

AN ABSTRACT OF THE THESIS OF

SUNG CHUN LEE for the MASTER OF SCIENCE  
(Name) (Degree)

in CHEMICAL ENGINEERING presented on Dec. 14, 1970  
(Major) (Date)

Title: DIFFUSION COEFFICIENTS OF ISOPROPYL ALCOHOL  
IN BINARY AND MULTICOMPONENT GAS SYSTEMS  
INVOLVING AIR AND ARGON

Abstract approved: Redacted for Privacy  
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Diffusion coefficients for isopropyl alcohol-air, isopropyl alcohol-argon, isopropyl alcohol-mixture of argon 1 : air 1, isopropyl alcohol-mixture of argon 1 : air 2, and carbon tetrachloride-air system were determined, using an Arnold cell technique. The measured carbon tetrachloride-air system diffusion coefficient was compared with previously measured values to verify the accuracy and reproducibility of the present experimental technique.

The following diffusion coefficients were obtained at 25°C.

D of $\text{CCl}_4$ - air	= 0.08002 $\text{cm}^2/\text{sec}$
D of $\text{CH}_3\text{CHOHCH}_3$ - air	= 0.10626 $\text{cm}^2/\text{sec}$
D of $\text{CH}_3\text{CHOHCH}_3$ - argon	= 0.08928 $\text{cm}^2/\text{sec}$
D of $\text{CH}_3\text{CHOHCH}_3$ - argon : air (1 : 1 in volume)	= 0.09425 $\text{cm}^2/\text{sec}$
D of $\text{CH}_3\text{CHOHCH}_3$ - argon : air (1 : 2 in volume)	= 0.09804 $\text{cm}^2/\text{sec}$

Diffusion Coefficients of Isopropyl Alcohol  
in Binary and Multicomponent Gas Systems  
Involving Air and Argon

by

Sung Chun Lee

A THESIS

submitted to

Oregon State University

in partial fulfillment of  
the requirements for the  
degree of

Master of Science

June 1971

APPROVED:

*Redacted for Privacy*

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Dean of Graduate School

Date thesis is presented

Dec 14, 1970

Typed by Muriel Davis for Sung Chun Lee

## ACKNOWLEDGMENTS

The author wishes to express his appreciation to the following:

Dr. C. E. Wicks for his help and encouragement during the course of this investigation.

The Department of Chemical Engineering whose facilities made this investigation possible.

Miss Hye Jung Choi who helped in typing the rough drafts of the thesis.

Finally, I would like to thank my parents for their financial support.

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## NOMENCLATURE

$C$	concentration of gas mixture	moles/liter
$C_{AB}$	Surtherland's constant	$^{\circ}\text{K}$
$C_1, C_2$	constants of integration	
$(D_{AB})_a$	apparent diffusion coefficient	$\text{cm}^2/\text{sec}$
$D_{AB}$	diffusion coefficient	$\text{cm}^2/\text{sec}$
$L$	effective diffusion path length in cell	cm
$L_a$	apparent diffusion path length	cm
$L_o$	diffusion path length at time zero	cm
$L_t$	diffusion path length at time $t$	cm
$\Delta L$	$L_s + L_e$ , end effects correction	cm
$\Delta L_e$	effective change in diffusion path length due to eddies or turbulence	cm
$\Delta L_s$	effective change in diffusion path length due to surface tension	cm
$l$	length of diffusion cell	cm
$m$	slope of experimental curve	sec/cm
$M_A$	molecular weight of A, diffusing vapor	gm
$M_B$	molecular weight of B, carrier gas	gm
$N_A$	diffusion flux of A	moles/sec $\text{cm}^2$
$N_B$	diffusion flux of B	moles/sec $\text{cm}^2$
$p_A$	partial pressure of diffusion substance A	mm Hg
$p_{AS}$	saturated vapor pressure of liquid	mm Hg



$p_{A1}$	saturated vapor pressure at the liquid surface	mm Hg
$p_{A2}$	partial pressure of the diffusing vapor A at top of the cell	mm Hg
$P$	total pressure of cell	mm Hg
$R$	gas constant	(mm Hg)(liter) / (mole)( $^{\circ}$ K)
$S$	cross-sectional area of diffusion cell	cm <sup>2</sup>
$t$	total diffusion time	sec
$T$	absolute temperature	$^{\circ}$ K
$T_b$	boiling temperature	$^{\circ}$ K
$u$	dummy variable defined by equation (30)	mm Hg
$v_{AZ}$	velocity of species A in Z direction (stationary coordinate)	
$V$	molar average velocity	
$V_b$	molal volume at normal boiling point	c. c. /gm. mole
$w$	dummy variable defined by equation (30)	mm Hg
$W$	wight of empty diffusion cell	gm
$W_A$	weight of liquid evaporated in time t	gm
$W_L$	average weight of the liquid in cell	gm
$x$	new variable defined by equation (39)	
$X$	new variable defined by equation (45)	
$y_A$	mole fraction of A	
$y_B$	mole fraction of B	

$z$	distance along diffusion path length	cm
$\theta$	new variable defined by equation (39)	
$\Theta$	new variable defined by equation (45)	
$\lambda$	constant	
$\sigma$	collision diameter	cm
$\Omega_{D, AB}$	collision integral for diffusion, function of $kT/\epsilon$	
$\rho_L$	density of liquid	$\text{g/cm}^3$
1	interface between gas and liquid	
2	top of the diffusion cell	

DIFFUSION COEFFICIENTS OF ISOPROPYL ALCOHOL  
IN BINARY AND MULTICOMPONENT GAS SYSTEMS  
INVOLVING AIR AND ARGON

INTRODUCTION

The diffusion process is important and fundamental in extraction, absorption and distillation operation. Though reliable diffusivity values are required in the design equations, one can get experimental values for only a few restricted materials. Experimental methods for measuring the diffusivity values have been developed (1, 2, 4, 5, 11, 14, 16, 18, 19, 20, 23, 24, 29, 30, 31) to provide reliable data points.

Diffusion is the transfer of a substance through a homogeneous phase resulting from concentration differences. This mechanism has been studied in many points of view, particularly by Fick and Maxwell-Stefan. The diffusion coefficient is the proportionality constant between the diffusion flux (rate of transfer across a unit area per unit time) and the gradient of the potential to that surface causing diffusion. The diffusion coefficient is a function of the concentration (partial pressure) of the diffusing substance, temperature, pressure, molecular weight of each substance in the homogeneous phase and interaction between molecules. Empirical equations (3, 9, 12, 13, 21, 27, 32) have been developed for predicting with fairly high accuracy the diffusion coefficients in gas systems.

Many experimental apparatus (1, 2, 4, 5, 14, 18, 20, 24, 29, 30, 31) have been studied for measuring the diffusion coefficients. The

method used to measure the diffusion coefficient in this thesis is the Arnold cell. The Arnold cell consists of a vertical tube of constant diameter which is partially filled with the diffusing liquid. The liquid level in the tube changes only after a long period of time. Therefore, one can assume the cell is operating as a pseudo-steady state with negligible error. The Arnold cell is maintained at constant temperature and pressure. The pure, non-diffusing gas flows across the open end of the tube and therefore, the partial pressure of the diffusing gas at the top of the tube is essentially zero.

This research project involves the measurement of diffusion coefficients for isopropyl alcohol in air, argon and the mixtures of the air and argon as well as the carbon tetrachloride in air. The diffusion cell used in this study was modeled after the Arnold cell of Wilke and Lee (31), by Larson (19) and later modified by Godfrey (11).

## THEORETICAL EVALUATIONS

Mass Diffusivity Equation

A more general flux relation is

$$\text{Flux} = - \left( \begin{array}{c} \text{overall} \\ \text{density} \end{array} \right) \left( \begin{array}{c} \text{diffusion} \\ \text{coefficient} \end{array} \right) \left( \begin{array}{c} \text{concentration} \\ \text{gradient} \end{array} \right)$$

or

$$J_A = - C D_{AB} \frac{dy_A}{dz} \quad (1)$$

The symbols in the equation are defined in the nomenclature. The molar flux in the Z-direction relative to the molar average velocity is

$$J_{AZ} = C_A (v_{AZ} - V_Z) \quad (2)$$

From equation (1) and (2)

$$J_{AZ} = C_A (v_{AZ} - V_Z) = - C D_{AB} \frac{dy_A}{dz}$$

$$C_A v_{AZ} = - C D_{AB} \frac{dy_A}{dz} + C_A V_Z \quad (3)$$

By definition of the molar-average velocity

$$V = \frac{\sum_{i=1}^n C_i v_i}{\sum_{i=1}^n C_i} = \frac{\sum_{i=1}^n C_i v_i}{C} \quad (4)$$

For the Z-direction

$$V_Z = \frac{1}{C} (C_A v_{AZ} + C_B v_{BZ})$$

or

$$C_A V_Z = y_A (C_A v_{AZ} + C_B v_{BZ}) \quad (5)$$

Substituting equation (5) into equation (3),

$$C_A v_{AZ} = -C D_{AB} \frac{dy_A}{dz} + y_A (C_A v_{AZ} + C_B v_{BZ}) \quad (6)$$

The quantities  $C_A v_{AZ}$  and  $C_B v_{BZ}$  are fluxes of component A and B relative to a fixed z-coordinate and therefore, one may express this type of molar flux relative to stationary coordinate by

$$\begin{aligned} N_A &= C_A v_A \\ N_B &= C_B v_B \end{aligned} \quad (7)$$

Rewriting equation (6) using these symbols, one obtains

$$N_{AZ} = -C D_{AB} \frac{dy_A}{dz} + y_A (N_{AZ} + N_{BZ}) \quad (8)$$

For the multicomponent mixture

$$N_{AZ} = -C D_{AM} \frac{dy_A}{dz} + y_A \sum_{i=1}^n N_i \quad (9)$$

Considering the control volume  $\Delta Z$  in Figure 1. A mass balance over this control volume for a steady-state operation can be expressed by

$$S N_{AZ} \Big|_Z - S N_{AZ} \Big|_{Z + \Delta Z} = 0$$

Dividing by  $\Delta Z$  and considering in the limit as  $\Delta Z$  approaches zero, we can get the differential equation,

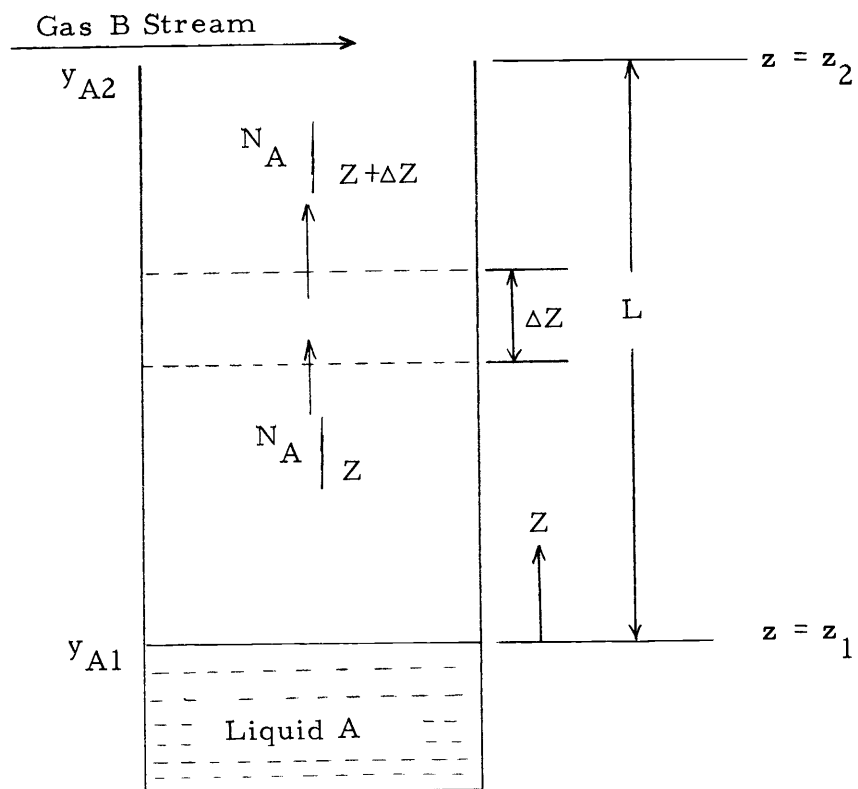


Figure 1. Diffusion of A through B in Steady State with B not in Motion.

$$\frac{dN_A}{dz} = 0 \quad (10)$$

This equation expresses a constant molar flux of A throughout the gas phase from  $z_1$  to  $z_2$ . Similarly, for the mass balance on Component B,

$$\frac{dN_B}{dz} = 0 \quad (11)$$

If gas B is insoluble in liquid A,  $N_{BZ}$  at plane  $z_1$  is zero and accordingly  $N_{BZ}$  is zero throughout the diffusion column. Thus component B is a stagnant gas.

From equation (8), when  $N_{BZ} = 0$ ,

$$N_{AZ} = \frac{-C D_{AB}}{(1 - y_A)} \frac{dy_A}{dz} \quad (12)$$

Since equation (10),

$$\frac{dN_A}{dz} = 0 \quad (10)$$

stipulate that

$$N_{AZ} = \text{constant} \quad (13)$$

along the diffusion path. The equation (12) can be integrated with two boundary conditions:

$$y_A = y_{A1} \quad \text{at } z = z_1$$

and

$$y_A = y_{A2} \quad \text{at } z = z_2$$



$$N_{AZ} \int_{z_1}^{z_2} dz = C D_{AB} \int_{y_{A1}}^{y_{A2}} \frac{dy_A}{1-y_A}$$

$$N_{AZ} (z_2 - z_1) = C D_{AB} \ell n \frac{(1-y_{A2})}{(1-y_{A1})}$$

$$N_{AZ} = \frac{C D_{AB}}{(z_2 - z_1)} \ell n \frac{(1-y_{A2})}{(1-y_{A1})} \quad (14)$$

If the gas is ideal,

$$C = \frac{n}{V} = \frac{P}{RT} \quad (15)$$

Equation (14) can be rearranged to the desired relationship,

$$N_{AZ} = \frac{P D_{AB}}{RT(z_2 - z_1)} \ell n \frac{(1-y_{A2})}{(1-y_{A1})} \quad (16)$$

To obtain the above equation, the following assumptions must be made:

1.  $D_{AB}$  is independent of concentration.
2. The gas is ideal.
3. Steady-state condition.
4. The liquid level remains constant (pseudo-steady state).

When the quasi-steady state may be assumed, the molar flux  $N_{AZ}$  is related to the amount of A leaving the liquid by

$$N_{AZ} = \frac{W_A}{S M_A t} \quad (17)$$

From equation (17) and equation (16)

$$D_{AB} = \frac{W_A RT (z_2 - z_1)}{SM_A t P \ln \frac{(1-y_{A2})}{(1-y_{A1})}} \quad (18)$$

The diffusion length,  $L = z_2 - z_1$ , is nearly constant. When pseudo-steady state conditions are assumed, one may evaluate  $L$  as the arithmetic average of the values at beginning and end of the diffusion period.

$$L = \frac{L_o + L_t}{2} \quad (19)$$

If one assumes that the gas rate is kept at such a rate that the partial pressure of the diffusing vapor  $A$  at the top of the tube is essentially zero,

$$p_{A2} = 0. \quad (20)$$

Also

$$y_A = \frac{p_A}{P} \quad (21)$$

By substituting equation (20) and equation (21) into equation (18), the following equation results

$$D_{AB} = \frac{W_A RTL}{SM_A t P \ln \frac{P}{P - p_{A1}}} \quad (22)$$

where  $p_{A1}$  is saturated vapor pressure at the liquid surface.

### Time to Reach Steady State

In order to use equation (22), it is necessary to determine the

time required to reach steady state. The general expression of the continuity equation for constant  $\rho$  and  $D_{AB}$  is

$$\frac{\partial C_A}{\partial t} + (\bar{v} \cdot \nabla C_A) = D_{AB} \nabla^2 C_A + R_A \quad (23)$$

If there is no chemical reaction,  $R_A$  is zero. When there is essentially no bulk contribution to the mass flux, equation (23) reduces to

$$\frac{\partial C_A}{\partial t} = D_{AB} \nabla^2 C_A \quad (24)$$

This is called Fick's second law of diffusion.

This equation may be written in cylindrical coordinates

$$\frac{\partial C_A}{\partial t} = D_{AB} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_A}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 C_A}{\partial \theta^2} + \frac{\partial^2 C_A}{\partial z^2} \right)$$

Since the gradient of concentration for  $r$  and  $\theta$  direction is zero in the Arnold diffusion cell,

$$\frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial z^2} \quad (25)$$

Also,

$$C_A = \frac{p_A}{RT}$$

At constant temperature

$$\frac{\partial p_A}{\partial t} = D_{AB} \frac{\partial^2 p_A}{\partial z^2} \quad (26)$$

If one assumes that the gas in the diffusion tube is initially saturated

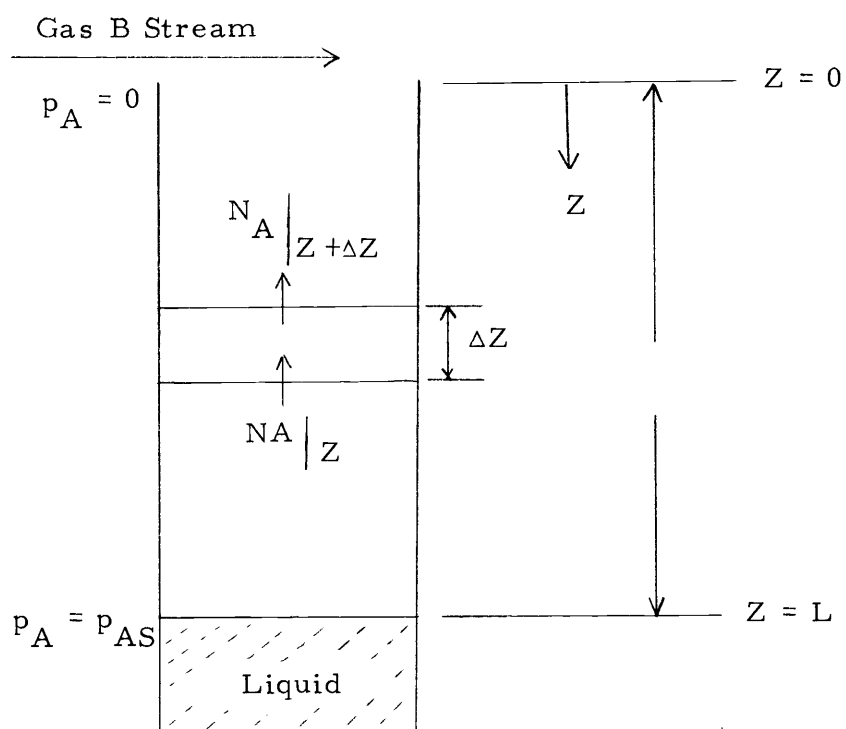


Figure 2. Unsteady State Diffusion

with vapor at partial pressure  $p_{AS}$ , the boundary conditions are

$$p_A = 0, \quad \text{at } z = 0 \quad \text{for all } t > 0 \quad (27)$$

$$p_A = p_{AS}, \quad \text{at } z = L \quad \text{for all } t \quad (28)$$

$$p_A = p_{AS}, \quad \text{when } t = 0 \quad \text{for all } z \quad (29)$$

Let 
$$p_A = u + w \quad (30)$$

where  $u$  and  $w$  satisfy the following equations

$$\frac{d^2 u}{dz^2} = 0 \quad (0 < z < L) \quad (31)$$

with boundary conditions

$$u = 0, \quad \text{at } z = 0 \quad (32)$$

$$u = p_{AS}, \quad \text{at } z = L \quad (33)$$

and the equation

$$\frac{\partial w}{\partial t} = D_{AB} \frac{\partial^2 w}{\partial z^2} \quad (0 < z < L) \quad (34)$$

with boundary conditions

$$w = 0, \quad \text{at } z = 0 \quad \text{and } z = L \quad (35)$$

$$w = p_{AS} - u, \quad \text{at } t = 0 \quad (36)$$

Integrating equation (31),

$$\frac{du}{dz} = C_1$$

$$u = C_1 z + C_2 \quad (37)$$

By the boundary conditions from equation (32) and equation (33)

$$C_2 = 0$$

$$C_1 = \frac{p_{AS}}{L}$$

Substituting these constants into equation (37), one obtains

$$u = \frac{p_{AS}}{L} z \quad (38)$$

$$\text{Let } \theta = \frac{D_{AB} t}{L^2} \quad \text{and} \quad x = \frac{z}{L} \quad (39)$$

The variables in equation (34) can be changed to

$$\frac{\partial w}{\partial \theta} \frac{\partial \theta}{\partial t} = D_{AB} \frac{\partial x}{\partial z} \frac{\partial}{\partial x} \left( \frac{\partial w}{\partial x} \frac{\partial x}{\partial z} \right) \quad (40)$$

Upon substituting equation (39) into equation (40),

$$\begin{aligned} \frac{\partial w}{\partial \theta} \frac{D_{AB}}{L^2} &= D_{AB} \frac{1}{L} \frac{\partial}{\partial x} \left( \frac{\partial w}{\partial x} \frac{1}{L} \right) \\ \frac{\partial w}{\partial \theta} &= \frac{\partial^2 w}{\partial x^2} \end{aligned} \quad (41)$$

Boundary conditions for new variables are:

$$1) \quad w = 0 \quad \text{at} \quad x = 0 \quad (42)$$

$$2) \quad w = 0 \quad \text{at} \quad x = 1 \quad (43)$$

$$\begin{aligned} 3) \quad w &= p_{AS} - u = p_{AS} - \frac{z}{L} p_{AS} \\ &= p_{AS} (1-x) \quad \text{at} \quad \theta = 0 \end{aligned} \quad (44)$$

Let  $w = X(x) \cdot \Theta(\theta)$  (45)

Substitute equation (45) into equation (41)

$$\frac{1}{\Theta} \frac{d\Theta}{d\theta} = \frac{1}{X} \frac{d^2 X}{dx^2} = -\lambda^2 \quad (46)$$

$$\frac{d^2 X}{dx^2} + \lambda^2 X = 0$$

$$X = C_1 \cos \lambda x + C_2 \sin \lambda x \quad (47)$$

From equation (46)

$$\frac{d\Theta}{\Theta} = -\lambda^2 d\theta$$

$$\ln \Theta = -\lambda^2 \theta + \ln C_3$$

$$\Theta = C_3 \exp(-\lambda^2 \theta) \quad (48)$$

Substitute equation (47) and equation (48) into equation (45)

$$w = (C_1 \cos \lambda x + C_2 \sin \lambda x) e^{-\lambda^2 \theta} \quad (49)$$

By the boundary condition of equation (42),

$$0 = (C_1 \cos 0 + C_2 \sin 0) e^{-\lambda^2 \theta}$$

$$C_1 = 0$$

$$w = C_2 \sin \lambda x \exp(-\lambda^2 \theta) \quad (50)$$

By the boundary condition of equation (43),

$$\begin{aligned}
0 &= C_2 \sin \lambda \exp(-\lambda^2 \theta) \\
\sin \lambda &= 0 \\
\lambda &= n \pi \quad \text{where } n = 1, 2, 3, \dots
\end{aligned} \tag{51}$$

Substitute equation (51) into equation (50)

$$\begin{aligned}
w &= C_2 \sin n \pi x \exp(-n^2 \pi^2 \theta) \\
w &= \sum_{n=1}^{\infty} A_n \sin n \pi x \exp(-n^2 \pi^2 \theta)
\end{aligned} \tag{52}$$

Applying the initial condition (equation (44)) for the equation (52) and multiplying both sides by  $\sin n \pi x$  and integrating, there results

$$\begin{aligned}
\int_0^1 p_{AS}(1-x) \sin n \pi x dx &= A_n \int_0^1 \sin^2 n \pi x dx \\
\int_0^1 p_{AS}(1-x) \sin n \pi x dx &= A_n \int_0^1 \frac{1 - \cos 2n \pi x}{2} dx \\
&= \frac{A_n}{2} \\
A_n &= 2 \int_0^1 p_{AS}(1-x) \sin n \pi x dx \\
&= 2 p_{AS} \left[ -\frac{\cos n \pi x}{n \pi} - \frac{1}{2 n^2 \pi^2} \sin n \pi x + \frac{x}{n \pi} \cos n \pi x \right] \Bigg|_0^1 \\
A_n &= \frac{2 p_{AS}}{n \pi}
\end{aligned} \tag{53}$$

From equation (52) and equation (53)



$$w = \sum_{n=1}^{\infty} \frac{2p_{AS}}{n\pi} \sin n\pi x e^{-n^2 \pi^2 \theta}$$

Since  $x = \frac{z}{L}$  and  $\theta = \frac{D_{AB}t}{L^2}$ ,

$$w = \sum_{n=1}^{\infty} \frac{2p_{AS}}{n\pi} \sin \frac{n\pi z}{L} \exp\left(-\frac{n^2 \pi^2 D_{AB}t}{L^2}\right)$$

$$w = \frac{2p_{AS}}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin \frac{n\pi z}{L} \exp\left(-\frac{n^2 \pi^2 D_{AB}t}{L^2}\right) \quad (54)$$

From equation (38), equation (54) and equation (30)

$$\begin{aligned} p_A &= u + w \\ &= p_{AS} \frac{z}{L} + \frac{2p_{AS}}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin \frac{n\pi z}{L} \exp\left(-\frac{n^2 \pi^2 D_{AB}t}{L^2}\right) \end{aligned}$$

$$\frac{p_A}{p_{AS}} = \frac{z}{L} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin \frac{n\pi z}{L} \exp\left(-\frac{n^2 \pi^2 D_{AB}t}{L^2}\right) \quad (55)$$

Differentiating equation (55) with respect to  $z$

$$\text{at } z = L, \quad t = t \quad \text{and} \quad z = L, \quad t = \infty,$$

$$\frac{1}{p_{AS}} \left( \frac{\partial p_A}{\partial z} \right)_{\substack{z=L \\ t=t}} = \frac{1}{L} + \frac{2}{L} \sum_{n=1}^{\infty} \cos n\pi \exp\left(-\frac{n^2 \pi^2 D_{AB}t}{L^2}\right)$$

and

```

]LIST, LEE
00001 :      PROGRAM LEE
00002 :      WRITE (61,199)
00003 :      T = 1.
00004 :      DO 10 I = 1,22
00005 :      SI = -0.10626*3.14**2.*T*60./10.**2.
00006 :      BETA = 1.-2.*(EXP(SI)-EXP(4.*SI)+EXP(9.*SI)-EXP(16.*SI)+EXP(
00007 :      C25.*SI)-EXP(36.*SI)
00008 :      WRITE(61,200)T,SI,BETA
00009 :      10  T = T+1.
00010 :      199 FORMAT(11X,'T'10X,'SI'10X,'BETA')
00011 :      200 FORMAT(3F13.5)
00012 :      END

```

]OUT,LEE

FORTRAN, I = LEE,R

NO ERRORS FOR LEE

RUN

TIME T (minute)	SI	BETA = $\frac{(N_A)_{t=t}}{(N_A)_{t=\infty}}$
1.00000	-.0.62861	.08825
2.00000	-1.25722	.44418
3.00000	-1.88583	.69765
4.00000	-2.51443	.83827
5.00000	-3.14304	.91370
6.00000	-3.77165	.95397
7.00000	-4.40026	.97545
8.00000	-5.02887	.98691
9.00000	-5.65748	.99302
10.00000	-6.28609	.99628
11.00000	-6.91470	.99801
12.00000	-7.54330	.99894
13.00000	-8.17191	.99944
14.00000	-8.80052	.99970
15.00000	-9.42913	.99984
16.00000	-10.05774	.99991
17.00000	-10.68635	.99995
18.00000	-11.31496	.99998
19.00000	-11.94356	.99999
20.00000	-12.57217	.99999
21.00000	-13.20078	1.00000
22.00000	-13.82939	1.00000

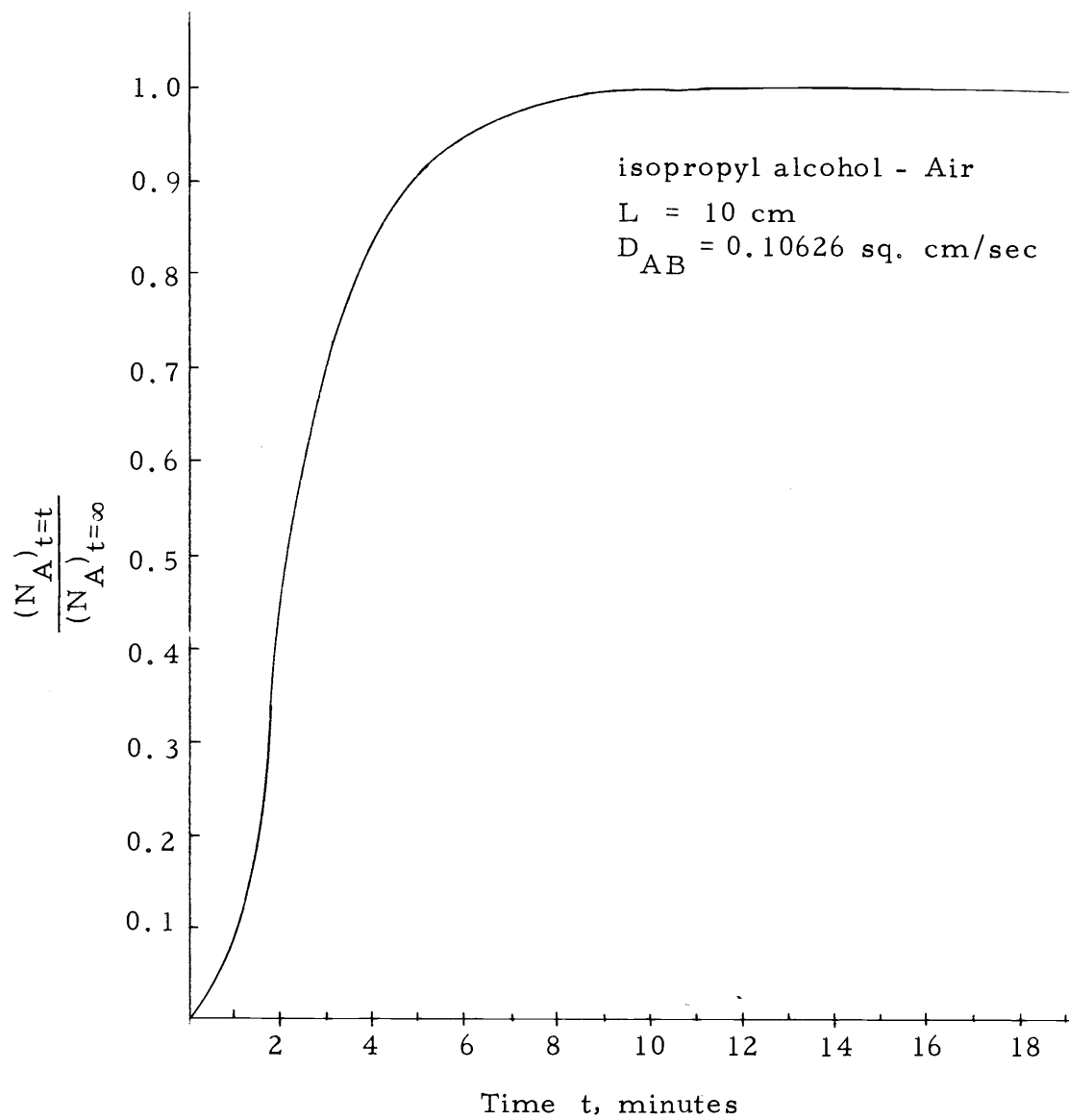


Figure 3. Approach to Steady State.

$$\frac{1}{p_{AS}} \left( \frac{\partial p_A}{\partial z} \right)_{z=L, t=\infty} = \frac{1}{L}$$

Since  $(N_A)_t = - \frac{D_{AB}}{RT} \frac{dp_A}{dz}$  , (56)

the ratio of the rate of diffusion at any time  $t$  to the rate of diffusion at time  $t = \infty$  is given by

$$\begin{aligned} \frac{(N_A)_{t=t}}{(N_A)_{t=\infty}} &= \frac{\left( \frac{\partial p_A}{\partial z} \right)_{z=L, t=t}}{\left( \frac{\partial p_A}{\partial z} \right)_{z=L, t=\infty}} \\ &= \frac{\frac{1}{L} \left( 1 + 2 \sum_{n=1}^{\infty} \cos n\pi \exp\left(-\frac{n^2 \pi^2 D_{AB} t}{L^2}\right) \right)}{\frac{1}{L}} \end{aligned} \quad (57)$$

Using the first six terms in the summation, one obtains

$$\begin{aligned} \frac{(N_A)_{t=t}}{(N_A)_{t=\infty}} &= 1 - 2 \exp\left(-\frac{\pi^2 D_{AB} t}{L^2}\right) + 2 \exp\left(-\frac{4\pi^2 D_{AB} t}{L^2}\right) - 2 \exp\left(-\frac{9\pi^2 D_{AB} t}{L^2}\right) \\ &\quad + 2 \exp\left(-\frac{16\pi^2 D_{AB} t}{L^2}\right) - 2 \exp\left(-\frac{25\pi^2 D_{AB} t}{L^2}\right) + 2 \exp\left(-\frac{36\pi^2 D_{AB} t}{L^2}\right) \end{aligned} \quad (58)$$

The required time for reaching steady state in the case of diffusion of isopropyl alcohol vapor into air when  $L$  equals 10 centimeters and the diffusivity is 0.10626 sq. cm. per second may be evaluated by equation (58), as illustrated in Figure 3. The diffusion rate

reaches 99.94% of the steady state rate in 13 minutes. The 13 minutes is only 2.5% of 10 hours.

Therefore, the assumption of steady state diffusion can be satisfied for the present experiments of 10 hours or longer duration.

### Evaluation of the End Effects

When gas flows across the open end of the tube, turbulence occurs at the mouth of the tube, and eddies will increase the diffusion rate and tend to decrease the diffusion path length by virtue of extending the region of vapor-free gas down into the tube. The surface tension makes the liquid surface downward concave, and this meniscus will cause to diminish the diffusion path length. Therefore, the effective diffusion path length will be shorter than that measuring at the center of the tube (Figure 4). Wilke and Lee (31) have shown these effects.

If six or eight different diffusion path lengths are chosen at the same experimental conditions, the evaluation for the end effects will be satisfied.

From equation (16)

$$N_{AZ} = \frac{P D_{AB}}{RT(z_2 - z_1)} \ell_n \frac{(1 - y_{A2})}{(1 - y_{A1})} \quad (16)$$

Since  $z_2 - z_1 = L$ ,

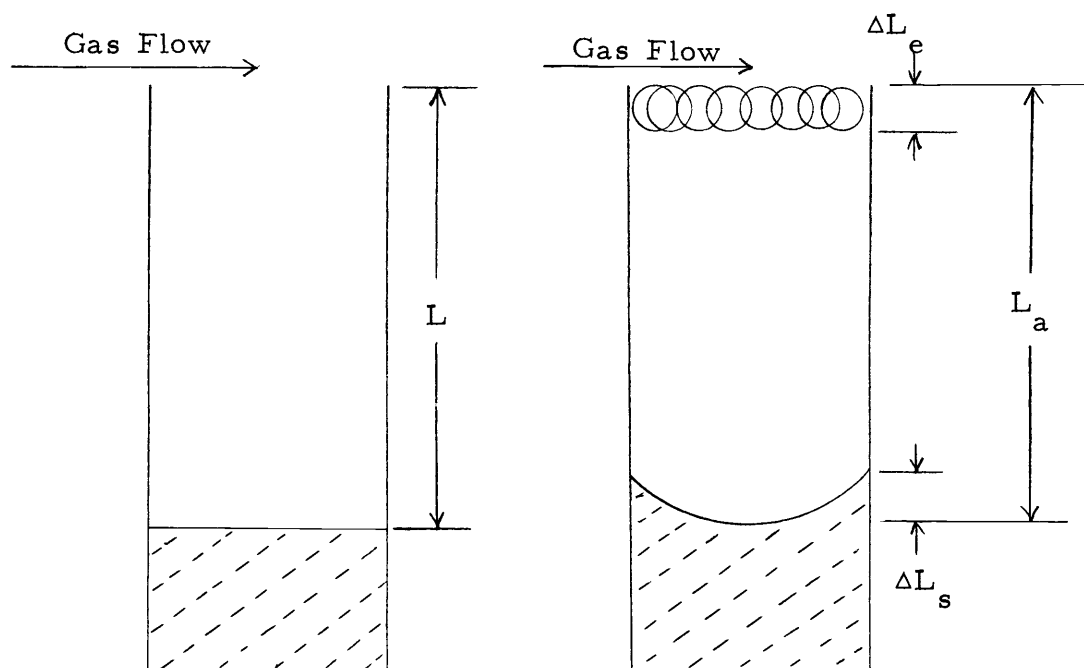


Figure 4. Apparent Path Length of Diffusion

$$N_{AZ} = \frac{P D_{AB}}{RTL} \ln \frac{(1-y_{A2})}{(1-y_{A1})} \quad (59)$$

Consider the effective diffusion path length as follows:

$$L = L_a - \Delta L_e - \Delta L_s = L_a - \Delta L \quad (60)$$

Applying true path length and apparent path length for the equation

(59) respectively,

$$N_{AZ} = \frac{D_{AB} P}{RT(L_a - \Delta L)} \ln \frac{(1-y_{A2})}{(1-y_{A1})} = \frac{(D_{AB})_a P}{RT L_a} \ln \frac{(1-y_{A2})}{(1-y_{A1})} \quad (61)$$

$$\frac{D_{AB}}{L_a - \Delta L} = \frac{(D_{AB})_a}{L_a}$$

$$\frac{1}{(D_{AB})_a} = - \frac{\Delta L}{D_{AB}} \cdot \frac{1}{L_a} + \frac{1}{D_{AB}} \quad (62)$$

Equation (62) gives a straight line, having a slope of  $-\Delta L/D_{AB}$  and an intercept of  $1/D_{AB}$  when  $1/(D_{AB})_a$  is plotted versus  $1/L_a$ . Therefore, diffusivity value,  $D_{AB}$  may be evaluated after reading the intercept.

## DESCRIPTION OF EXPERIMENTAL APPARATUS

Figure 5 illustrates the schematic diagram of the entire apparatus. The diffusion chamber was 7.8 cm. in inside diameter and 10.5 cm. in height. A diffusion tube holder was connected to the bottom of the chamber. The diffusion chamber and the holder, as illustrated in Figure 6, were made of brass to obtain satisfactory heat conduction from the constant temperature bath. The diffusion cell (0.946048 cm. inside diameter, 14.17 cm. inside height, made of type-304 stainless steel) just slipped into the diffusion tube holder (1.3 cm. outside diameter, 13 cm. height) to give good heat transfer.

A 20 cm. inside diameter, gas inlet tube was connected to a bundle of one-eighth inch copper tubing in order to reduce any gas disturbance or eddies. A copper-constantan thermocouple was placed at the gas outlet tube. This thermocouple was connected to a potentiometer for measuring correct temperature within the diffusion chamber. A water manometer was connected to the pressure tap which was placed in the side of the diffusion gas chamber for measuring the pressure within the chamber. The diffusion chamber and tube were immersed in a water bath maintained at  $25^{\circ} \pm 0.002^{\circ}\text{C}$ . A thermotrol, Model 1053A made by Hallekainen Instruments, was used to maintain the constant bath temperature. The circulating water to control the bath temperature was pumped to the constant



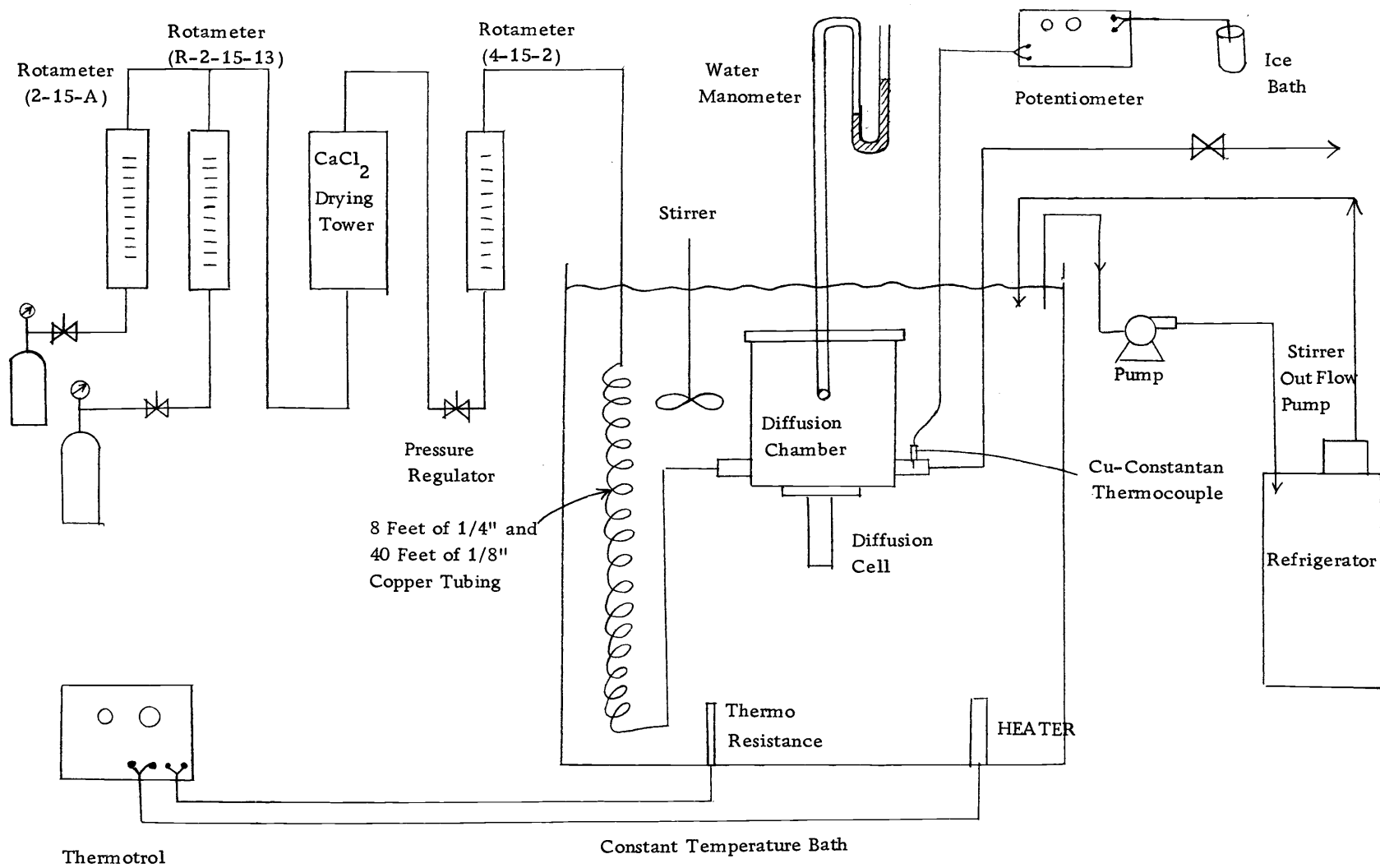


Figure 5. Flow Diagram of Apparatus.

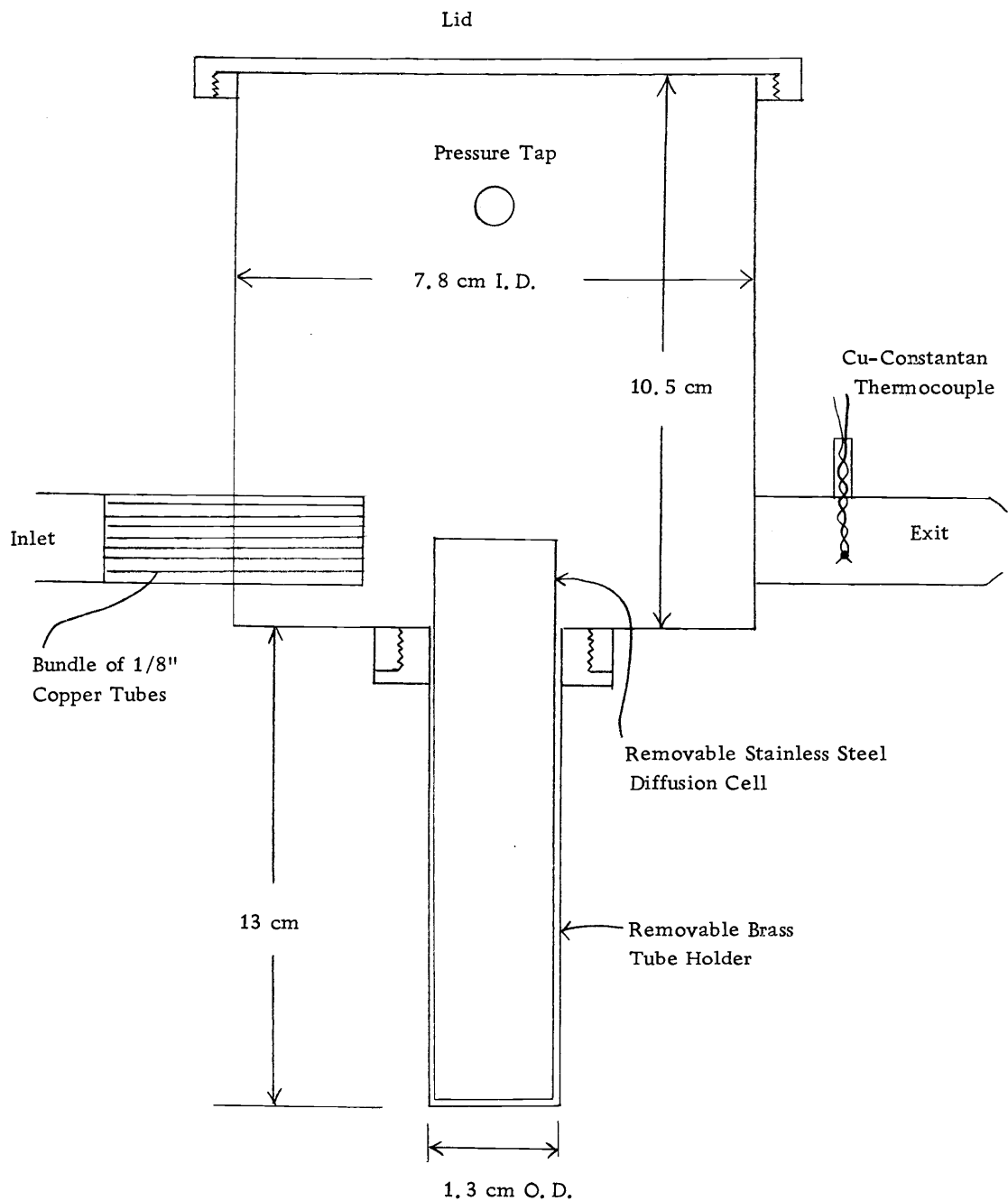


Figure 6. Cross Section of Diffusion Cell and Chamber.

temperature bath from the refrigerating unit (Amico temperature bath Model 4-86E). To eliminate vibration, the stirring motor for the water bath was installed independently on the concrete floor of the laboratory. The gas was passed through an eight foot coil of 1/4-inch and a 40 foot coil of 1/8-inch copper tubing immersed in the water bath before entering the diffusion chamber.

The drying tower was used to remove any moisture in the gas. It was packed three-quarters full with eight mesh anhydrous calcium chloride and one-quarter full with glass wool. The rotameter was used to measure the gas flow rate at the diffusion cell. Three rotameters (size R-2-15-A, size R-2-15-B, size 4-15-2, Brooks Instrument Co.) were calibrated using a wet-test meter made by Precision Scientific Co. Figures 7, 8 and 9 represent the gas flow rate versus rotameter reading. A pressure regulator was arranged just before the rotameters to maintain constant pressure at the entrance to the rotameter and constant flow rate. A stainless steel tank, 18 inches in diameter and 22 inches in height was enclosed in a glass woolbox, 22 inches x 22 inches x 25 inches, for the constant temperature bath.

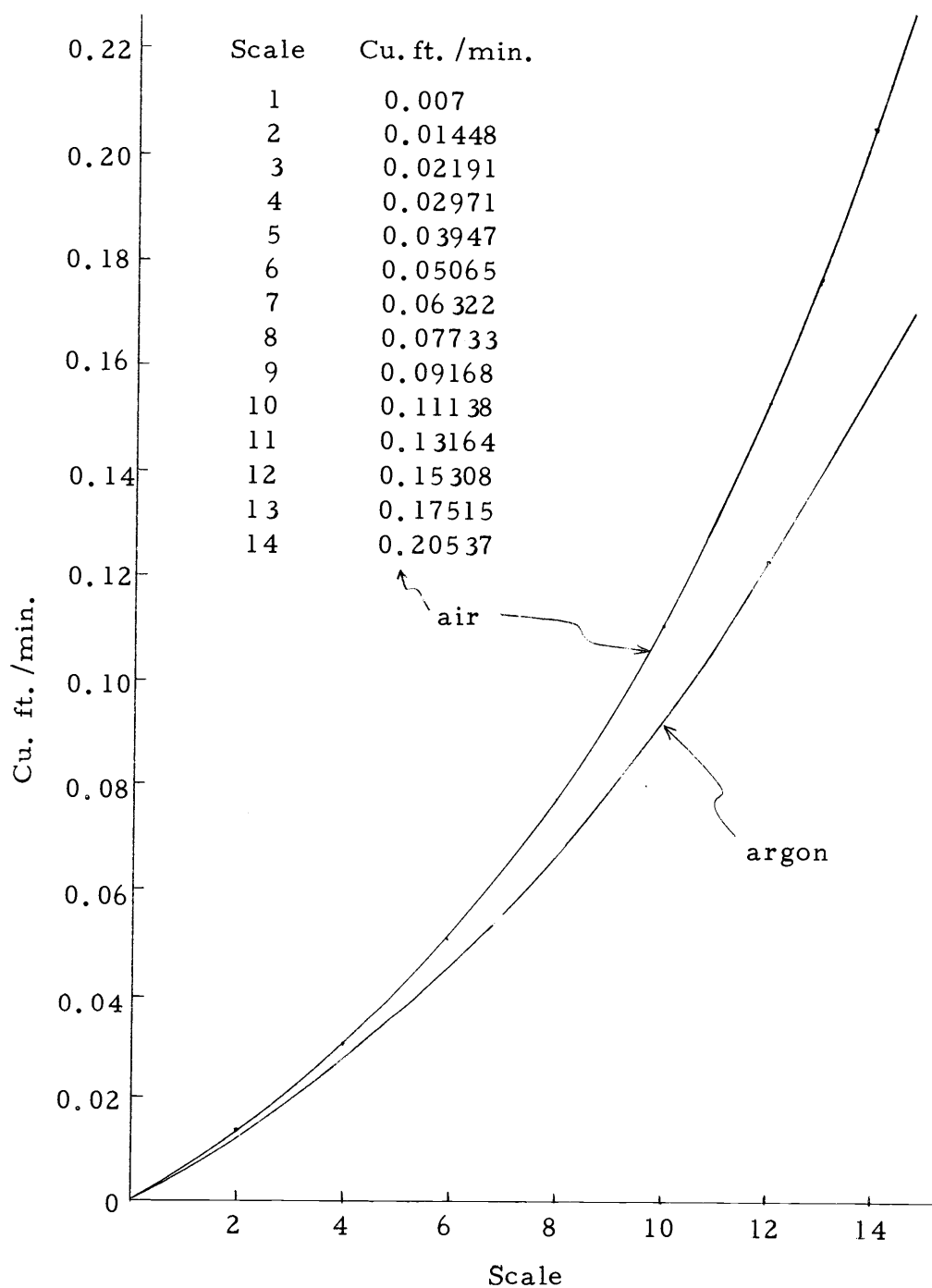


Figure 7. Calibration Curve of Rotameter Size 4-15-2 for Air and Argon.

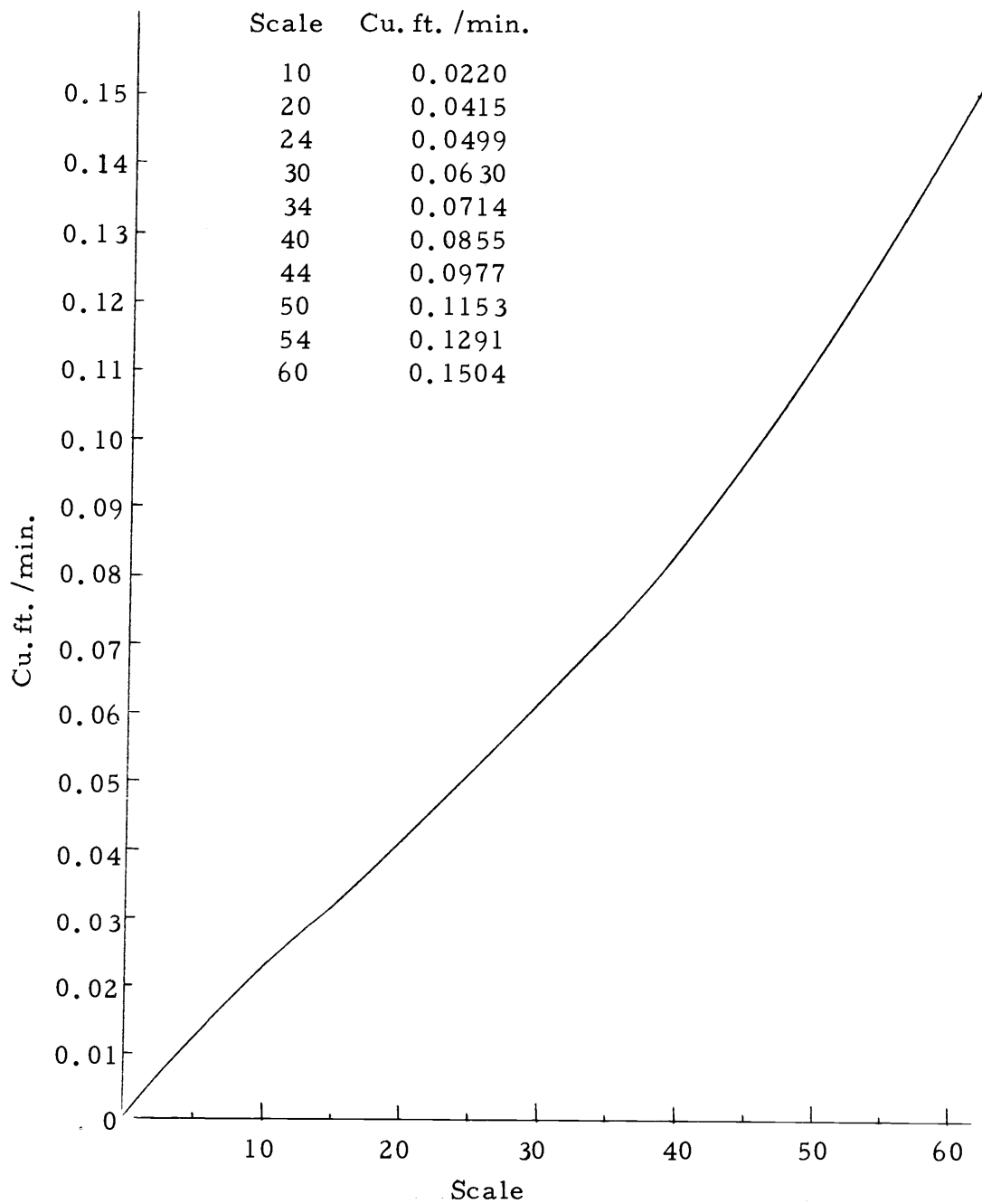


Figure 8. Calibration Curve of Rotameter Size R-3-15-B for Air.

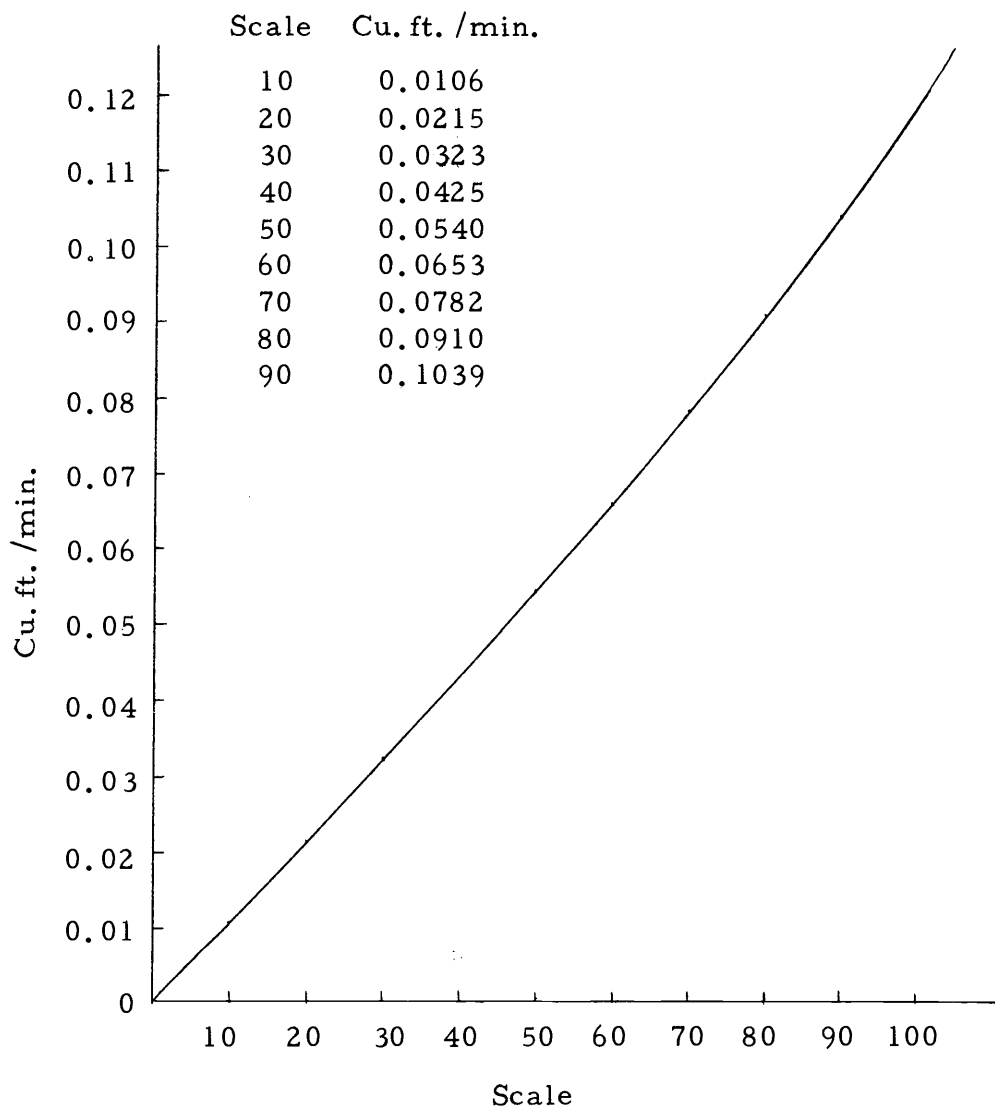


Figure 9. Calibration Curve of Rotameter Size R-2-15-A for Argon.

## EXPERIMENTAL PROCEDURE

The dials of thermotrol were adjusted to obtain the required temperature in the bath after reading the potentiometer temperature scale (copper-constantan thermocouple). The pressure regulator valves were open and controlled to give required flow rate in the rotameter, and the system was filled with the carrier gas from the gas cylinder.

The diffusion cell was filled to a desired level with liquid, and a small plastic pipe, with one of its ends connected to a vacuum line, was slowly inserted into the diffusion cell in order to remove any liquid drops on the wall. The diffusion cell was then stoppered and weighed on a balance proven accurate to  $\pm 0.01$  milligrams. The lid of the diffusion chamber was opened and the diffusion cell was slipped into the holder. The diffusion cell was left for a while to get moderate heat transfer from the constant temperature bath. The stopper was removed and then the time was recorded. The lid was replaced and the diffusion chamber was completely immersed in the water bath.

The flow rate, water manometer reading, atmospheric pressure, time and the temperature at the cell exit were periodically recorded throughout the run. The running time was 10 to 13 hours. At the end of the run the diffusion cell was taken out, stoppered, and weighed.

## EXPERIMENTAL RESULTS

Tables 6 through 11, located in Appendix IV, indicate the diffusivity values obtained by simple linear regression analysis of equation (62) for the various investigated systems. Figures 10 through 14 represent the straight lines when the reciprocal of the apparent diffusion coefficient was plotted against the reciprocal of the apparent diffusion path length. These data points are also tabulated in Appendix III. The intercept value was read on the axis as  $1/L_a$  goes to zero, and the diffusion coefficient was determined from the reciprocal of the intercept value. The end effects correction,  $\Delta L$ , was calculated from the slope of the straight line and the diffusion coefficient. Table 1 represents these experimental results.

Table 1. Experimental Results

System	Experimental $D_{AB}$ (cm <sup>2</sup> /sec) at 25°C, 1 atm	$\Delta L$ cm
CCl <sub>4</sub> - Air	0.08002	0.418
CH <sub>3</sub> CHOH CH <sub>3</sub> - Air	0.10626	0.491
CH <sub>3</sub> CHOH CH <sub>3</sub> - Argon	0.08928	0.673
CH <sub>3</sub> CHOH CH <sub>3</sub> - Argon: Air (1:1 in volume)	0.09425	0.805
CH <sub>3</sub> CHOH CH <sub>3</sub> - Argon: Air (1:2 in volume)	0.09804	0.650



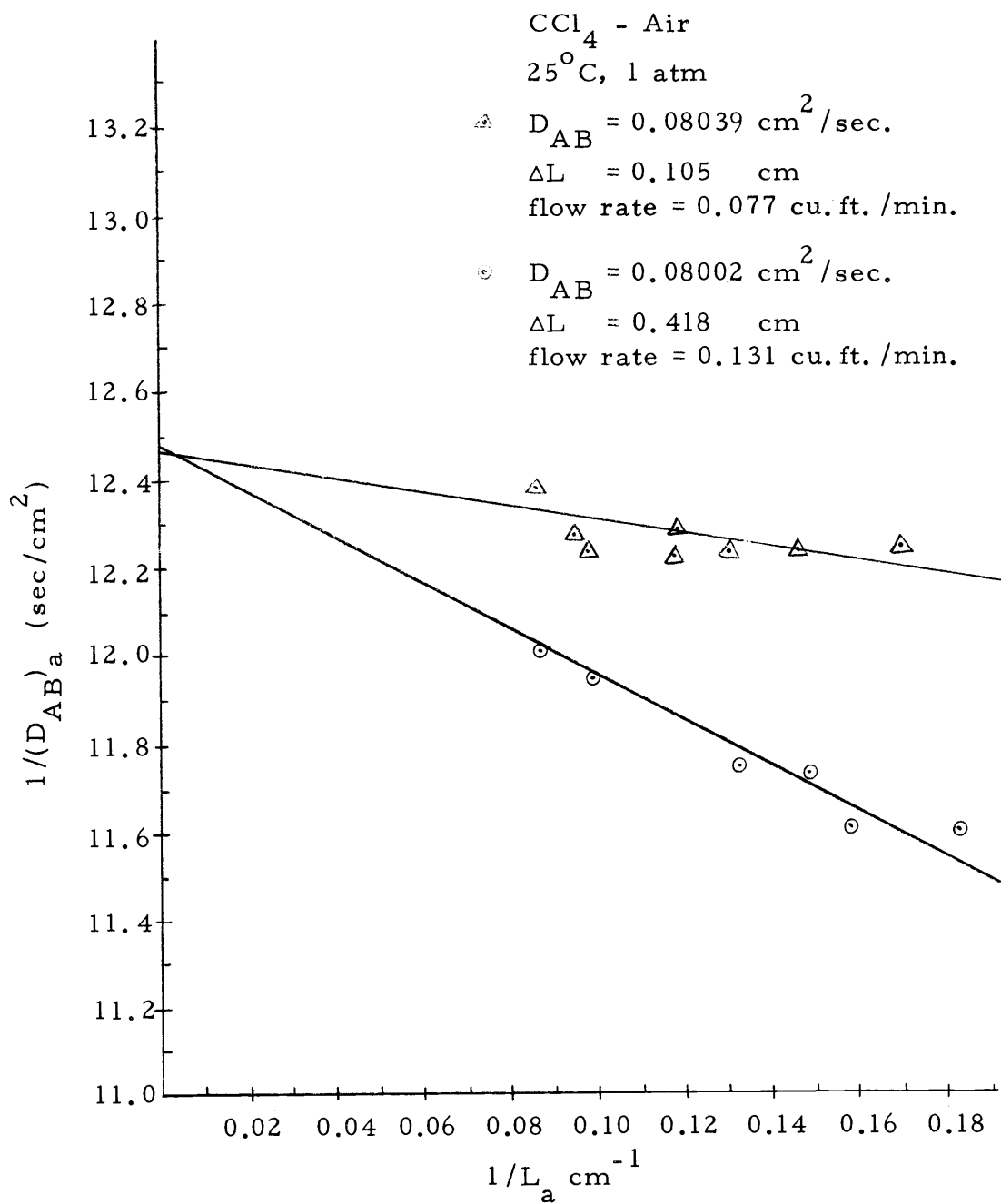


Figure 10. Diffusion Coefficient of Carbon Tetrachloride in Air.

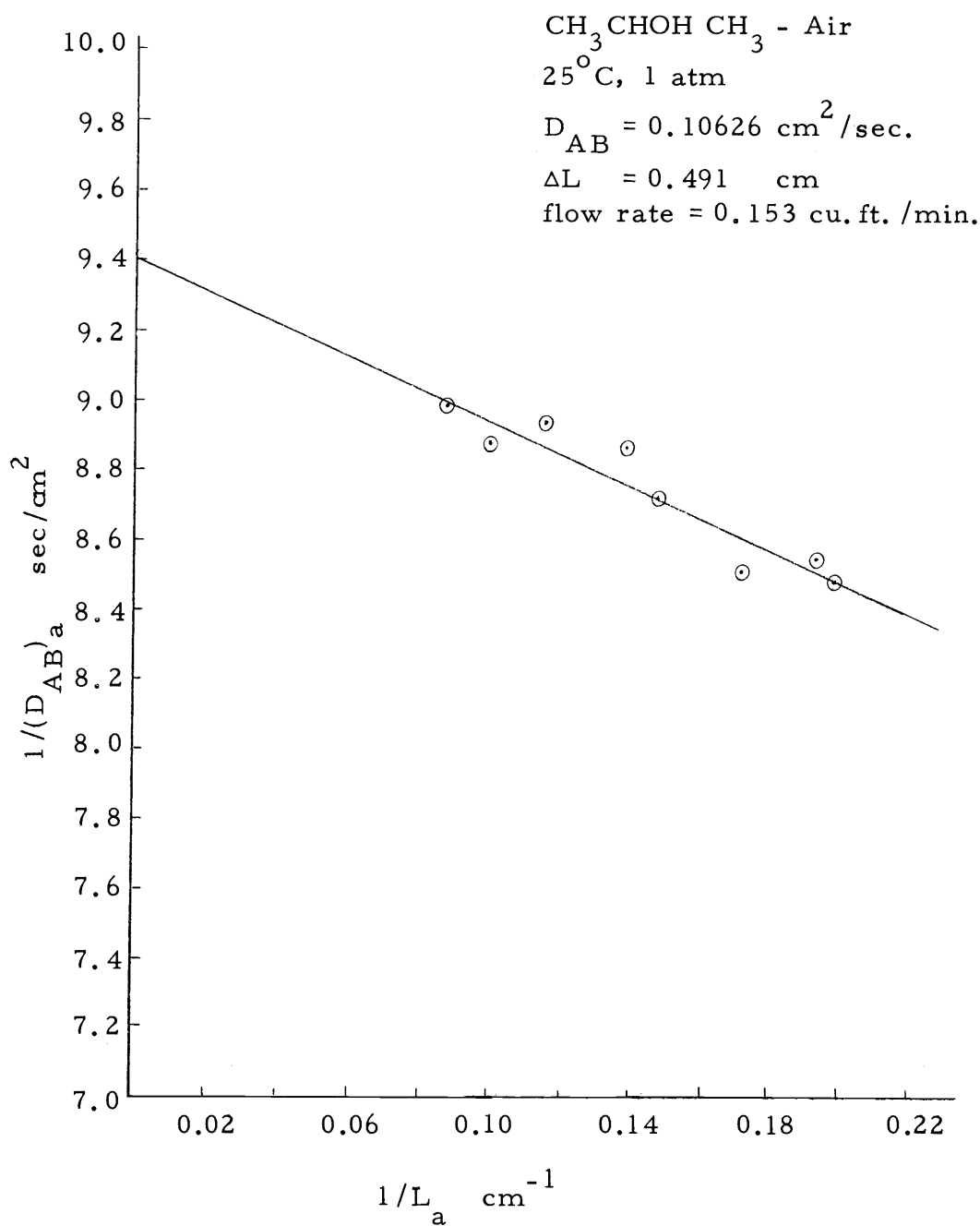


Figure 11. Diffusion Coefficient of Isopropyl Alcohol in Air.

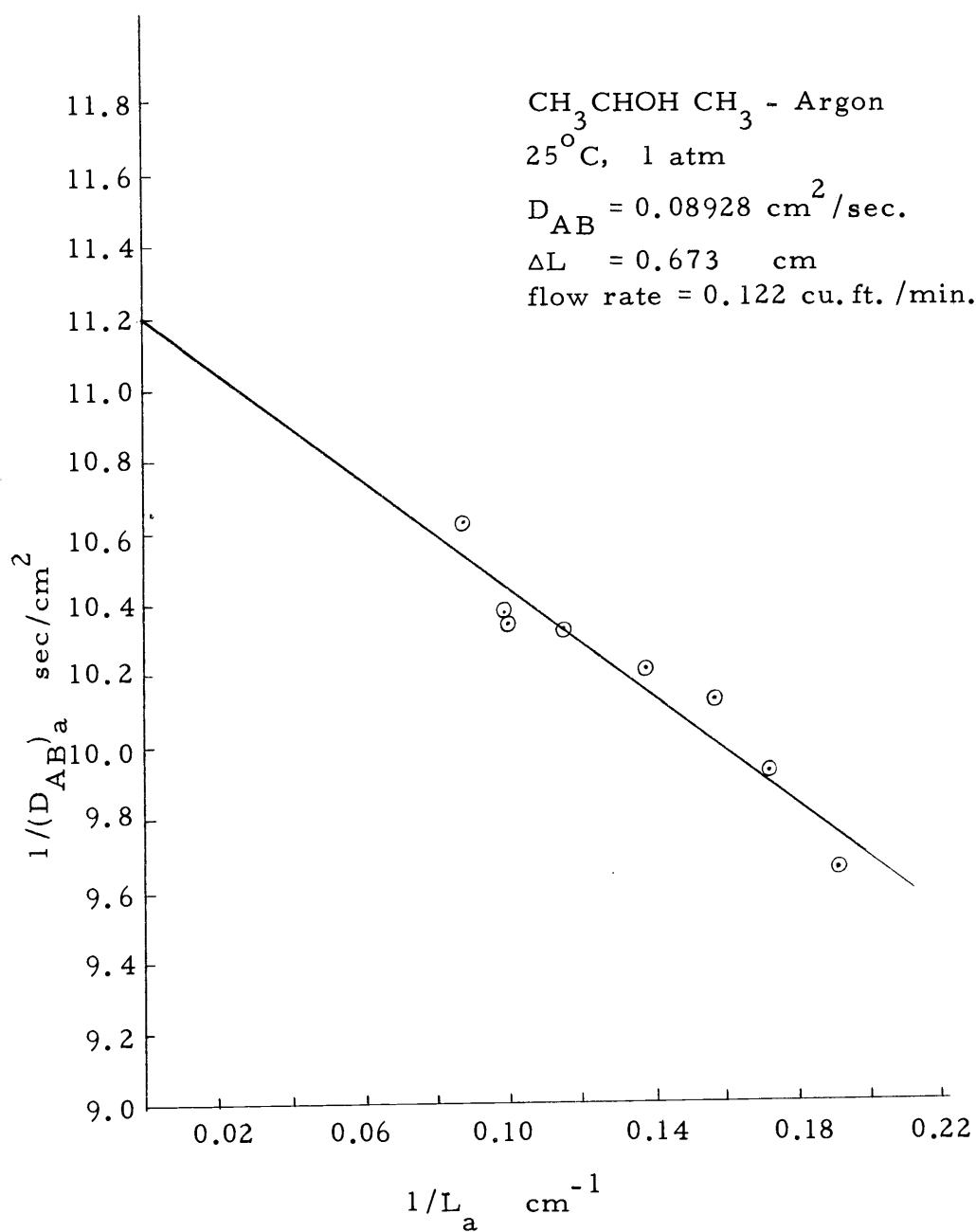


Figure 12. Diffusion Coefficient of Isopropyl Alcohol in Argon.

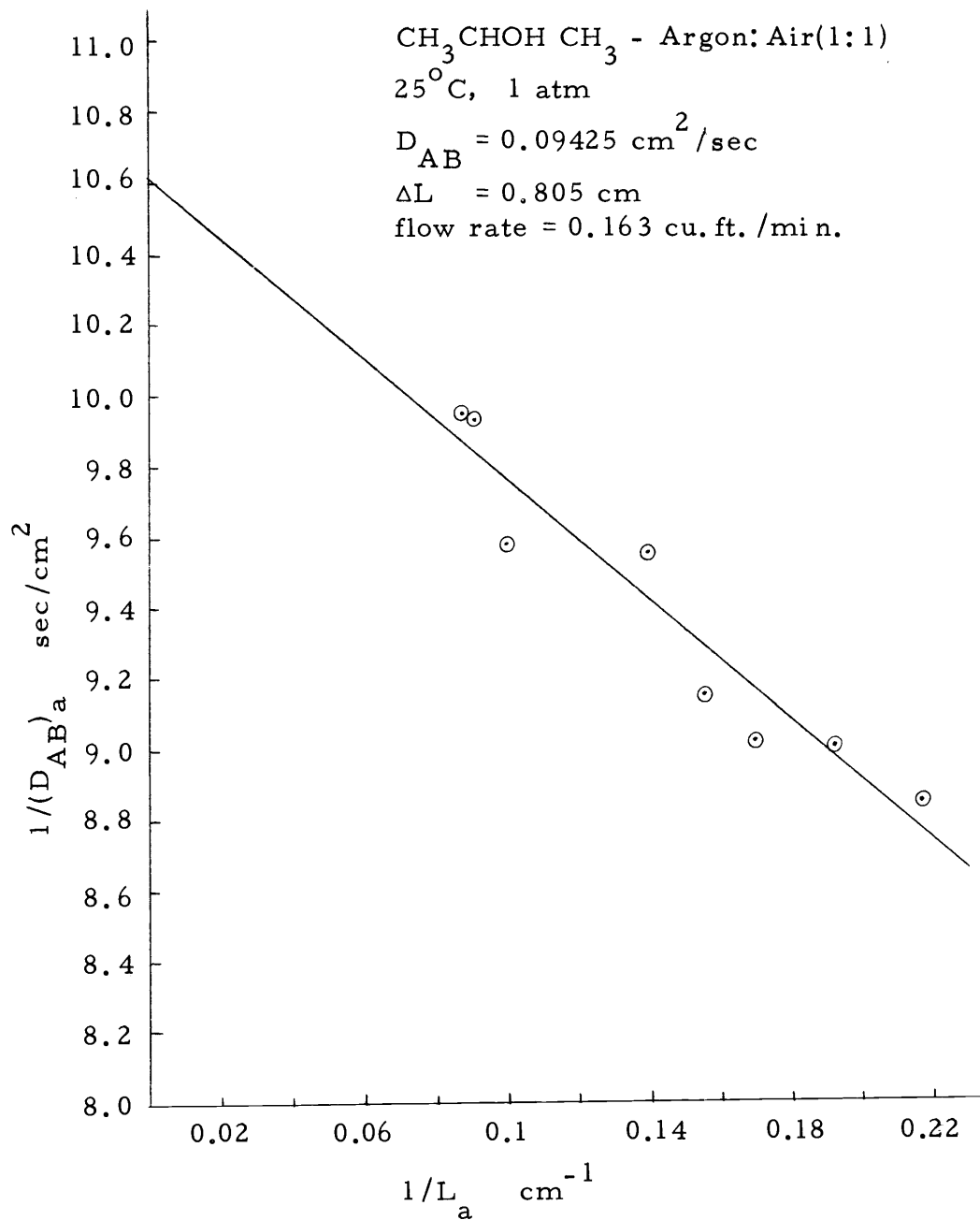


Figure 13. Diffusion Coefficient of Isopropyl Alcohol in Argon: Air (1:1 in volume)

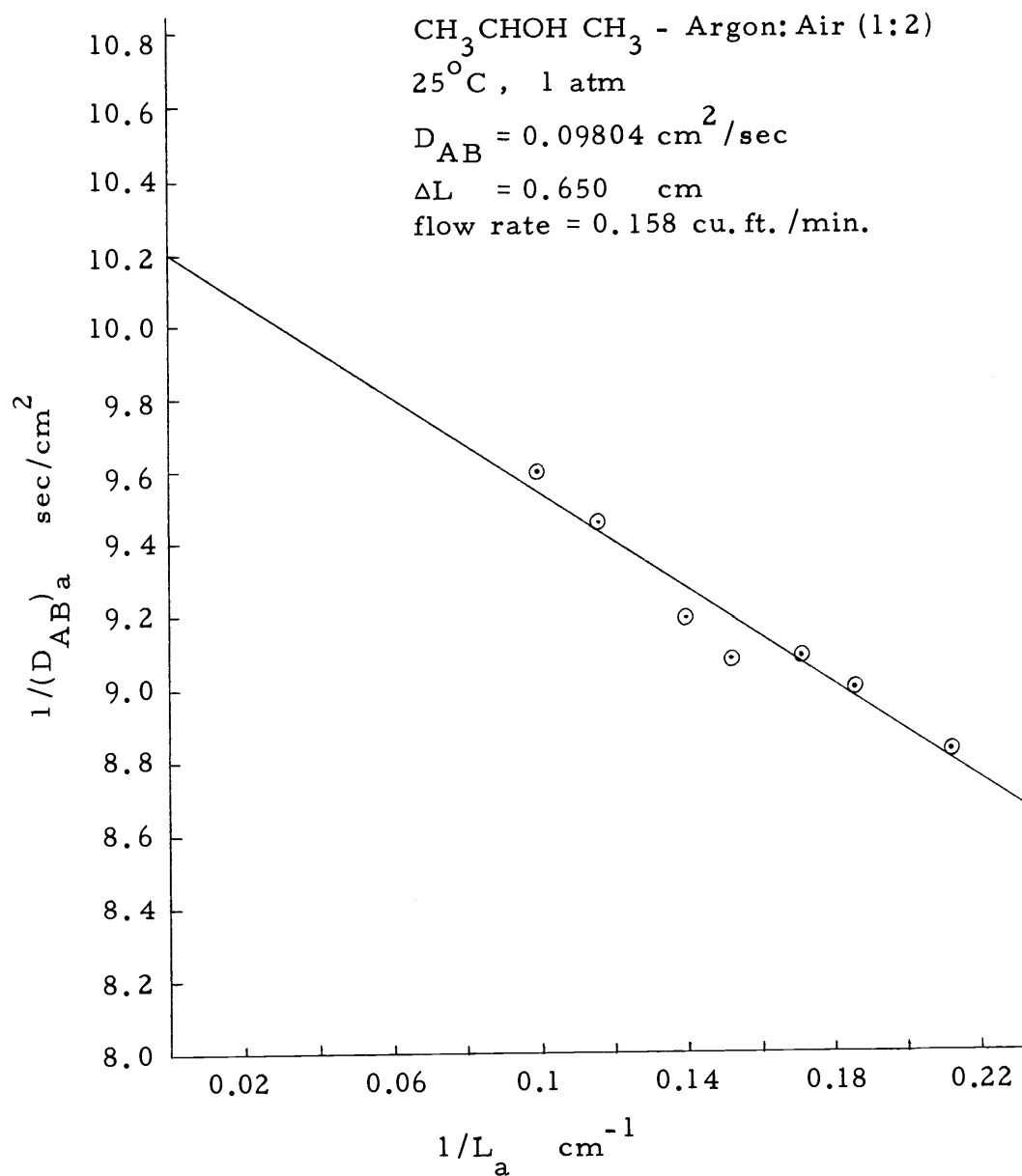


Figure 14. Diffusion Coefficient of Isopropyl Alcohol in Argon: Air (1:2 in volume)

SUMMARY FOR EMPIRICAL EQUATIONS FOR  
THE DIFFUSION COEFFICIENT

Arnold Method

After using Sutherland constant  $C_{AB}$  to account for deviation from hard spheres, Arnold (3) developed the following equation:

$$D = \frac{0.00837 \left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2}}{P(V_{bA}^{1/3} + V_{bB}^{1/3})^2} \frac{T^{5/2}}{T + C_{AB}} \quad (63)$$

where

$$C_{AB} = 1.47 F \sqrt{T_{bA} \times T_{bB}}$$

and  $F$  depends on the ratio  $V_{bB}/V_{bA}$ .

Hirschfelder, Bird and Spatz Method for Non-polar Compounds

The collision integral  $\Omega_{D, AB}$  for the potential energy of attraction between two nonpolar gases has been calculated by Hirschfelder, Bird and Spatz as a function of  $(kT/\epsilon)_{AB}$ . The values of  $\epsilon/k$  and  $\sigma$  are obtained from viscosity data, and expressed in the following formulas:

$$\begin{aligned} \sigma_{AB} &= \frac{1}{2} (\sigma_A + \sigma_B) & \epsilon_{AB} &= \sqrt{\epsilon_A \epsilon_B} \\ \sigma &= 0.841 V_c^{1/3} & \epsilon/k &= 0.77 T_c \end{aligned} \quad (64)$$

Hirschfelder, Bird and Spotz (12, 13) developed the following equation:

$$D_{AB} = \frac{0.0018583 T^{3/2} \left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2}}{P \sigma_{AB}^2 \Omega_{D, AB}} \quad (65)$$

### Wilke and Lee Method

Wilke and Lee (32) modified Hirschfelder, Bird and Spotz method and developed the following equation:

$$D_{AB} = \frac{B T^{3/2} \left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2}}{P \sigma_{AB}^2 \Omega_{D, AB} (1 - \Delta)} \quad (66)$$

where  $B \times 10^4 = 10.7 - 2.46 \left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2}$

and  $\Delta = f \left( \frac{M_A}{M_B}, \frac{kT}{\epsilon_{AB}} \right)$

### Othmer Method

Chen and Othmer (21) developed the following equation in which the critical temperature and volume were used.

$$D_{AB} = \frac{0.43 \left( \frac{T}{100} \right)^{1.81} \left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{0.5}}{P \left( \frac{T_{cA} T_{cB}}{10,000} \right)^{0.1405} \left[ \left( \frac{V_{cA}}{100} \right)^{0.4} + \left( \frac{V_{cB}}{100} \right)^{0.4} \right]^2} \quad (67)$$

Wilke Method in Multicomponent Gases

Wilke (33, 34) derived the following equation for the effective diffusion coefficient of a gas with respect to a multicomponent mixture of stagnant gases:

$$D_{A, \text{mix}} = \frac{1}{\frac{y_B}{D_{AB}} + \frac{y_C}{D_{AC}} + \frac{y_D}{D_{AD}} + \dots} \quad (68)$$

Table 2 indicates the results of calculated diffusion coefficients using above equations.



Table 2. Comparison of Theoretically Calculated Diffusion Coefficients and Experimental Diffusion Coefficients.

	$\text{CCl}_4$ -Air	$\text{CH}_3\text{CHOHCH}_3$ in Air	$\text{CH}_3\text{CHOHCH}_3$ in Argon
Experimental	0.08002	0.10626	0.08928
Arnold	0.08149	0.09806	0.08829
Hirschfelder, Bird and Spatz	0.07485		
Wilke and Lee	0.08158	0.10490	0.09456
Othmer	0.07942	0.10022	0.09293
-----			
	$\text{CH}_3\text{CHOHCH}_3$ in Argon: Air (1 : 1)	$\text{CH}_3\text{CHOHCH}_3$ in Argon: Air (1 : 2)	
Experimental	0.09425	0.09804	
Wilke and Lee Multicomponent	0.09704	0.09993	

## DISCUSSION OF RESULTS

The experimental diffusion coefficients for carbon tetrachloride and isopropyl alcohol in binary and multicomponent gas systems involving air and argon were compared with the theoretically calculated diffusion coefficients in Table 2. In order to testify the accuracy and the reproducibility of the present work, the result of the carbon tetrachloride-air system was compared with the results previously studied by Larson (19) and the calculated values. The present value of the carbon tetrachloride was 3.6 percent smaller than that of Larson. This difference may have arisen from a slight error in measuring the cross-sectional area of the diffusion cell or from any leak from the stopper during the weighing. Mass flow rate is proportional to the cross-sectional area of the diffusion cell and therefore, accurate measurement of the cross-sectional area is critical.

In general, the slope of the curve increased with increasing flow rate, thus producing increased end effects. The diffusion coefficient will usually increase with decreasing molecular weight of the carrier gas for a given diffusing gas at a fixed temperature. For example, diffusivity of isopropyl alcohol-air system is greater than that of isopropyl alcohol-argon system since the molecular weight of air is smaller than that of argon. Moreover, the diffusivity is also

affected by the intermolecular forces.

There are some cooling zones in the interface between liquid and gas phase owing to vaporization at the surface. A temperature gradient at the surface of the liquid could cause convection currents which might introduce an error in the diffusion coefficient measurement. Wilke and Lee (31) have measured the magnitude of this cooling effect and indicated that it can be neglected except for liquids which possess high volatility at the temperatures used. If the relatively large end-effect corrections are required, the experimental data cannot be regarded as highly precise. However, the present experimental values are believed sufficiently accurate and useful as a source of data for possible engineering applications involving diffusion of these substances.

The dipole moments of the carbon tetrachloride and isopropyl alcohol are zero debye and 1.66 debye, respectively. Therefore, the carbon tetrachloride is a non-polar molecule and the isopropyl alcohol is a polar molecule. The equation of Hirschfelder, Bird and Spatz should only be expected to be reliable for carbon tetrachloride in this present work since it is the only non-polar compound.

The diffusion coefficient for the isopropyl alcohol-air system was 1.3 percent and 6 percent higher than those obtained empirically by the Wilke and Lee equation and the Othmer equation, respectively.

The value of isopropyl alcohol-argon system was 1.1 percent

higher than the value obtained by the Arnold equation, and 3.9 percent and 5.6 percent smaller than the value obtained by the Othmer equation and the Wilke and Lee equation, respectively.

The diffusion coefficient for the isopropyl alcohol-mixture of argon 1:air 1 in volume was 2.96 percent smaller than that calculated by the Wilke and Lee multicomponent equation. The diffusion coefficient for the isopropyl alcohol-mixture of argon 1:air 2 in volume was 1.9 percent smaller than that obtained by the Wilke and Lee multicomponent equation. Table 3 presents the percent deviation between experimental value and theoretically calculated value.

Table 3. The Percent Deviation Between Experimental and Empirically Calculated Value

	$\text{CCl}_4$ -Air	$\text{CH}_3\text{CHOHCH}_3$ in Air	$\text{CH}_3\text{CHOHCH}_3$ in Argon
Experimental	0.08002	0.10626	0.08928
Arnold	-1.8%	8.4%	1.1%
Hirschfelder, Bird and Spatz	6.8%		
Wilke and Lee	-1.9%	1.3%	-5.6%
Othmer	0.8%	6.0%	-3.9%
-----			
	$\text{CH}_3\text{CHOHCH}_3$ in Argon: Air (1 : 1)	$\text{CH}_3\text{CHOHCH}_3$ in Argon: Air (1 : 2)	
Experimental	0.09425	0.09804	
Wilke and Lee Multicomponent	-2.96%	-1.9%	

## BIBLIOGRAPHY

1. Altshuller, A.P. and T.R. Cohen. Application of diffusion cells to the production of known concentrations of gaseous hydrocarbons. *Analytical Chem.* 32(7), 802, 1960.
2. Andrew, S.P.S. A simple method of measuring gaseous diffusion coefficients. *Chemical Engineering Science* 4, 269. 1955.
3. Arnold, J.H. Studies in diffusion. *Ind. Eng. Chem.* 22(10), 1091. 1930.
4. Berry, V.J. and R. C. Koeller. Diffusion in compressed binary gaseous systems. *A.I.Ch.E. Journal.* 6(2), 274. 1960.
5. Brockett, C.P. Apparatus for the quantitative observation of gaseous diffusion. *J. Chem. Educ.* 43(4), 207. 1966.
6. Carslaw, H.S. Introduction to mathematical theory of conduction of heat in solids. New York, Dover publication, 1945.
7. Chemical Rubber Publishing Company. Handbook of chemistry and physics. 49th Ed. 1969.
8. Chen, H. T. and D. F. Othmer. Correlating diffusion coefficients in binary gas systems. *Ind. Eng. Chem., process Design Develop.* 1(4), 249. 1962.
9. Fuller, E.N., P.D. Schetter and J. C. Giddings. A new method for prediction of binary gas-phase diffusion coefficients. *Ind. Eng. Chem.* 58(5), 19. 1966.
10. Gilliland, E. R. Diffusion coefficients in gaseous systems. *Ind. Eng. Chem.* 26(6), 681. 1934.
11. Godfrey, J. H. Diffusion coefficients of binary gas systems. Master's thesis. Corvallis, Oregon State University. 1968 42 numb. leaves.
12. Hirschfelder, J. O., R. B. Bird and E. L. Spatz. The transport properties of gases and gaseous mixtures. *Chem. Rev.* 44, 205, 1949.

13. Hirschfelder, J.O., C.F. Curtiss and R.B. Bird. Molecular theory of gases and liquids. pp. 538-540. p. 1110. Wiley, New York, 1954.
14. Hudson, G.H., J.C. McCoubrey and A.R. Ubbelohde. Vapor diffusion coefficients and collision parameters for cyclic molecules. Transactions, Faraday Society, 56, 1144. 1960.
15. International Critical Table, McGraw-Hill, New York, 1930.
16. Jorgensen, F. and H. Watts. The determination of vapour diffusion coefficients. Chemistry and Industry. 1440. September 1961.
17. Kobe, K.A. and R.E. Lynn. The critical properties of elements and compounds. J. Chem. Rev., 52, 117-236. 1953.
18. Kohn, J.P. and N. Romero. Molecular diffusion coefficients in binary gaseous systems at one atmosphere pressure. J. Chem. Eng. Data. 10(2), 125. 1965
19. Larson, E.M. Diffusion coefficients of chlorinated hydrocarbons in air. Master's thesis. Corvallis, Oregon State University. 1964. 42 numb. leaves.
20. Nelson, E.T. The measurement of vapour diffusivities in coalgas and some common gases. J. Applied Chem. 6, 286. 1956.
21. Othmer, D.F. and N.H. Chen. New generalized equation for gas diffusion coefficient. J. Chem. Eng. Data. 7(1), 37. 1962.
22. Perry, J.H. Chemical Engineers Handbook. 3d Ed. McGraw-Hill, New York, 1950.
23. Pochettino, A. Su Gli Elementi Cinetici Molecolari. Nuovo Cimento, N9, Ser. 6, V.8, 2<sup>o</sup> sem. - Fasc 7<sup>o</sup> . p. 5. 1915.
24. Reamer, H.H. and B.H. Sage. Diffusion coefficients in hydrocarbon systems. J. Chem. Eng. Data. 8, 34, 1963.
25. Reid, R.C. and T.K. Sherwood. Properties of gases and liquid. McGraw-Hill, New York, 1958. p. 52.

26. Rossini, F.D. Amer. Petroleum Inst. Research Proj. 44.
27. Saksena, M.P. and S.C. Saxena. Calculation of diffusion coefficients of binary gas mixtures. Indian J. Pure Appl. Phys. 4(31), 109. 1966.
28. Slattery, J.C. and R.B. Bird. Calculation of diffusion coefficient of dilute gases and of the self-diffusion coefficient of dense gases. A.I. Ch.E. Journal 4(2), 137. 1958.
29. Walker, R.E. and A.A. Westenberg. Molecular diffusion studies in gases at high temperature. I. The point source technique. J. Chem. Phys. 29(5), 1139. 1958. IV. Results and interpretation of the CO<sub>2</sub>-O<sub>2</sub>, CH<sub>4</sub>-O<sub>2</sub>, H<sub>2</sub>-O<sub>2</sub>, and H<sub>2</sub>O-O<sub>2</sub> systems. J. Chem. Physics, 32(2), 436. 1960.
30. Walker, R.E. and A.A. Westenberg. Measurement of multi-component diffusion coefficients for the CO<sub>2</sub>-He-N<sub>2</sub> systems using the point source technique. J. Chemical Physics 32(5), 1314. 1960.
31. Wilke, C.R. and C.Y. Lee. Measurement of vapor diffusion coefficients. Industrial and Eng. Chem. 46(11) 2381. 1954.
32. Wilke, C.R. and C.Y. Lee. Estimation of diffusion coefficients for gases and vapors. Industrial and Engineering Chemistry. 47(6), 1253. 1955.
33. Wilke, C.R. and D.F. Fairbanks. Diffusion coefficients in multicomponent gas mixtures. Ind. Eng. Chem. 42(3), 471. 1950.
34. Wilke, C.R. Diffusional properties of multicomponent gases. Chem. Eng. Progress. 46(2), 95. 1950.



## APPENDICES

## APPENDIX I

Calculation

From equation (22),

$$D_{AB} = \frac{W_A R T L}{S M_A t P \ln \frac{P}{P - p_{A1}}} \quad (22)$$

Where  $p_{A1}$  is saturated vapor pressure at the liquid surface. Substituting for quantities that remain constant for all runs, equation (22) reduces to

$$D_{AB} = \frac{(82.057 \frac{\text{atm cm}^3}{\text{gr mole } ^\circ\text{K}})(760 \frac{\text{mm Hg}}{\text{atm}}) T W_A L}{(0.702934 \text{ cm}^2)(2.3026) M_A t P \log \frac{P}{P - p_{A1}}}$$

$$D_{AB} = (3.85287 \times 10^4) \frac{T W_A L}{M_A t P \log \frac{P}{P - p_{A1}}} \quad (69)$$

For apparent diffusion coefficient and apparent diffusion path length,

$$(D_{AB})_a = (3.85297 \times 10^4) \frac{T W_A L_a}{M_A t P \log \frac{P}{P - p_{A1}}} \quad (70)$$

The apparent diffusion path length,  $L_a$ , can be calculated from the cross-sectional area of the cell and the density of the liquid.

$$L_a = \ell - \frac{W_L}{S\rho_L} = 14.17 - \frac{W_L}{0.702934 \rho_L} \quad (71)$$

The magnitude of the end effect correction can be determined from the slope of the curves in Figures 10 through 14. From the equation (62), the end effect correction can be calculated by

$$L = -m D_{AB} \quad (72)$$

where  $m$  is the slope of the curve.

### Sample Calculation

Weight of cell, holder and stopper = 52.7863 gm.

Beginning: Weight of cell, holder, stopper and  $\text{CH}_3\text{CHOHCH}_3$   
= 56.6421 gm.

End: Weight of cell, holder, stopper and  $\text{CH}_3\text{CHOHCH}_3$   
= 56.5880 gm.

$W_A = 0.0541$  gm.

$t = 33870$  sec.

$$L_o = 14.17 - \frac{3.8558}{0.702934 \times 0.7812} = 7.14838$$

$$L_t = 14.17 - \frac{3.8017}{0.549132} = 7.2469$$

$$L_a = \frac{7.14838 + 7.2469}{2} = 7.19764$$

$$\frac{1}{L_a} = 0.13893$$

$$P = \text{atmospheric pressure} + \text{cell pressure} = 758.9 + \frac{2.85}{13.6} \times 10$$

$$= 758.9 + 2.10 = 761$$

$$p_s = 43.582 \text{ mm Hg} \quad M_A = 60.09 \text{ gm./mole}$$

$$(D_{AB})_a = (3.85297 \times 10^4) \frac{(298)(0.0541)(7.19764)}{(60.09)(33870)(761) \log \left( \frac{761}{761 - 43.582} \right)}$$

$$(D_{AB})_a = 0.11269 \text{ cm}^2/\text{sec}$$

correcting  $(D_{AB})_a$  to 760 mm Hg

$$(D_{AB})_a = (0.11269) \left( \frac{761}{760} \right) = 0.11283 \text{ cm}^2/\text{sec}$$

$$\frac{1}{(D_{BA})_a} = 8.86289 \text{ sec/cm}^2$$

### Sample Calculation for Empirical Equations

(a) Arnold Method for  $\text{CCl}_4$  - Air System

$$\frac{V_b \text{ of } \text{CCl}_4}{V_b \text{ of air}} = \frac{276}{82} = 3.334$$

$F_{bB}/V_{bA}$	1	2	3	4	5	6	8	10
F	1.0	0.980	0.953	0.92	0.894	0.875	0.838	0.805

$$F = 0.953 - 0.334 \times 0.033 = 0.953 - 0.011038 = 0.941962$$

$$C = 1.47 F \sqrt{T_{bA} T_{bB}} = 1.47 \times 0.941962 \sqrt{350 \times 78.39} = 229.358$$

$$D_{AB} = \frac{0.00837 \left( \frac{1}{153.84} + \frac{1}{28.97} \right)^{1/2} 298^{5/2}}{1(102^{1/3} + 29.9^{1/3})^2 (298 + 229.358)} = 0.081494 \text{ cm}^2/\text{sec}$$

(b) Hirschfelder, Bird and Spatz Method for  $\text{CCL}_4$  - Air System

$$\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B) = \frac{1}{2}(5.881 + 3.617) = 4.749 \text{ \AA}$$

$$\epsilon_{AB}/k = \sqrt{\epsilon_A \epsilon_B} = \sqrt{327 \times 97} = 178.095 \text{ }^\circ\text{K}$$

$$kT/\epsilon_{AB} = \frac{298}{178.095} = 1.67326$$

$$\Omega_{D,AB} = 1.153 - \frac{0.02326 \times 0.013}{0.05} = 1.14696$$

$$D_{AB} = \frac{0.00185 (298)^{3/2} \left( \frac{1}{153.84} + \frac{1}{28.97} \right)^{1/2}}{1 (4.749)^2 1.14696} = 0.07485 \text{ cm}^2/\text{sec}$$

(c) Wilke and Lee for Multicomponent System (Argon : Air = 1 : 2)

$$D_{A\text{-mix}} = \frac{1}{\frac{y_B}{D_{AB}} + \frac{y_C}{D_{AC}}} = \frac{1}{\frac{1/3}{0.089284} + \frac{2/3}{0.10626}}$$

$$= 0.09993 \text{ cm}^2/\text{sec}$$

## APPENDIX II

Table 4. Physical Properties of the Involved Chemicals

	Argon	Air	Isopropyl Alcohol	CCl <sub>4</sub>	Reference
B. P. $T_b$ ( $^{\circ}$ K)	87.3	78.39	355.2	350	(22)
Critical Tem. $T_c$ ( $^{\circ}$ K)	150.7	132.3	508	556.4	(22)
Critical Press. $P_c$ (atm)	48	37.2	53	45	(22)
Critical Vol. $V_c$ (cm <sup>2</sup> /gm mole)	75.2	86.6	220	276	(17)
Molal Vol. at Normal B. P. $V_b$ (cm <sup>2</sup> /gm mole)	27.9	29.9	102	82	(26,22)
$\epsilon/k$ ( $^{\circ}$ K)	124	97	391.16	327	(13)
$\sigma$ ( $\text{A}^{\circ}$ )	3.418	3.617	5.077	5.881	(13)
Molecular Weight	39.94	28.97	60.09	153.84	(22)
Density (gm/cm <sup>3</sup> )	0.0017828	0.0012928	0.7812	1.595	(22)
Saturated Vapor Press. at 25 $^{\circ}$ C, $p_{AS}$ (mm Hg)			43.582	113.1	(22)
Dipole Moment (debye)			1.66	0	(7)

## APPENDIX III

Table 5. Experimental Data at 25°C.

Run No.	$W_A$ gm	t sec	$L_a$ cm	Cell Pressure in $H_2O$ gage (cm)	Atmospheric Pressure mm Hg	$(D_{AB})_a$ $cm^2/sec$
CCl <sub>4</sub> in air; flow rate = 0.077 cu. ft. /min.						
1	0.1967	38880	11.4667	1.1	757.92	0.080785
2	0.2565	36720	8.3524	1.2	759.2	0.081408
3	0.2965	38760	7.6463	1.2	760.03	0.081709
4	0.5586	55920	5.8625	1.3	758.6	0.081679
5	0.3357	39180	6.8129	1.2	761.35	0.081675
6	0.2211	38760	10.1648	1.2	760.95	0.081129
7	0.3566	51480	8.4613	1.3	757	0.081526
8	0.2079	37200	10.51247	1.3	755	0.081511
CCl <sub>4</sub> in air; flow rate = 0.131 cu. ft. /min.						
9	0.2126	41020	11.4334	2.5	758.15	0.082679
10	0.3474	35790	6.3300	2.5	761.5	0.086139
11	0.2396	40320	10.0571	2.55	760.2	0.083633
12	0.3084	38175	7.5353	2.55	759.1	0.085052
13	0.3882	42765	6.7088	2.65	760.43	0.085253
14	0.3896	34585	5.4572	2.7	761.5	0.086198
Isopropyl alcohol in air; flow rate = 0.153 cu. ft. /min.						
15	0.0541	33870	7.1976	2.85	758.9	0.11283
16	0.0360	36130	11.3587	3.1	759.7	0.11122
17	0.04875	36690	8.6070	3.1	757.05	0.11198
18	0.07475	36065	5.7857	3.1	757.15	0.11744
19	0.0438	38065	9.9761	3.1	758.38	0.11261
20	0.0785	32828	5.0215	3.1	758.83	0.11787
21	0.0635	36575	6.7331	3.1	757.78	0.11458
22	0.0853	36840	5.1537	3.1	758.2	0.11703
Isopropyl alcohol in argon; flow rate = 0.122 cu. ft. /min.						
23	0.05332	38485	7.1945	3.1	759.45	0.097922
24	0.03145	37235	11.3548	3.15	759	0.094163
25	0.07645	42915	5.8072	3.15	753.35	0.10079
26	0.04337	37990	8.6357	3.15	759.3	0.096845
27	0.04023	40835	9.9826	3.15	758.05	0.096439
28	0.07445	36595	5.1942	3.15	757.75	0.10358
29	0.03874	38980	9.9711	3.1	754.2	0.096664
30	0.0573	36280	6.3708	3.1	759.02	0.098793

Continued on next page

Table 5 continued.

Run No.	$W_A$ gm	t sec	$L_a$ cm	Cell Pressure in $H_2O$ gage (cm)	Atmospheric Pressure mm Hg	$(D_{AB})_a$ $cm^2/sec$
Isopropyl alcohol in argon:air (1:1); flow rate = 0.163 cu. ft. /min.						
31	0.03138	34685	11.3385	4.2	757.25	0.10059
32	0.0384	36135	9.9579	4.1	761.85	0.10440
33	0.0402	42925	10.9542	4.15	758.12	0.10071
34	0.0736	42605	6.4392	4.1	759.32	0.10937
35	0.08525	39385	5.1925	4.0	763.35	0.1111
36	0.0729	38095	5.8886	4.15	760.15	0.11092
37	0.09565	38340	4.6050	4.15	760.15	0.11308
38	0.06395	42930	7.1226	4.15	761.5	0.10464
Isopropyl alcohol in argon:air (1:2); flow rate = 0.158 cu. ft. /min.						
39	0.06345	40742	7.1288	3.85	757.07	0.10883
40	0.03625	33910	9.9500	3.85	756.95	0.10420
41	0.0703	36965	5.8441	3.7	764.37	0.10998
42	0.04884	39057	8.5935	3.8	760.25	0.10576
43	0.00849	40084	5.3592	3.75	756.47	0.11114
44	0.0632	36960	6.5525	3.75	758.97	0.11008
45	0.09036	36965	4.7163	3.8	758.63	0.11337



## APPENDIX IV

Table 6. Diffusion Coefficient of Carbon Tetrachloride in Air.

.EDIT

]INPUT	$X = 1/L_a$	$Y=1/(D_{AB})_a$
00001:	0.08720	12.378
00002:	0.11972	12.283
00003:	0.13078	12.238
00004:	0.17057	12.242
00005:	0.14678	12.243
00006:	0.09837	12.326
00007:	0.11818	12.265
00008:	0.09512	12.268
00009:		

]OUT, LEC

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 \*\*\*\*\*

PROBLEM IDENTIFICATION - PROBLEM.

SAMPLE SIZE = 8

SUM OF X	.96672
MEAN OF X	.12084
STANDARD DEVIATION OF X	.02816
STANDARD ERROR OF MEAN	.00996
MAXIMUM X	.17057
MINIMUM X	.08720
RANGE OF X	.08337

SUM OF Y	98.24300
MEAN OF Y	12.28037
STANDARD DEVIATION OF Y	.04881
STANDARD ERROR OF MEAN	.01726
MAXIMUM Y	12.37800
MINIMUM Y	12.23800
RANGE OF Y	.14000

REGRESSION LINE  $Y = A + B * X$ 

A =	12.438243	STANDARD ERROR OF A =	.057501
B =	-1.306423	STANDARD ERROR OF B =	.464928

 $D_{AB} = 1/A = 0.08039$  at flow rate 0.077 cu. ft./min.

CORRELATION COEFFICIENT R = -0.753800205

ANALYSIS OF VARIANCE

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE
TOTAL	7	.01667	.0024
REGRESSION	1	.00947	.0095
ERROR	6	.00720	.0012

Table 7. Diffusion Coefficient of Carbon Tetrachloride in Air.

```

]INPUT      X=1/La      Y=1/(DAB)a
00001:     0.08746     12.094
00002:     0.15797     11.609
00003:     0.09943     11.956
00004:     0.13270     11.757
00005:     0.14905     11.729
00006:     0.18324     11.601
00007:
]OUT,LED

```

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PROBLEM IDENTIFICATION - PROBLEM.

SAMPLE SIZE = 6

```

SUM OF X                .80985
MEAN OF X               .13498
STANDARD DEVIATION OF X .03628
STANDARD ERROR OF MEAN .01481
MAXIMUM X               .18324
MINIMUM X               .08746
RANGE OF X              .09578

SUM OF Y                70.74600
MEAN OF Y               11.79100
STANDARD DEVIATION OF Y .19660
STANDARD ERROR OF MEAN .08026
MAXIMUM Y               12.09400
MINIMUM Y               11.60100
RANGE OF Y              .49300

```

REGRESSION LINE  $Y = A + B * X$

A = 12.496617 STANDARD ERROR OF A = .098984

B = -5.227763 STANDARD ERROR OF B = .712222

$D_{AB} = 1/A = 0.08002$  at flow rate 0.131 cu. ft. /min.

CORRELATION COEFFICIENT R = -0.964825174

#### ANALYSIS OF VARIANCE

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE
TOTAL	5	.19326	.0387
REGRESSION	1	.17990	.1799
ERROR	4	.01336	.0033

Table 8. Diffusion Coefficient of Isopropyl Alcohol in Air.

```

#EDIT

JINPUT      X=1/La      Y=1/(DAB)a
00001:      0.13893      8.86289
00002:      0.08803      8.99118
00003:      0.11618      8.93016
00004:      0.17283      8.51498
00005:      0.10023      8.88020
00006:      0.19914      8.48392
00007:      0.14852      8.72752
00008:      0.19403      8.54481
00009:

] OUT,LEB

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PROBLEM IDENTIFICATION - PROBLEM.

SAMPLE SIZE =          8

SUM OF X                      1.15789
MEAN OF X                      .14474
STANDARD DEVIATION OF X        .04181
STANDARD ERROR OF MEAN        .01478
MAXIMUM X                      .19914
MINIMUM X                      .08803
RANGE OF X                     .11111

SUM OF Y                      69.93566
MEAN OF Y                      8.74196
STANDARD DEVIATION OF Y        .20299
STANDARD ERROR OF MEAN        .07177
MAXIMUM Y                      8.99118
MINIMUM Y                      8.48392
RANGE OF Y                     .50726

REGRESSION LINE   Y = A + B * X

A =          9.410710      STANDARD ERROR OF A =          .091180
B =         -4.620494      STANDARD ERROR OF B =          .608161
      DAB=1/A=0.10626      at flow rate 0.153 cu. ft./min.
CORRELATION COEFFICIENT R = -0.951756660

```

## ANALYSIS OF VARIANCE

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE
TOTAL	7	.28845	.0412
REGRESSION	1	.26129	.2613
ERROR	6	.02716	.0045

Table 9. Diffusion Coefficient of Isopropyl Alcohol in Argon.

]LIST,LEE	X=1/L <sup>a</sup>	Y=1/(D <sub>AB</sub> ) <sup>a</sup>
00001:	0.13899	10.21220
00002:	0.08806	10.61988
00003:	0.17219	9.92161
00004:	0.11579	10.32577
00005:	0.10017	10.36924
00006:	0.19252	9.65344
00007:	0.10029	10.34511
00008:	0.15696	10.12217

] OUT,LEA

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PROBLEM IDENTIFICATION - PROBLEM.

SAMPLE SIZE = 8

SUM OF X	1.06497
MEAN OF X	.13312
STANDARD DEVIATION OF X	.03808
STANDARD ERROR OF MEAN	.01346
MAXIMUM X	.19252
MINIMUM X	.08806
RANGE OF X	.10446

SUM OF Y	81.56942
MEAN OF Y	10.19618
STANDARD DEVIATION OF Y	.29860
STANDARD ERROR OF MEAN	.10557
MAXIMUM Y	10.61988
MINIMUM Y	9.65344
RANGE OF Y	.96644

REGRESSION LINE  $Y = A + B * X$ 

A = 11.200185 STANDARD ERROR OF A = .120624

B = -7.542056 STANDARD ERROR OF B = .875325

 $D_{AB}=1/A=0.08928$  at flow rate 0.122 cu. ft./min.

CORRELATION COEFFICIENT R = -0.961886072

## ANALYSIS OF VARIANCE

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE
TOTAL	7	.62413	.0892
REGRESSION	1	.57746	.5775
ERROR	6	.04667	.0078

Table 10. Diffusion Coefficient of Isopropyl Alcohol in Argon:Air (1:1 in volume).

] INPUT	$X=1/L_a$	$Y=1/(D_{AB})_a$
00001:	0.08818	9.94095
00002:	0.10042	9.57854
00003:	0.09128	9.92950
00004:	0.15529	9.14327
00005:	0.19258	9.00090
00006:	0.16982	9.01550
00007:	0.21715	8.84329
00008:	0.14039	9.55657

] OUT,LEG

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PROBLEM IDENTIFICATION - PROBLEM.

SAMPLE SIZE = 8

SUM OF X	1.15511
MEAN OF X	.14439
STANDARD DEVIATION OF X	.04827
STANDARD ERROR OF MEAN	.01707
MAXIMUM X	.21715
MINIMUM X	.08818
RANGE OF X	.12897
SUM OF Y	75.00852
MEAN OF Y	9.37606
STANDARD DEVIATION OF Y	.43223
STANDARD ERROR OF MEAN	.15282
MAXIMUM Y	9.94095
MINIMUM Y	8.84329
RANGE OF Y	1.09766

REGRESSION LINE  $Y = A + B * X$ 

A = 10.609333 STANDARD ERROR OF A = .165965

B = -8.541304 STANDARD ERROR OF B = 1.097036

 $D_{AB}=1/A=0.09425$  at flow rate 0.163 cu. ft./min.

CORRELATION COEFFICIENT R = -0.953905252

## ANALYSIS OF VARIANCE

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE
TOTAL	7	1.30776	.1868
REGRESSION	1	1.18998	1.1900
ERROR	6	.11778	.0196

Table 11. Diffusion Coefficient of Isopropyl Alcohol - Argon:Air (1:2 in volume).

] INPUT

00001: 0.14027 9.18864  
 00002: 0.10050 9.59692  
 00003: 0.17111 9.09256  
 00004: 0.11636 9.45537  
 00005: 0.18659 8.99766  
 00006: 0.15261 9.08430  
 00007: 0.21203 8.82067

00008:

] OUT,LE3E

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PROBLEM IDENTIFICATION - PROBLEM.

SAMPLE SIZE = 7

SUM OF X 1.07947  
 MEAN OF X .15421  
 STANDARD DEVIATION OF X .03914  
 STANDARD ERROR OF MEAN .01479  
 MAXIMUM X .21203  
 MINIMUM X .10050  
 RANGE OF X .11153

SUM OF Y 64.23612  
 MEAN OF Y 9.17659  
 STANDARD DEVIATION OF Y .26734  
 STANDARD ERROR OF MEAN .10104  
 MAXIMUM Y 9.59692  
 MINIMUM Y 8.82067  
 RANGE OF Y .77625

REGRESSION LINE  $Y = A + B * X$ 

A = 10.199028 STANDARD ERROR OF A = .116282

B = -6.630173 STANDARD ERROR OF B = .734053

 $D_{AB} = 1/A = 0.09804$  at flow rate 0.158 cu. ft. /min.CORRELATION COEFFICIENT  $R = -0.970696304$ 

## ANALYSIS OF VARIANCE

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE
TOTAL	6	.42881	.0715
REGRESSION	1	.40405	.4041
ERROR	5	.02476	.0050