The time was immediately recorded. The water level in the bath, which was about an inch below the lid, was raised by adding water previously heated to within  $\pm 1^{\circ}\text{C}$  of the bath temperature until the whole diffusion cell was under water. The pressure in the diffusion cell, the equilibrium cell temperature, the temperature of the exit end of the diffusion cell, the rotameter reading, room temperature, and atmospheric pressure were all recorded. All these readings were recorded at regular intervals during the course of a run.

At the end of a run the water was drained from the bath to a level below the lid, and then the diffusion tube was removed from the diffusion cell, stoppered immediately and the time recorded. All the other readings were noted at the same time. The tube was then



weighed. Hence the loss in weight of the liquid due to evaporation was determined.

The temperature of the bath (B) was maintained constant at  $50^{\circ}\text{C}$  for the chloroform runs and at  $55^{\circ}\text{C}$  for the methanol runs. The temperature of the bath (R) was varied depending on what concentration of the vapor in the air stream was desired.

At least four runs were taken for each air-stream concentration. For each air-stream concentration the liquid level was varied by adding or removing liquid from the diffusion tube thus varying the diffusion path length. The results were then extrapolated to infinite path length. A Sample Calculation is shown in Appendix V.

The concentration of the vapor in the air stream was evaluated by knowing the saturation temperature, i. e., the bath (R) temperature. Assuming Dalton's law, the mole fraction of the solvent in the air stream is equal to the vapor pressure of the solvent at that temperature divided by total pressure in the cell. To make sure that equilibrium was reached in the equilibrium cell, during early runs the weight loss of the solvent was determined and the partial pressure was calculated using the air flow rate and the weight of solvent lost. It was found that the stream was saturated in the equilibrium cell (Appendix IV).

## RESULTS

The discussion in Appendix II indicates that if the reciprocal of apparent diffusion coefficient,  $\frac{1}{D_a}$ , is plotted against the reciprocal of apparent diffusion path,  $\frac{1}{Z_a}$ , a straight line must be obtained which, if extrapolated to infinite  $Z_a$ , should give the concentration average diffusion coefficient,  $\bar{D}_{AB}$ . Figures (5) and (6) represent such plots for the air-chloroform and air-methanol systems, respectively. The best straight line was determined by the method of least squares. The actual diffusion coefficients at infinite path length are presented in Table I.

It can be seen from the data in Table I that the variation in diffusion coefficients for air-chloroform system in the range of concentration from 0 to 0.5664 was of the order of ten percent, while for air-methanol system in the range of 0 to 0.4734 the concentration variation is only about 1.02 percent.

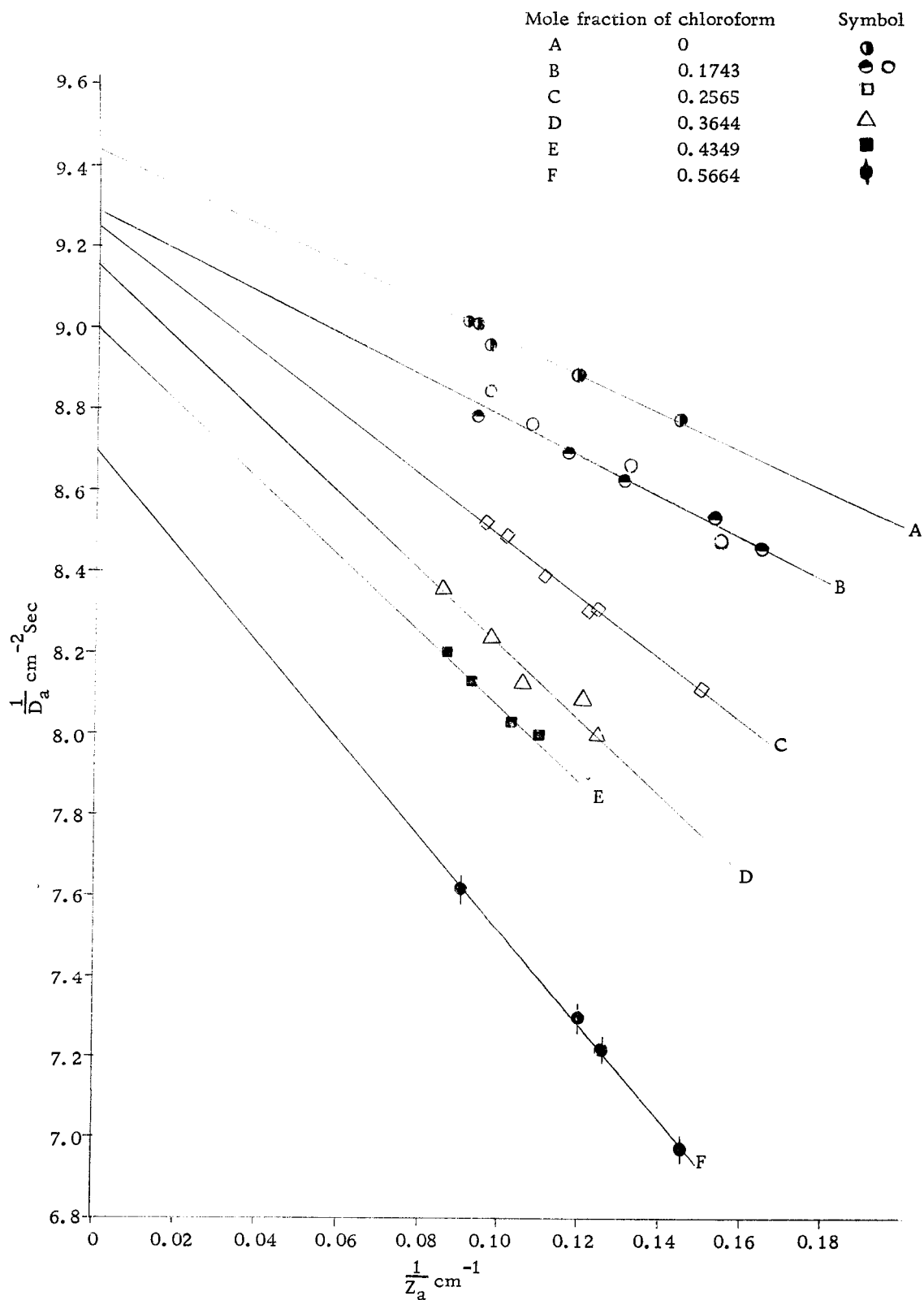


Figure 5. Experimental results for chloroform-air system at 50°C and 1 atmosphere.

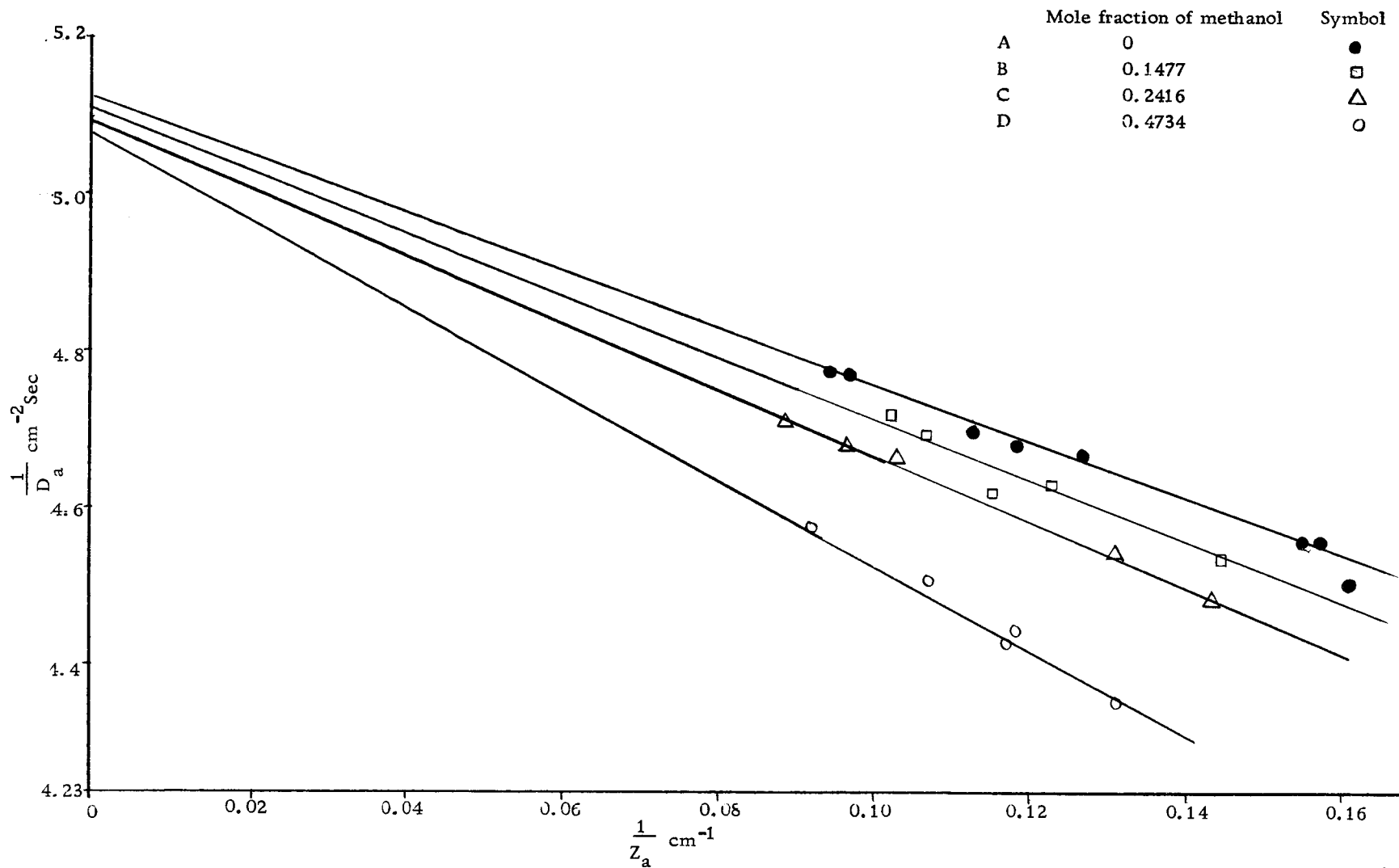


Figure 6. Experimental results for methanol-air system at 55°C and 1 atmosphere.

Table 1. Experimental results.

System	Concentration at liquid surface $X_{A_1}$	Concentration in the air stream $X_{A_2}$	Diffusion Coefficient $\bar{D}_{AB}$ cm <sup>2</sup> / sec
air-chloroform at 50°C and 1 atmosphere	0.6813	0	0.1059
	0.6815	0.1743	0.1073
	0.6817	0.2565	0.1081
	0.6815	0.3644	0.1096
	0.6825	0.4349	0.1110
	0.6829	0.5664	0.1148
air-methanol at 55°C and 1 atmosphere	0.666	0	0.1951
	0.665	0.1477	0.1957
	0.666	0.2416	0.1962
	0.666	0.4734	0.1971

## DISCUSSION OF RESULTS

The concentration average diffusion coefficients, calculated by extrapolating the results to infinite path length, were at 50°C for the air-chloroform system and at 55°C for the air-methanol system. Diffusion coefficients for these systems at these temperatures were not found in literature. Hence the diffusion coefficients for each system at zero concentration in the air stream was converted to the respective values at 25°C using the collision integrals. The values are tabulated in Table 2.

Table 2. Diffusion coefficients at 25.5°C and 1 atmosphere.

System	Present work $\bar{D}_{AB}$ cm <sup>2</sup> /sec	Previous work $D_{AB}$ cm <sup>2</sup> /sec	Investigator(s)
air-chloroform	0.09217	0.09042	Larson (21)
air-methanol	0.1697	0.1620	Othmer (26)

The result for the air-chloroform system was within two percent of the result reported by Larson (21), while for the air-methanol system the variation from the reported values was of the order of 4.5 percent. Larson (21) used the same end effect corrections. Othmer (26) did not indicate whether the values were corrected for eddies and end-effects.

Several additional experiments were carried out for the

chloroform-air system at  $X_{A_2} = 0.174$  in order to check the reproducibility of the results. These experimental points are shown in Figure 5 along with the original determinations at 17.4 percent chloroform. It can be seen that the reproducibility is within approximately one percent (o represents these points in Figure 5).

Since the variation of the diffusion coefficient with the concentration in the air stream for the air-methanol system was only of the order of one percent, no correlation was attempted, since little error would arise in a design calculation if the diffusion coefficient for this system were assumed to be constant with concentration. For the air-chloroform system the variation is of the order of ten percent over the concentration range of 0 to 56 percent, and hence attempts were made to obtain a functional relationship between the diffusion coefficient and the concentration as defined by equation (6).

(1)  $F(X_A)$  is a linear function of mole fraction:

$$F(X_A) = a + bX_A \quad (15)$$

where  $a$  and  $b$  are constants. The concentration average diffusion coefficient,  $\bar{D}_{AB}$ , is defined as

$$\bar{D}_{AB} = \frac{- \int_{X_{A_1}}^{X_{A_2}} \frac{F(X_A) dX_A}{1-X_A}}{\ln \left( \frac{1-X_{A_2}}{1-X_{A_1}} \right)} \quad (11)$$

Substituting equation (15) into (11) and integrating over the concentration range yields,

$$\bar{D}_{AB} = (a + b) + \frac{b(X_{A_2} - X_{A_1})}{\ln \left( \frac{1 - X_{A_2}}{1 - X_{A_1}} \right)} \quad (16)$$

The experimental data gives  $\bar{D}_{AB}$  as a function of  $X_{A_2}$  for constant pressure, temperature and  $X_{A_1}$ . According to equation (16) if these experimental values of  $\bar{D}_{AB}$  are plotted against

$$\frac{X_{A_2} - X_{A_1}}{\ln \left( \frac{1 - X_{A_2}}{1 - X_{A_1}} \right)} \quad \text{a straight line should result. However, as shown in}$$

Figure 7, it was found that this linear relationship holds upon

$X_{A_2} = 0.3$  and not beyond that concentration. Hence the linear relationship assumed does not hold at all concentrations.

(2) Form suggested by Amdur and Schatzki (2, See equation 2, page 3):

$$\text{Define } F(X_A) = a + \frac{bX_A}{1+X_A} \quad (17)$$

Substitute (17) in (11) and integrate to get,



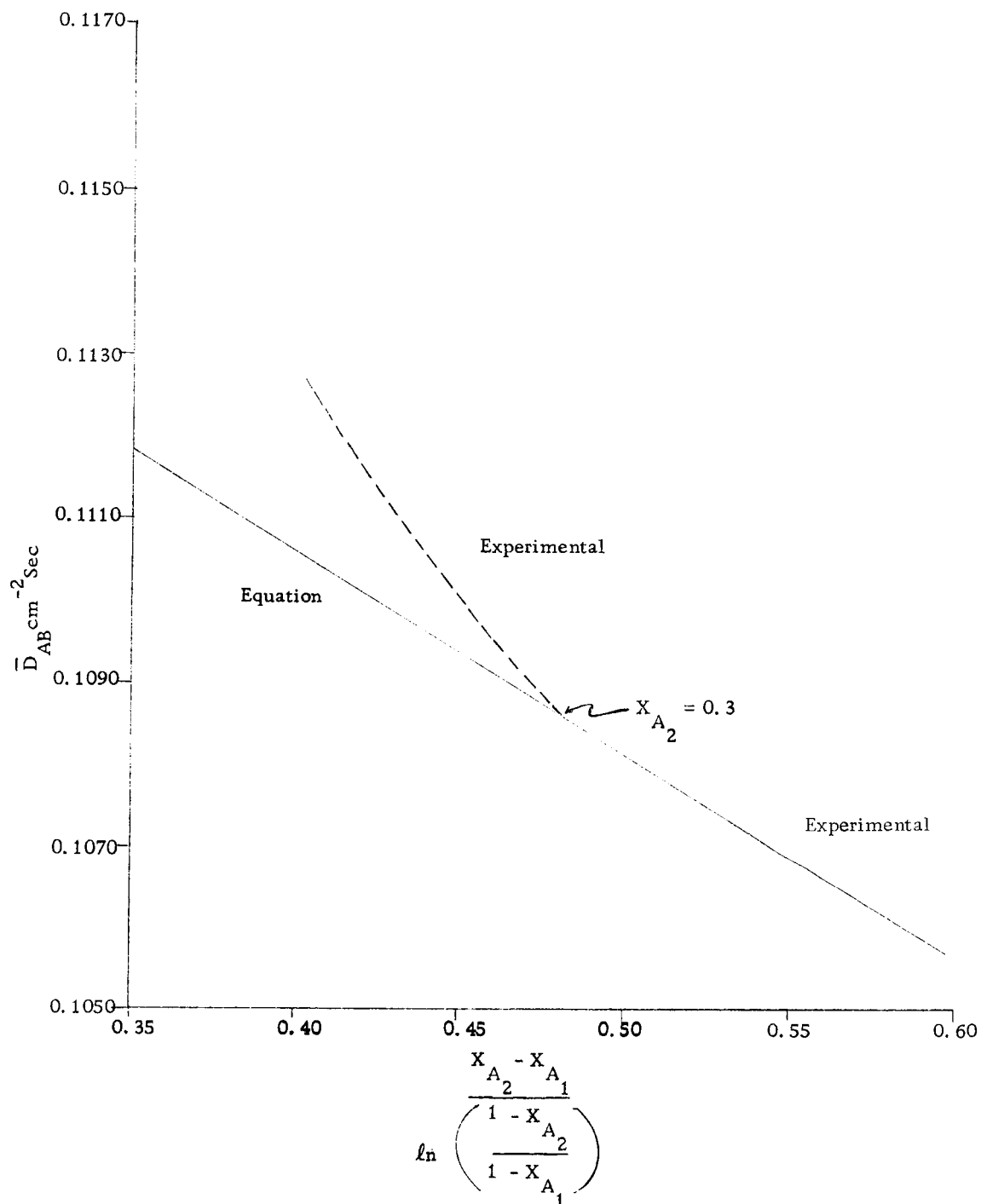


Figure 7. Variation of diffusion coefficient as a linear function of mole fraction for chloroform-air system at 50°C and 1 atmosphere.

$$\bar{D}_{AB} = \left( \frac{1}{2} b - a \right) - \frac{\frac{1}{2} b \ln\left(\frac{1 + X_{A2}}{1 + X_{A1}}\right)}{\ln\left(\frac{1 - X_{A2}}{1 - X_{A1}}\right)} \quad (18)$$

From equation (18), a plot of  $\bar{D}_{AB}$  vs

$$\frac{\frac{\ln\left(\frac{1 + X_{A2}}{1 + X_{A1}}\right)}{1 - X_{A2}}}{\ln\left(\frac{1 - X_{A2}}{1 - X_{A1}}\right)}$$

should give a straight line. No linear relation was observed. Hence the assumed function was incorrect.

(3)  $F(X_A)$  is a quadratic function of mole fraction:

Define

$$F(X_A) = a + bX_A + cX_A^2 \quad (19)$$

Substituting equation (19) into equation (11) and integrating we get,

$$\bar{D}_{AB} = (a+b+c) + (b+c) \frac{(X_{A2} - X_{A1})}{\ln\left(\frac{1 - X_{A2}}{1 - X_{A1}}\right)} + \frac{c}{2} \frac{X_{A2}^2 - X_{A1}^2}{\ln\left(\frac{1 - X_{A2}}{1 - X_{A1}}\right)} \quad (20)$$

Constants  $a$ ,  $b$  and  $c$  are redefined as

$$a + b + c = A \quad (21)$$

$$b + c = B \quad (22)$$

$$\frac{c}{2} = C' \quad (23)$$

Substitution of (21), (22), and (23) into (20) yields

$$\bar{D}_{AB} = A + B \frac{X_{A_2} - X_{A_1}}{\ln \frac{1-X_{A_2}}{1-X_{A_1}}} + C' \frac{X_{A_2}^2 - X_{A_1}^2}{\ln \left( \frac{1-X_{A_2}}{1-X_{A_1}} \right)} \quad (24)$$

The experimental data give six sets of values of  $\bar{D}_{AB}$  corresponding to six sets of values of  $X_{A_1}$  and  $X_{A_2}$ . The method of regression was used to find the best possible values of A, B, and C'; the calculations were done on an IBM 1620 digital computer. Then equation (19) is given by,

$$F(X_A) = (0.10296) - (0.0349) X_A + (0.0853) X_A^2 \quad (25)$$

By definition, the point value of the diffusion coefficients is given by equation (6)

$$D_{AB} = F(X_A) \quad (6)$$

From equation (6) and (25) we get

$$D_{AB} = (0.10296) - (0.0349) X_A + (0.0853) X_A^2 \quad (26)$$

The calculated values from equation (26) fit within one percent to

experimental value. Figure 8 is a plot of  $D_{AB}$  vs  $X_A$ . As can be seen there is a minima in the curve. To determine whether the minima was due to a molecular weight effect, a new function was defined in terms of mass fractions, thus including the molecular weight.

(4)  $F(\omega_A)$  is a quadratic function of weight fraction:

$$F(\omega_A) = a + b\omega_A + c\omega_A^2 \quad (27)$$

where

$$\omega_A = \frac{X_A M_A}{X_A M_A + X_B M_B} = \text{weight fraction} \quad (28)$$

Equation (27) is analogous to equation (6), the difference being that the function is defined in terms of weight fraction,  $\omega_A$ . Substituting (28) into (27) and using this equation in equation (11) the integration is carried out. The coefficients  $a$ ,  $b$ , and  $c$  were then determined using regression methods. The function obtained is

$$F(\omega_A) = (0.1422) + (0.0017)\omega_A + (0.0181)\omega_A^2 \quad (28)$$

The calculated values from equation (28) fit the experimental value within one percent.  $F(\omega_A)$  gives the point value of the diffusion coefficient for a given  $\omega_A$ . The values are plotted in Figure 9.

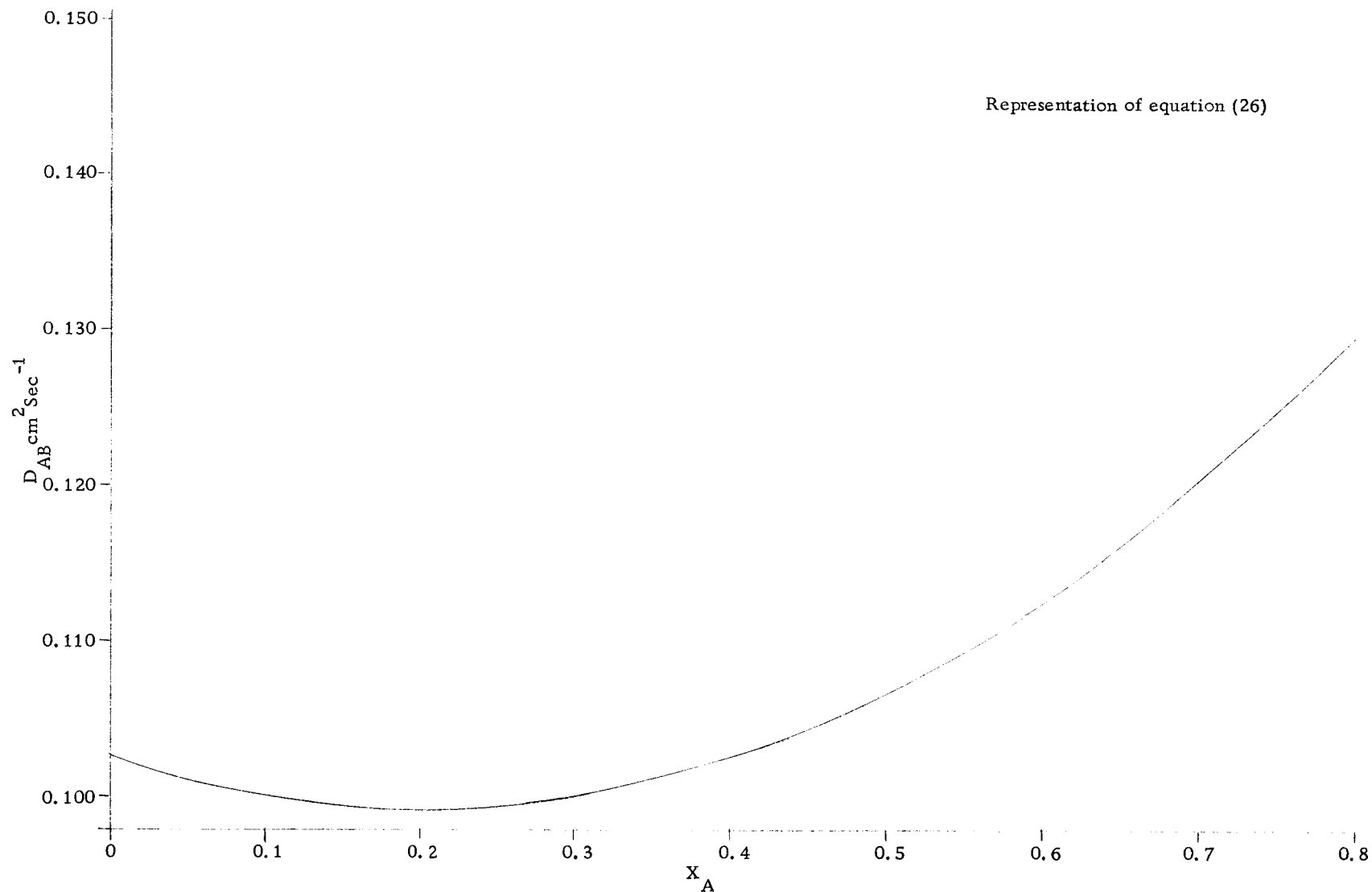


Figure 8. Variation of diffusion coefficient as a quadratic function of mole fraction for chloroform-air system at 50°C and 1 atmosphere.

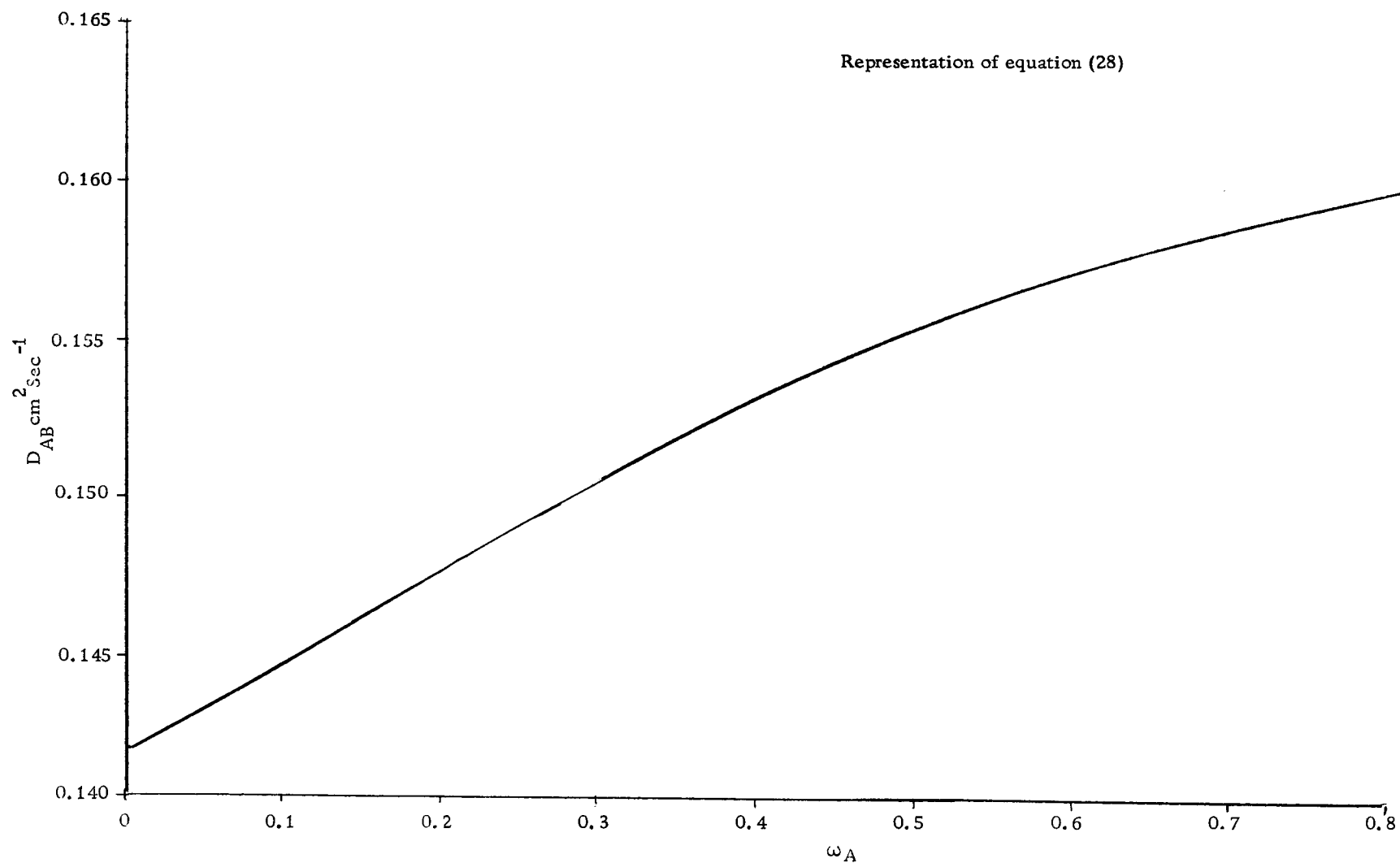


Figure 9. Variation of diffusion coefficient as a quadratic function of weight fraction for chloroform-air system at 50°C and 1 atmosphere

## Conclusion

Schäfer et al. (28) have shown experimentally that the difference in molecular weights of the two diffusing species has a pronounced effect on the variation of diffusion coefficient with concentration. A definite conclusion that can be derived from their work is that the diffusion coefficient becomes more dependent on the concentration of the heavier gas as the difference in molecular weight of the two diffusing species increases. Analyzing the present work from this standpoint, it is clear that the dependency of diffusion coefficient is more in chloroform-air system than methanol-air system, since in the former case the difference in molecular weight is 90 while in the latter case it is only 3. The curve (Figure 9) obtained for the chloroform-air system by plotting  $D_{AB}$  vs  $\omega_A$  is similar to the curves Schäfer et al. have presented in their paper. Thus it is concluded that the stronger dependency of diffusion coefficient on concentration in chloroform-air system than in methanol-air system is due to molecular sizes of the diffusing species.

From the analysis of the different functional relationships to predict the concentration dependency of the diffusion coefficients, it is concluded that the quadratic form of the equation in weight fraction (equation (27)) is the best possible correlation.

## RECOMMENDATIONS

It is recommended that further data be taken for systems in which the two components have large difference in molecular weights. In this manner, it can then be ascertained whether the form of the correlation given by equation (28) is generally useful. In addition, such factors as molecular size and intermolecular forces should be investigated.



## BIBLIOGRAPHY

1. Altshuller, A. P. and T. R. Cohen. Application of diffusion cells to the production of known concentrations of gaseous hydrocarbons. *Analytical Chemistry* 32:802-810. 1960.
2. Amdur, I. and T. F. Schatzki. Composition dependence of diffusion coefficient in the system A - X<sub>e</sub>. *Journal of Chemical Physics* 29:1425-1426. 1958.
3. Andrews, S. P. S. A simple method of measuring gaseous diffusion coefficients. *Chemical Engineering Science* 4:269-272. 1955.
4. Arnold, J. H. Studies in diffusion: I. Estimation of diffusibility in gaseous systems. *Industrial and Engineering Chemistry* 22:1091-1095. 1930.
5. \_\_\_\_\_. Unsteady-state vaporisation and absorption. *Transactions of the A.I.Ch.E.* 40:361-378. 1944.
6. Berry, V. J. and R. C. Koeller. Diffusion in compressed binary gaseous systems. *A.I.Ch.E. Journal* 6:275-280. 1960.
7. Bird, R. B., W. E. Stewart and E. N. Lightfoot. *Transport phenomena*. London, Wiley, 1960. 780 p.
8. Carslaw, H. S. *Introduction to mathematical theory of heat in solids*. 2d ed. New York, Dover, 1945. 510p.
9. Chemical Rubber Company. *Handbook of Chemistry and Physics*. 40th ed. Cleveland, Ohio, 1958. 3456 p.
10. Cummings, G. A. McD. and A. R. Ubbelohde. Collision diameters of flexible hydrocarbon molecules in the vapor phase. *Journal of the Chemical Society*, 1953, p. 3751-3755.
11. Cummings, G. A. McD., E. McLaughlin and A. R. Ubbelohde. Collision parameters of C<sub>6</sub>-C<sub>9</sub> hydrocarbons in the vapor phase: the hydrogen effect. *Journal of the Chemical Society*, 1955, p. 1141.

12. Fair, J. R. and B. J. Lerner. A generalized correlation of diffusion coefficients. A.I.Ch.E. Journal 2:13-18. 1956.
13. Foust, A. S. et al. Principles of unit operations. New York, Wiley, 1960. 578 p.
14. Gambil, W. R. Predict diffusion coefficients. Chemical Engineering 65:125. June 2, 1958.
15. Gilliland, E. R. Diffusion coefficients in gaseous systems. Industrial and Engineering Chemistry 26:681-685. 1934.
16. Guryunova, N. A. and E. V. Kuvshinskii. The determination of the diffusion coefficients of the vapors of cyclohexane, chloroform and acetone in air. Zhurnal Tekhnicheskoi Fiziki 18:1421-1425. 1948. (Tr. by James R. Divine, Chemical Engineering Dept., Oregon State University, 1963)
17. Hirschfelder, J. O., C. F. Curtiss and R. B. Bird. Molecular theory of gases and liquids. New York, Wiley, 1954. 1219 p.
18. Hirschfelder, J. O., R. B. Bird and E. L. Spotz. Transport properties of gases and gaseous mixtures. II. Chemical Reviews 44:205-231. 1949.
19. Jeans, J. H. Dynamical theory of gases. 4th ed. New York, Dover, 1954. 444 p.
20. Jordan, T. E. Vapor pressure of organic compounds. New York, Interscience, 1954. 266 p.
21. Larson, Edward M. Diffusion coefficients of chlorinated hydrocarbons in air. Master's thesis. Corvallis, Oregon State University, 1963. 42 numb. leaves.
22. Lee, C. Y. and C. R. Wilke. Measurement of vapor diffusion coefficient. Industrial and Engineering Chemistry 46:2381-2387. 1954.
23. Lonius, Anton. Dependence of gas diffusion coefficient on the mixing ratio. Oak Ridge, Tenn., 1963. 14 p. (Atomic Energy Commission Publication AEC-TR-5938; translated from Annalen der Physik) (microcard)

24. McAdams, W. H. Heat transmission. 3rd ed. New York, McGraw Hill, 1954. 532 p.
25. Othmer, D. F. New generalized equations of gas diffusion coefficients. Journal of Chemical and Engineering Data 7:37-41. 1962.
26. Othmer, Donald F. and Hung Tsung Chen. Correlating diffusion coefficients in binary gas systems. Journal of Chemical and Engineering Data 7:249-254. 1962.
27. \_\_\_\_\_. Correlating diffusion coefficients in binary gas systems. Industrial and Engineering Chemistry: Process design and Development. 1:249-254. 1962.
28. Perry, J. H. Chemical engineers' handbook. 4th ed. New York, McGraw-Hill. 1963.
29. Reid, R. C. and T. K. Sherwood. Properties of gases and liquids. New York, McGraw-Hill, 1958. 386 p.
30. Schäfer, K., H. Corte and H. Moesta. Über die Messung der Temperatur und Konzentrations--abhängigkeit des Diffusions Koeffizienten von Gasen. Zeitschrift für Electrochemie und Angewandte Physikalische Chemie. 55:662-664, 1951.
31. Stull, D. R. Vapor pressures of pure substances: organic compounds. Industrial and Engineering Chemistry. 39:517-550. 1947.
32. Wilke, C. R. and D. F. Fairbanks. Diffusion coefficient in multi-component gas mixtures. Industrial and Engineering Chemistry 42:471-475. 1950.
33. Wilke, C.R. and C.Y. Lee. Measurement of vapor diffusion coefficients of gases and vapors. Industrial and Engineering Chemistry 47:1253. 1955.

## NOMENCLATURE

$a, b, c, A, B, C'$	- constants	
$C$	- molar concentration of gas mixture	$\frac{\text{gm moles}}{\text{liter}}$
$C_{12}^*$	- function of temperature and inter-molecular potential	
$C_p$	- specific heat of the liquid	$\frac{\text{Btu}}{\text{lbm } ^\circ\text{F}}$
$Da$	- apparent diffusion coefficient	$\text{cm}^2/\text{sec}$
$D_{AB}$	- diffusion coefficient of A through B	$\text{cm}^2/\text{sec}$
$\bar{D}_{AB}$	- concentration average diffusion coefficient defined by equation (11)	$\text{cm}^2/\text{sec}$
$f_d$	- concentration dependent function defined by equation (2)	
$F(X_A)$	- a concentration dependent function of diffusing species A	
$g$	- acceleration due to gravity	$\frac{\text{ft}}{\text{hr}^2}$
$h$	- heat transfer coefficient on the liquid side in the diffusion tube	$\frac{\text{Btu}}{\text{hr ft}^2 ^\circ\text{F}}$
$k_f$	- thermal conductivity of the liquid at the film temperature	$\frac{\text{Btu}}{\text{hr ft } ^\circ\text{F}}$
$L$	- length of the diffusion tube	cm
$\ell$	- length of the liquid column in the tube	cm

$m_1, m_2$	- molecular weight of species 1 and 2	
$M_A, M_B$	- molecular weight of species A and B	
$n$	- exponent in heat-transfer correlation	
$N_A$	- diffusion flux of A	$\frac{\text{gm moles}}{\text{sec cm}^2}$
$N_B$	- diffusion flux of B	$\frac{\text{gm moles}}{\text{sec cm}^2}$
$P_d$	- diffusion cell pressure	mm Hg
$P_e$	- equilibrium cell pressure	mm Hg
$p$	- partial pressure of diffusion species	mm Hg
$P$	- total pressure of the system	mm Hg
$P_s$	- vapor pressure of the liquid	mm Hg
$P_{\text{atm}}$	- atmospheric pressure	mm Hg
$R$	- gas constant	$\frac{(\text{mmHg})(\text{liter})}{\text{gm mole } ^\circ\text{K}}$
$S$	- cross sectional area of the diffusion tube	$\text{cm}^2$
$T$	- temperature	$^\circ\text{K}$
$T_{L_i}$	- initial temperature of the liquid	$^\circ\text{K}$
$T_{L_f}$	- final temperature of the liquid	$^\circ\text{K}$
$T_s$	- temperature of the diffusion tube wall	$^\circ\text{R}$
$T_d$	- diffusion cell temperature	$^\circ\text{K}$
$T_e$	- equilibrium cell temperature	$^\circ\text{K}$

$\omega_A$	- weight fraction of the diffusing species	
$w$	- weight of the liquid taken in the tube for a run	gm
$W_A$	- weight of A evaporated	gm
$W_L$	- weight of diffusion tube and liquid	gm
$X_A$	- mole fraction of A	
$X_{A_1}$	- mole fraction of A at the surface of the liquid in the diffusion tube	
$X_{A_2}$	- mole fraction of A at the mouth of the diffusion tube	
$X_B$	- mole fraction of B	
$Z, Z_1, Z_2$	- distance along diffusion path	cm
$Z_a$	- apparent diffusion path length	cm
$\Delta Z$	- correction due to end effects	cm
$\beta_f$	- coefficient of cubical expansion	$\frac{1}{^\circ\text{F}}$
$\theta$	- diffusion time	sec
$\rho_A$	- density of liquid at film temperature	$\text{gm/cm}^3$
$\mu$	- viscosity of the liquid at film temperature	$\frac{\text{lbm}}{\text{ft hr}}$
$\Phi$	- $\frac{k_f}{L} (0.13) \left[ \frac{L^3 \rho_f^2 g \beta C_p}{\mu_f k_f} \right]^{1/3}$	$\frac{\text{Btu}}{\text{hr ft}^2}$
$\Omega_D$	- collision integral for diffusion	

## APPENDICES

## APPENDIX I

### DERIVATION OF PERTINENT MASS-TRANSFER EQUATIONS



Fick's first law governing the diffusion of species A into species B, with respect to fixed spatial coordinates, can be written as (7)

$$N_A = X_A (N_A + N_B) - CD_{AB} \nabla X_A \quad (29)$$

A mass balance on each component gives

$$\frac{dN_A}{dZ} = 0 \quad (30)$$

$$\frac{dN_B}{dZ} = 0 \quad (31)$$

If species B is insoluble in A, then from (30) and (31)  $N_B$  is zero for all values of  $Z$ .

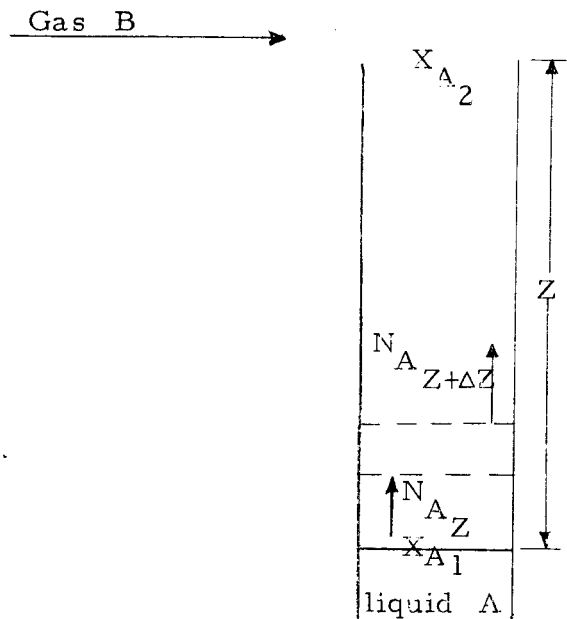


Figure 10. Diffusion model for diffusion of A through stagnant B.

Equation (29) can then be written as

$$N_A = \frac{-CD_{AB}}{1-X_A} \frac{dX_A}{dZ} \quad (32)$$

Under steady state conditions where temperature, pressure,  $X_{A_1}$  and  $X_{A_2}$  are constant,  $N_A$  and  $D_{AB}$  are fixed

$$\frac{1}{1-X_A} \frac{dX_A}{dZ} = C_1 \quad (33)$$

where  $C_1$  is a constant.

Integrate (33) with the boundary conditions at

$$Z = Z \quad X_A = X_{A_1} \quad (34)$$

$$Z = 0 \quad X_A = X_{A_2} \quad (35)$$

to get

$$C_1 = \frac{\ln \frac{1-X_{A_1}}{1-X_{A_2}}}{Z} \quad (36)$$

Equation (36) can then be substituted into equation (33) to give

$$\frac{dX_A}{dZ} = \frac{1-X_A}{Z} \ln \left( \frac{1-X_{A_1}}{1-X_{A_2}} \right) \quad (37)$$

Equation (37) is substituted into equation (32) to get

$$N_A = \frac{CD_{AB}}{Z} \ell n \frac{1-X_{A2}}{1-X_{A1}} \quad (38)$$

With the assumption of ideal gases,  $C = \frac{P}{RT}$ , and  $N_A$  can be expressed as  $\frac{WA}{\theta SM_A}$ , we then get

$$D_{AB} = \frac{W_A RT Z}{\theta S P M_A} \ell n \frac{1-X_{A1}}{1-X_{A2}} \quad (5)$$

For an apparent value of diffusion path,  $Z_a$ , we get a value of the apparent diffusion coefficient using equation (5). The concentration average diffusion coefficient (which is defined in equation (11)) is obtained by extrapolating the result to infinite path length.

## APPENDIX II

### CORRELATION TO END-EFFECTS

Lee and Wilke's (22) Treatment on End Effect Correction to Mass-Transfer

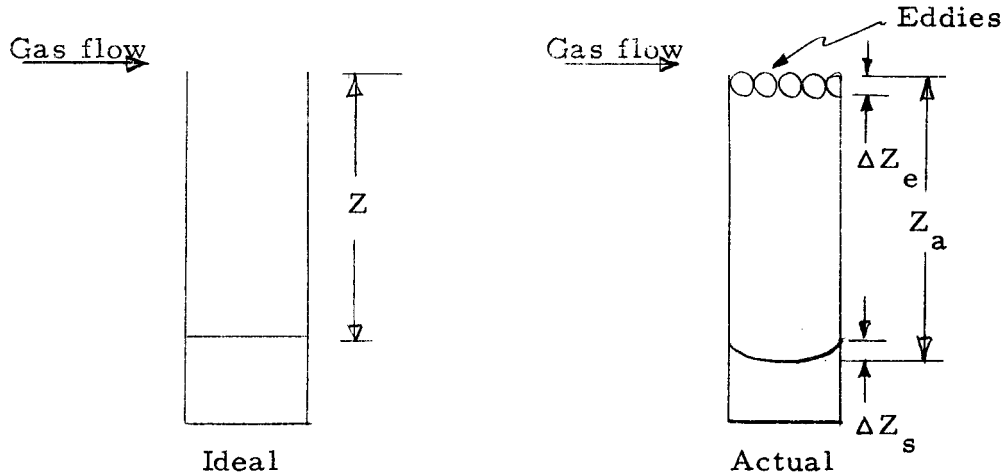


Figure 11. Model for end effect corrections.

The above figure indicates the effective diffusion path in relation to the apparent path; the difference is caused by turbulence.

The effective average diffusion path is given by

$$Z = Z_a - \Delta Z_s - \Delta Z_e = Z_a - \Delta Z \quad (39)$$

where

$Z$  is the effective diffusion path

$Z_a$  is the apparent diffusion path

$\Delta Z_c$  and  $\Delta Z_s$  are the effects of turbulence on the diffusion path at the mouth of the tube and the effect of liquid meniscus at the liquid level, respectively.

In terms of the apparent diffusion coefficient  $D_a$ , equation (38) may be rewritten as

$$N_A = \frac{PD_a}{RTZ_a} \ln \frac{1-X_{A2}}{1-X_{A1}} \quad (38)$$

But,

$$N_A = \frac{P\bar{D}_{AB}}{RT(Z_a - \Delta Z)} \ln \left( \frac{1-X_{A2}}{1-X_{A1}} \right) \quad (40)$$

Combination of the equations (38) and (40) yields

$$\frac{1}{D_a} = -\frac{\Delta Z}{\bar{D}_{AB}} \frac{1}{Z_a} + \frac{1}{\bar{D}_{AB}} \quad (41)$$

Equation (41) is the equation of a straight line with a slope of  $-\frac{\Delta Z}{\bar{D}_{AB}}$

and intercept of  $\frac{1}{\bar{D}_{AB}}$ . Hence if  $\frac{1}{D_a}$  is plotted against  $\frac{1}{Z_a}$

and extrapolated to infinite path length, the intercept is the reciprocal of the diffusion coefficient,  $\bar{D}_{AB}$ .

### APPENDIX III

#### TRANSIENT HEAT-TRANSFER EFFECT

McAdams (24) recommends the following equation for calculating the heat transfer coefficient for liquids in the laminar flow range for natural convection:

$$\frac{hL}{k_f} = 0.59 \left[ \frac{\ell^3 \rho_A^2 g \beta_f \Delta T}{\mu_f^2} \left( \frac{C_p \mu}{k} \right)_f \right]^{1/4} \quad (42)$$

The properties of the liquids (chloroform and methanol) are found from Perry (28). The properties are listed in Table 3 below, with appropriate units to be used in equation (42).

Table 3. Properties of chloroform and methanol.

Property	Units	Chloroform	Methanol
density $\rho_A$	$\frac{\ell \text{ b m}}{\text{ft}^3}$	93	49.5
acceleration due to gravity, $g$	$\frac{\text{ft}}{\text{hr}^2}$	$4.17 \times 10^8$	$4.17 \times 10^8$
coefficient of cubical expansion, $\beta$	$\frac{1}{F}$	$6.5 \times 10^{-4}$	$6.5 \times 10^{-4}$
viscosity, $\mu$	$\frac{\ell \text{ b m}}{\text{ft hr}}$	1.2095	1.2095
specific heat, $C_p$	$\frac{\text{Btu}}{\ell \text{ b m } F}$	0.233	0.338
thermal conductivity, $k$	$\frac{\text{Btu}}{\text{hr ft } F}$	0.08	0.124
length of liquid column, $\ell$	ft	0.3281	0.3281
maximum film temperature	F	44	54



Using equation (42) and the properties from Table 3 we get,

$$\text{for the chloroform-air system } h = 36.0 \frac{\text{Btu}}{\text{hr ft}^2 \text{ } ^\circ\text{F}}, \quad \text{and}$$

$$\text{for the methanol-air system } h = 27.9 \frac{\text{Btu}}{\text{hr ft}^2 \text{ } ^\circ\text{F}}$$

A heat balance on a fluid element gives,

$$h (T_S - T_L) A = w C_p \frac{dT_L}{d\theta} \quad (43)$$

where

$w$  = weight of the liquid,  $\ell\text{bm}$

$C_p$  = specific heat of the liquid  $\frac{\text{Btu}}{\ell\text{bm } ^\circ\text{F}}$

$A$  = surface area of the tube where heat transfer is taking place  $= 3.20 \times 10^{-2} \text{ ft}^2$

$T_S, T_L$  = tube surface temperature and liquid temperature

Considering the fluid properties at the given temperature to be constant the heat transfer coefficient in equation (42) can be redefined as

$$h = \Phi \Delta T^n \quad (44)$$

where

$$\Phi = \frac{k_f}{L} (0.59) \left[ \frac{L^3 \rho_A^2 g \beta C_p}{\mu_f k_f} \right]^{1/4}$$

$$n = 1/4$$

$$\Delta T = T_S - T_L$$

$$\text{For the chloroform-air system} \quad \Phi = 13.75 \frac{\text{Btu}}{\text{hr ft}^2}$$

$$\text{For the methanol-air system} \quad \Phi = 12.2 \frac{\text{Btu}}{\text{hr ft}^2}$$

Substituting equation (44) into equation (43) and integrating we get,

$$\theta = \frac{wC}{n\Phi A} \left[ \frac{1}{(T_S - T_{L_f})^n} - \frac{1}{(T_S - T_{L_i})^n} \right] \quad (45)$$

where

$T_{L_i}$  = initial temperature of the liquid, °F

$T_{L_f}$  = final temperature of the liquid, °F

$T_S$  = surface temperature of the tube, °F

From equation (45), assuming the final temperature of the liquid approaches within 1° F of the bath temperature, a calculation of time to reach this temperature yields,

$$\theta = 1.78 \text{ minute for the chloroform-air system}$$

and

$$\theta = 1.61 \text{ minute for the methanol-air system .}$$

## APPENDIX IV

### DIFFUSION PATH AND EQUILIBRIUM CALCULATIONS

### Calculation of the Diffusion Pathlength

In the calculation of diffusion coefficients the arithmetic average of the initial and final path lengths has been used. The following discussion proves that the arithmetic average is a rigorous value of the diffusion path in this particular case.

Consider the model given in Figure 12.

$$N_A = \frac{CD_{AB}}{Z} \ln \frac{1-X_{A_2}}{1-X_{A_1}} \quad (38)$$

Assume that the liquid level falls slowly so that at the end of the time  $\theta$  the level is indicated by  $Z_2$  as shown in Figure 12.

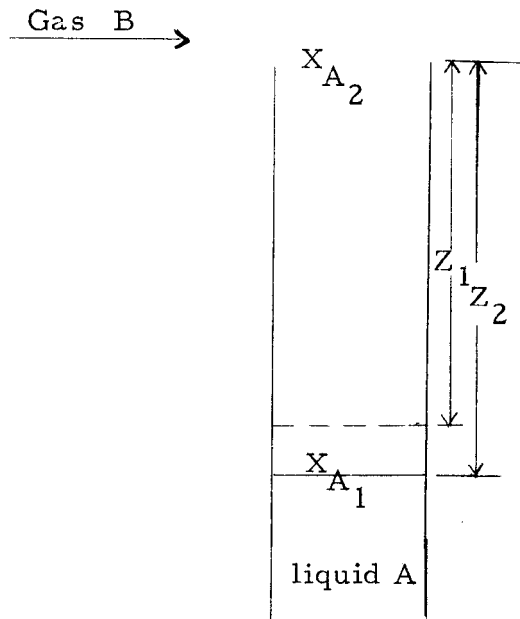


Figure 12. Model for diffusion path.

The molar flux,  $N_A$ , is related to the rate at which the liquid level falls by

$$N_A = -\rho_A \frac{dZ}{d\theta} \quad (39)$$

where  $\rho_A$  is the molar density of the liquid.

Equation (39) is substituted into equation (38) to get

$$\rho_A \frac{dZ}{d\theta} = \frac{PD_{AB}}{RTZ} \ln \frac{1-X_{A2}}{1-X_{A1}} \quad (40)$$

Separate variables, integrate with limits from  $\theta$  to 0 to  $\theta = \theta$  and from  $Z = Z_1$  to  $Z = Z_2$ , and rearrange to get,

$$D_{AB} = \frac{RT}{P\theta} \frac{\rho_A \left( \frac{Z_2^2 - Z_1^2}{2} \right)}{\ln \left( \frac{1-X_{A2}}{1-X_{A1}} \right)} \quad (41)$$

If the diffusion path length is taken as the arithmetic average of initial and final paths, then equation (38) can be written as

$$N_A = \frac{PD_{AB}}{RT} \frac{\ln \left( \frac{1-X_{A2}}{1-X_{A1}} \right)}{\frac{Z_1 + Z_2}{2}} \quad (42)$$

When the liquid level drops from  $Z_1$  to  $Z_2$  during the evaporation period the molal flux is given by

$$N_A = \frac{Z_2 - Z_1}{\theta} \rho_A \quad (43)$$

If equation (43) is substituted into (42) we get

$$\frac{Z_2 - Z_1}{\theta} \rho_A = \frac{P}{RT} \frac{D_{AB}}{\frac{Z_1 + Z_2}{2}} \ln \frac{1 - X_{A_2}}{1 - X_{A_1}}$$

or

$$D_{AB} = \frac{RT \rho_A \frac{Z_2^2 - Z_1^2}{2}}{\theta P \ln \left( \frac{1 - X_{A_2}}{1 - X_{A_1}} \right)} \quad (44)$$

Equations (44) and (41) are identical. Hence the arithmetic average is completely rigorous.

Table 4. Equilibrium calculations.

System	Run no.	Corrected air flow rate  cu ft/ min	Vapor pressure mm Hg	Equilibrium cell pressure mm Hg	Theoretical mole fraction of solvent	Weight of solvent consumed gm	Moles of air	Moles of solvent	Mole fraction of solvent calculated $X_{A_2}$
air- chloro- form	8	0.06322	210	1210.77	0.1739	1168	0.1052	0.02154	0.171
	28	0.02817	683	1209.5	0.5650	3000	0.04345	0.05532	0.560
air- methanol	44	0.07973	158	1070.3	0.147	314	0.1280	0.0220	0.139
	53	0.05348	505	1065.0	0.475	1070	0.0816	0.0736	0.472

## APPENDIX V

## SAMPLE CALCULATION



The diffusion path is calculated using the dimensions of the tube and the density of the liquid.

$$\text{Height of the liquid in the tube} = L - \frac{W_L - W}{S \rho_A}$$

L is measured to be 14.17 cm.

#### Calculation of run number 14.

Weight of the empty diffusion tube	=	63.14200 gm
Initial weight of the tube + $\text{CHCl}_3$	=	71.92750 gm
Final weight of the tube + $\text{CHCl}_3$	=	70.14080 gm
Weight loss by diffusion $W_A$	=	1.78670 gm
Time of diffusion $\theta$	=	36,180 sec.
Initial weight of $\text{CHCl}_3$ alone	=	8.78550 gm
Initial diffusion path	=	$14.17 - \frac{8.78550}{(0.70713)(1.485)}$
	=	5.80 cm
Final weight of $\text{CHCl}_3$ alone	=	6.9988 gm
Final diffusion path	=	$14.17 - \frac{6.9988}{(0.70713)(1.485)}$
	=	7.51 cm
Average diffusion path $Z$	=	$\frac{5.80+7.51}{2} = 6.655 \text{ cm}$
Total pressure $P$	=	768.02 mm Hg
Diffusion cell temperature $T$	=	50° C
Equilibrium cell temperature	=	36.3°C
Equilibrium cell pressure	=	1118.92 mm Hg

Vapor pressure of  $\text{CHCl}_3$  at  $36.3^\circ\text{C}$  = 310 mm Hg  
(Equilibrium cell temperature)

Vapor pressure of  $\text{CHCl}_3$  at  $50^\circ\text{C}$  = 522 mm Hg

$$X_{A_1} = \frac{522}{768.02} = 0.680$$

$$X_{A_2} = \frac{310}{1118.92} = 0.2605$$

$$D_{AB} = \frac{W_A RTZ}{\theta \text{SPM}_A \ln\left(\frac{1-X_{A_2}}{1-X_{A_1}}\right)} \quad (5)$$

where  $D_a$  is the apparent diffusion coefficient

$$R = 62.32 \times 10^3 \frac{\text{mm Hg} \cdot \text{liter}}{\text{mole } ^\circ\text{K}}$$

$$T = 323.16^\circ\text{K}$$

$$S. = 0.70713 \text{ cm}^2$$

$$M_A = 119.39$$

$$\begin{aligned} D_a &= \frac{(1.7860)(62.32 \times 10^3)(323.16)(6.655)}{(36,180)(0.70713)(768.02)(119.39) \ln\left(\frac{1-0.2605}{1-0.680}\right)} \\ &= 0.1220 \text{ cm}^2/\text{sec} \end{aligned}$$

Correcting  $D_a$  to 760 mm Hg

$$D_a \text{ at } 760 \text{ mm Hg and } 50^\circ\text{C} = \frac{768.02}{760} (0.1220) = 0.1232 \text{ cm}^2/\text{sec}$$

$$\frac{1}{D_a} = 8.116 \text{ sec cm}^{-2}$$

$$\frac{1}{Z_a} = 0.1503 \text{ cm}^{-1}$$

These values are then used to determine the actual concentration average diffusion coefficient by plotting  $\frac{1}{D_a}$  vs  $\frac{1}{Z_a}$  and fitting a straight line by the method of least squares. The intercept of this straight line on the  $\frac{1}{D_a}$  axis gives the actual concentration average diffusion coefficient,  $\bar{D}_{AB}$ .

## APPENDIX VI

### EXPERIMENTAL RESULTS

Table 5. Experimental Data - Chloroform-air system at 50°C and 1 atmosphere.

Run Number	Weight lost by diffusion tube gm	Diffusion time sec	Average diffusion path cm	Diffusion cell pressure inch H <sub>2</sub> O	Equilibrium cell pressure inch Hg	Equilibrium cell temperature °C	Atmospheric pressure mmHg	X <sub>A1</sub>	X <sub>A2</sub>	Apparent diffusion coefficient Da cm <sup>2</sup> /sec
1	0.39859	36,000	10.405	3.20	--	--	760.3	0.6812	0	0.1110
2	3.39750	39,600	6.960	3.56	--	--	761.7	0.6792	0	0.1174
3	2.19012	36,600	6.955	3.07	--	--	759.4	0.6822	0	0.1140
4	1.90120	38,700	8.390	3.06	--	--	758.15	0.6834	0	0.1127
5	1.41863	36,000	10.355	3.40	--	--	758.80	0.6822	0	0.1116
6	1.39090	37,500	10.890	3.35	--	--	760.90	0.6805	0	0.1110
7	1.46078	38,700	10.620	3.20	--	--	762.50	0.6800	0	0.1108
8	1.15469	36,000	10.76	3.60	17.72	26	760.77	0.6801	0.1739	0.1139
9	1.70448	36,600	7.67	3.59	17.92	26	755.80	0.6845	0.1736	0.1159
10	2.09505	38,400	6.575	3.50	17.60	26	757.4	0.6844	0.1744	0.1171
11	1.56765	38,800	8.62	3.50	17.81	26	761.2	0.6800	0.1732	0.1148
12	2.32338	39,660	6.08	2.90	17.87	26	764.2	0.6784	0.1724	0.1182
13	1.47075	36,120	8.20	3.90	17.75	36.1	757.88	0.6825	0.2566	0.1205
14	1.78670	36,180	6.655	3.80	18.00	36.1	760.92	0.6800	0.2605	0.1232
15	1.43103	36,000	8.155	3.54	17.98	36.1	759.90	0.6811	0.2548	0.1203
16	1.30456	36,240	8.97	3.50	17.82	36.1	759.05	0.6819	0.2558	0.1191
17	1.24837	38,760	9.855	3.75	17.90	36.10	760.60	0.6801	0.2550	0.1177
18	1.13015	36,240	10.850	3.55	17.82	36.10	755.70	0.6847	0.2566	0.1174
19	0.86475	38,520	11.605	3.54	17.70	45.2	761.90	0.6792	0.3631	0.1195

Table 5. (continued)

Run Number	Weight lost by diffusion tube gm	Diffusion time sec	Average diffusion path cm	Diffusion cell pressure inch H <sub>2</sub> O	Equilibrium cell pressure inch Hg	Equilibrium cell temperature °C	Atmospheric pressure mm Hg	X <sub>A1</sub>	X <sub>A2</sub>	Apparent diffusion coefficient Da cm <sup>2</sup> /sec
20	1.22113	36,360	8.045	3.79	17.61	45.2	763.40	0.6776	0.3637	0.1243
21	1.26438	39,120	8.320	3.70	17.70	45.2	763.25	0.6784	0.3628	0.1235
22	1.04525	36,240	9.425	3.60	17.48	45.2	756.9	0.6837	0.3661	0.1231
23	0.96665	35,880	10.025	3.80	17.61	45.2	758.6	0.6817	0.3654	0.1213
24	0.72977	36,900	11.28	3.68	17.53	50.2	757.7	0.6828	0.4365	0.1220
25	0.97778	37,980	9.10	3.675	17.87	50.2	757.9	0.6816	0.4335	0.1253
26	0.76392	36,060	10.69	3.720	17.70	50.2	760.5	0.6826	0.4339	0.1230
26(a)	0.88075	38,820	9.73	2.975	17.60	50.2	759.1	0.6832	0.4354	0.1199
26(b)	1.80245	37,200	5.29	3.230	17.60	50.2	758.8	0.6825	0.4355	0.1389
27	0.59490	35,880	8.290	3.60	17.70	58.0	758.0	0.6831	0.5654	0.1370
28	0.76363	36,300	7.145	3.50	17.68	58.0	759.5	0.6815	0.5650	0.1432
29	0.47073	39,600	11.09	3.72	17.45	58.0	756.2	0.6841	0.5682	0.1314
30	0.63665	36,600	7.95	3.80	17.73	58.0	756.9	0.6832	0.5672	0.1384
31	2.35250	70,660	10.345	3.50	17.58	26	757.63	0.6831	0.1744	0.1129
32	1.77052	38,100	7.615	3.60	17.70	26	756.0	0.6847	0.1742	0.1153
33	1.82457	48,660	9.335	3.60	17.8	26	755.6	0.6847	0.1740	0.1140
34	2.04275	36,600	6.51	3.60	17.70	26	760.73	0.6863	0.1744	0.1180

Table 6. Experimental Data - Methanol-air system at 55°C and 1 atmosphere

Run Number	Weight lost by diffusion tube gm	Diffusion time sec	Average diffusion path cm	Diffusion cell pressure inch H <sub>2</sub> O	Equilibrium cell pressure inch Hg	Equilibrium cell temperature °C	Atmospheric pressure mm Hg	X <sub>A1</sub>	X <sub>A2</sub>	Apparent diffusion coefficient Da cm <sup>2</sup> /sec
35	1.17710	37,500	12.92	0.6	--	--	759.0	0.666	0	0.2191
36	1.0093	42,900	8.425	0.6	--	--	759.3	0.666	0	0.2136
37	1.04379	47,280	8.84	0.40	--	--	763.45	0.665	0	0.2128
38	0.74980	40,500	10.44	0.45	--	--	760.4	0.666	0	0.2091
39	1.14761	61,380	10.355	0.40	--	--	760.95	0.666	0	0.2093
40	1.25580	37,860	6.215	0.40	--	--	758.15	0.667	0	0.2226
41	0.92065	36,660	7.85	0.40	--	--	762.4	0.665	0	0.2144
42	1.38260	43,380	6.335	0.40	--	--	761.7	0.666	0	0.2193
43	0.6422	37,260	9.725	0.60	12.22	30	759.9	0.666	0.1478	0.2121
44	0.8108	38,400	8.115	0.60	12.0	30	764.25	0.663	0.1470	0.2161
45	0.7240	41,160	9.46	0.60	12.10	30	764.25	0.663	0.1478	0.2130
46	0.73667	37,080	8.65	0.60	12.12	30	757.0	0.668	0.1480	0.2170
47	0.90521	36,300	6.945	0.60	12.0	30	759.1	0.666	0.1480	0.2208
48	0.80165	36,000	6.97	0.60	12.2	40	760.0	0.666	0.241	0.2232
49	0.5908	39,590	9.72	0.80	12.0	40	757.0	0.667	0.242	0.2146
50	0.79122	39,600	7.645	0.80	12.0	40	759.5	0.665	0.242	0.2124
51	0.55110	38,520	10.32	0.60	12.0	40	761.4	0.665	0.242	0.2137
52	0.79122	39,600	7.645	0.60	12.1	40	764.0	0.663	0.241	0.2209
53	0.30166	39,480	10.875	0.60	12.0	55	759.0	0.666	0.475	0.2181
54	0.42153	41,400	8.495	0.60	12.0	55	762.2	0.665	0.473	0.2258
55	0.48125	41,760	7.640	0.60	12.0	55	762.4	0.665	0.473	0.2298
56	0.43158	42,540	8.455	0.60	12.0	55	760.4	0.666	0.473	0.2252
57	0.28156	37,800	9.325	0.60	12.0	55	760.0	0.666	0.473	0.2222

## APPENDIX VII

## VAPOR-PRESSURE DATA



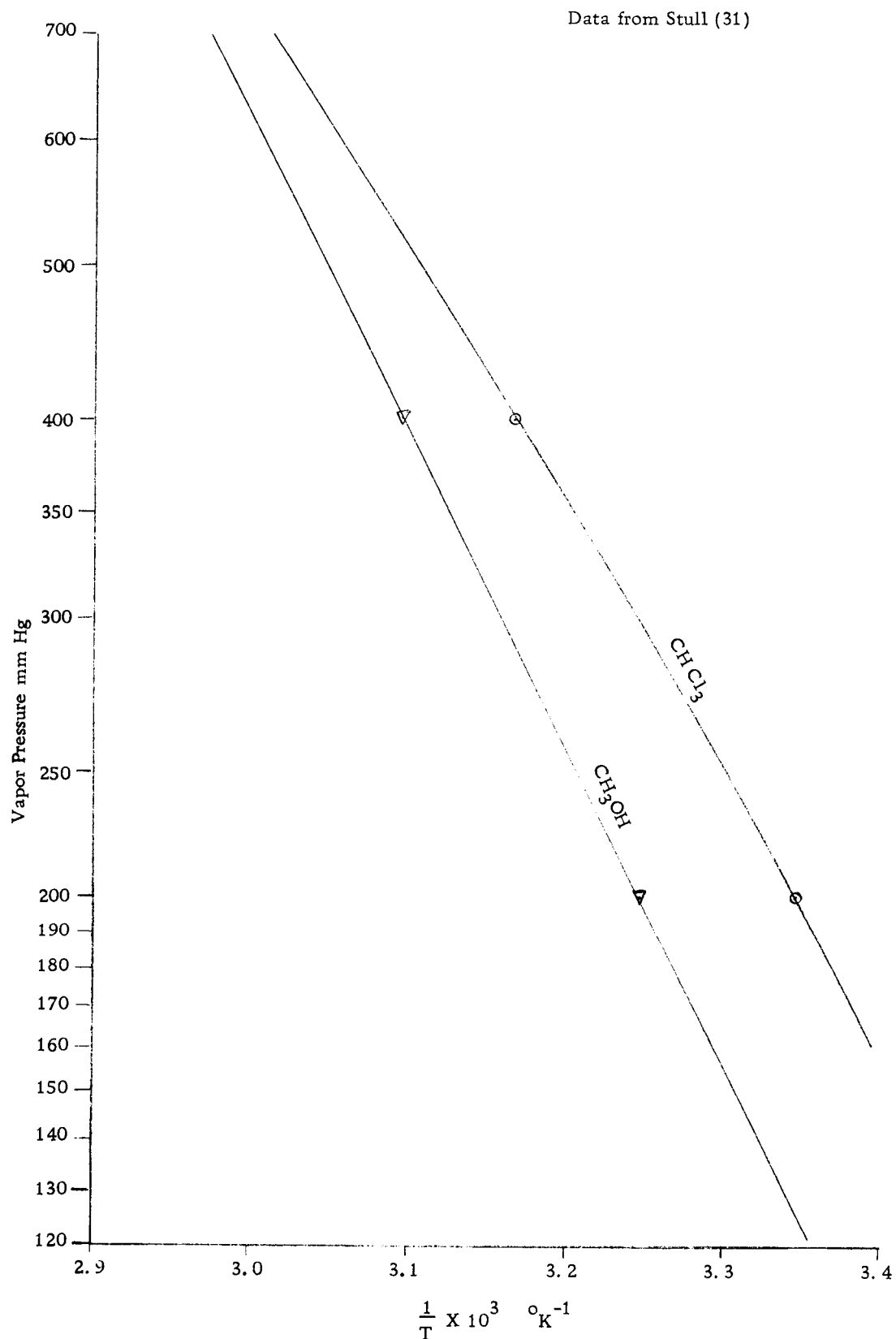


Figure 13. Vapor pressure data for chloroform and methanol.