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MASS TRANSFER INTO CYLINDRICAL LIQUID FILMS

MEASUREMENT OF LIQUID DIFFUSIVITIES

BY

RONALD F. LOVENGUTH

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

AT

NEWARK COLLEGE OF ENGINEERING

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Newark, New Jersey

1964

APPROVAL OF THESIS

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ABSTRACT

This thesis was undertaken to augment and validate the previous work of Ratcliff and Reid in the area of diffusion of immiscible liquids. Their novel approach to this particular problem of liquid diffusion led the author to consider an experimental technique that has been used in gas-liquid studies. A short wetted-wall column was used to determine the rate of mass transfer of benzene and toluene into thin cylindrical films of water. A general analytical solution for the rate of mass transfer has been derived and is given below. This solution was checked using the system benzene-water.

$$G = 3.63 \left(\frac{\pi(\rho_w - \rho_B)g}{\mu_1} \right)^{1/6} R^{2/3} L^{1/2} D_{AB}^{1/2} Q^{1/3} C_{R_0}$$

The calculated diffusivity from the experimental results for the system benzene-water with the author's above derived equation gave a result which was approximately thirteen percent lower than that reported by Ratcliff and Reid in their study of the same system using spherical films of water.

The system toluene-water was also studied and data is presented.

TABLE OF CONTENTS

Title	1
Approval	ii
Acknowledgements	iii
Abstract	iv
Table of Contents	v
List of Figures	vi
List of Tables	vi
Introduction	1
Theory	4
Experimental	
Apparatus	9
Procedure	9
Analysis	11
End Effects	14
Method of Calculation	16
Conclusion	30
Table of Nomenclature	33
References	34
Appendix	35

LIST OF FIGURES

Figure 1	Inclined Fluid Flow	4
Figure 2	Diffusion Into Falling Film	6
Figure 3	Schematic Of The Flow System	10
Figure 4	The Absorber	12
Figure 5	Benzene Absorption Versus Flow Rate	27
Figure 6	Benzene Absorption Versus Flow Rate	28
Figure 7	Toluene Absorption Versus Flow Rate	29
Figure 8	Solubility Of Benzene And Toluene In Water	37

LIST OF TABLES

Table 1	Benzene Run Number 1	20
Table 2	Benzene Run Number 2	21
Table 3	Benzene Run Number 3	22
Table 4	Benzene Run Number 4	23
Table 5	Benzene Run Number 5	24
Table 6	Toluene Run Number 1	25
Table 7	Toluene Run Number 2	26
Table 8	Comparison Of Diffusion Coefficients	32

INTRODUCTION

Liquid diffusivities are measured by either a diaphragm cell technique or by methods employing unsteady state diffusion^(4,5). The apparatus used in measuring the diffusion coefficients is essentially the same as that employed for gases. However, since the diffusion coefficients for liquids are of the order of four powers of ten smaller than those for gases, the corresponding apparatus for liquid diffusion studies is of the order of one-one hundredth the size used for gases, assuming one would like the observation time to be the same as that used for gases. This restriction on the apparatus is brought about because the concentration distribution is essentially a function of x^2/Dt , x being the linear dimensions of the apparatus, D the diffusion coefficient, and t the observation time. This experimental handicap makes the determination of diffusion coefficients of liquids rather difficult. However, if suitable methods of analysis are available, the rather small apparatus could be sufficient.

In the case of measurement of diffusion coefficients of immiscible liquids, the small size, the difficulty in obtaining samples, and the method of analysis present tremendous problems in the obtaining of data of reliable

accuracy. This is attested to by the fact that in recent compilations of data, values on diffusion coefficients for immiscible liquids are not reported.⁽⁴⁾

With these problems in mind, a steady state method for the determination of diffusion coefficients of immiscible liquids was introduced by Ratcliff and Reid⁽⁷⁾ using thin films of water flowing over a sphere immersed in an "atmosphere" of another fluid. Their work was an outgrowth of the previous work of Davidson and Cullen,⁽³⁾ involving the absorption of sparingly soluble gases in spherical films of water. Ratcliff and Reid, using the same physical model as Davidson and Cullen, namely, that the velocity profile of the film of water at any point on the sphere could be represented by assuming the flow to be that of an inclined plane tangent to the surface, developed an analytical expression for the rate of mass transfer of the fluid studied. The diffusion coefficient D , was expressed as a function of the parameters of the system, and the physical properties of the fluids.

Similarly, in this thesis, an expression for the rate of mass transfer for cylindrical films of water was developed using a modification of the same velocity profile assumed by Ratcliff and Reid in their experiments with spherical films. The diffusion coefficient obtained in

this work for benzene was lower by approximately thirteen percent than that obtained by Ratcliff and Reid.

Since the diffusion coefficients of immiscible liquids are nowhere to be found in the literature, the system toluene-water was also studied and the results for both organics compared against the engineering empirical expressions of both Wilke-Chang and Othmer-Thaker. The Othmer-Thaker expression was found to give results closer to the author's value than Wilke's expression.

THEORY

Consider a liquid film flow over the outside of a cylindrical body in the "atmosphere" of a second liquid. For thin films the flow may be represented by a vertical plate tangent to the surface of the cylindrical body. Assuming this physical situation and little shear at the interface, a velocity profile can be obtained.

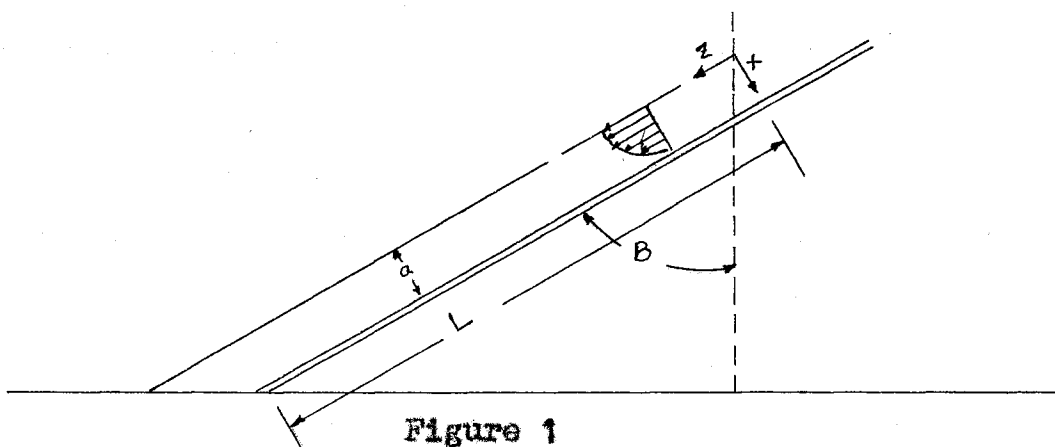


Figure 1

By equating viscous and gravity forces from the above diagram (fig. 1) the following differential equation is obtained.

$$\frac{d\tau_{xz}}{dx} = (\rho_w - \rho_s)g \cos B \quad (1)$$

which gives

$$\tau_{xz} = (\rho_w - \rho_s)g x \cos B + C_1 \quad (1a)$$

the boundary condition for equation (1a) being, $x = 0$
 $\tau_{xz} = 0$ and the equation can then be written as,

$$\tau_{xz} = (\rho_w - \rho_B) g x \cos B \quad (1a')$$

Also, since the fluids are Newtonian we have,

$$\tau_{xz} = -\mu \frac{dV_z}{dx} \quad (1b)$$

Substituting this into equation 1a' gives,

$$\frac{dV_z}{dx} = - \frac{(\rho_w - \rho_B) g \cos B}{\mu_1} x \quad (2)$$

integrating giving

$$V_z = - \frac{(\rho_w - \rho_B) g \cos B}{2\mu_1} x^2 + C_2 \quad (3)$$

the boundary condition being at $x = a$, $V_z = 0$, the constant being evaluated and producing

$$C_2 = \frac{(\rho_w - \rho_B) g \cos B}{2\mu_1} a^2 \quad (3a)$$

The velocity profile is then

$$V_z = \frac{(\rho_w - \rho_B) g a^2 \cos B}{2\mu_1} \left[1 - \frac{x^2}{a^2} \right] \quad (4)$$

However, for the particular case in which we are interested $\cos B = 1$, when $B = 0$ for a vertical plate.

This gives,

$$V_z = \frac{(\rho_w - \rho_B) a^2}{2\mu_1} \left[1 - \frac{x^2}{a^2} \right] \quad (5)$$

The maximum velocity may be obtained by letting $x = 0$, then

$$V_{z_{max}} = \frac{(\rho_w - \rho_B) a^2 g}{2 \mu_1} \quad (6)$$

Another equation of interest is the volume rate of flow

$$Q = \int_0^w \int_0^a v_z dx dy \quad (7)$$

which gives for a vertical plate.

$$Q = \frac{(\rho_w - \rho_B) W a^3}{3 \mu_1} \quad (8)$$

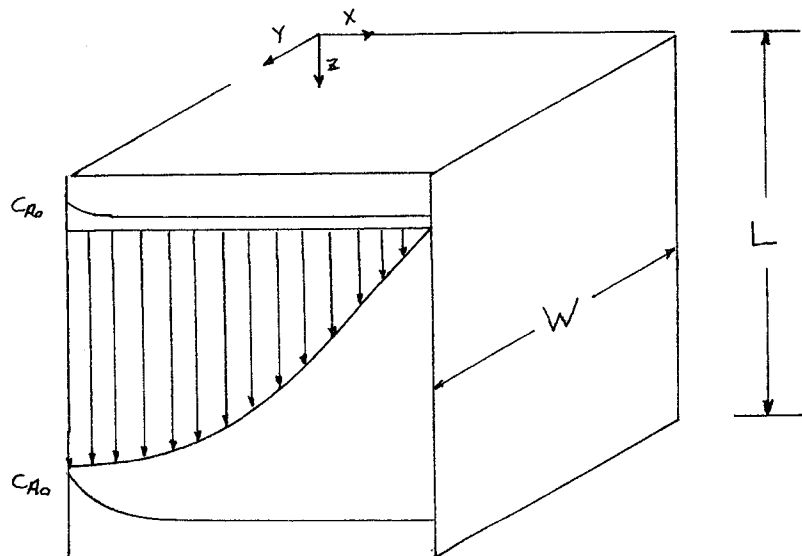
For a cylindrical body W may be replaced without too much error by $2 R$. Then we have

$$Q = \frac{2(\rho_w - \rho_B) \pi R a^3}{3 \mu_1} \quad (9)$$

The Diffusion Equation

Consider the case where we have absorption into a falling film as shown below.

Figure 2



The assumption that the liquid will not penetrate very far into the film will be used to solve the differential equation. From the general diffusion equation (1) with constant density and diffusivity we have,

$$V_z \frac{dC_A}{dz} = D_{AB} \frac{d^2C_A}{dx^2} \quad (10)$$

for V_z we substitute $V_z \max \left(1 - \frac{x^2}{\delta^2}\right)$. However for thin films with small penetration equation (10) can be written as,

$$V_{z \max} \frac{dC_A}{dz} = D_{AB} \frac{d^2C_A}{dx^2} \quad (11)$$

The solution, by the method of "combination of variables" (1) has been worked out and gives the following concentration profile.

$$\frac{C_A}{C_{A_0}} = \operatorname{erfc} \frac{x}{\sqrt{4D_{AB}V_{z \max} z}} \quad (12)$$

Total Material Transferred

The local mass flux at surface $x = 0$ at a position z down the column is

$$N_{A_x}(z) \Big|_{x=0} = -D_{AB} \frac{dC_A}{dx} \Big|_{x=0} = C_{A_0} \frac{\sqrt{D_{AB}V_{z \max}}}{\pi z} \quad (13)$$

the total material for the entire surface $2\pi RL$ is then

$$G = 2\pi RL C_{A_0} \frac{\sqrt{4D_{AB}V_{z \max}}}{\pi L} \quad (14)$$

which is obtained from the following integration,

$$G = \int_0^{2\pi R} \int_0^L N_{A_x} \Big|_{x=0} dz dy \quad (15)$$

but we have

$$v_{max} = \frac{(\rho_w - \rho_B) g a^2}{2\mu_1} \quad (5)$$

and

$$a^2 = \left[\frac{3\mu_1 Q}{2\pi R (\rho_w - \rho_B) g} \right]^{2/3} \quad (16)$$

Equation (16) can be obtained by determining the film thickness of the inclined plate flow. Therefore,

$$v_{z,max} = \frac{(\rho_w - \rho_B)}{2\mu_1} \left[\frac{3\mu_1 Q}{2\pi R (\rho_w - \rho_B) g} \right]^{2/3} \quad (17)$$

Substituting this expression into equation (14) we have

$$G = 3.63 \left[\frac{\pi(\rho_w - \rho_B) g}{\mu_1} \right]^{1/6} R^{2/3} L^{1/2} D_{AB}^{1/2} C_{A_0} Q^{1/3} \quad (18)$$

EXPERIMENTAL

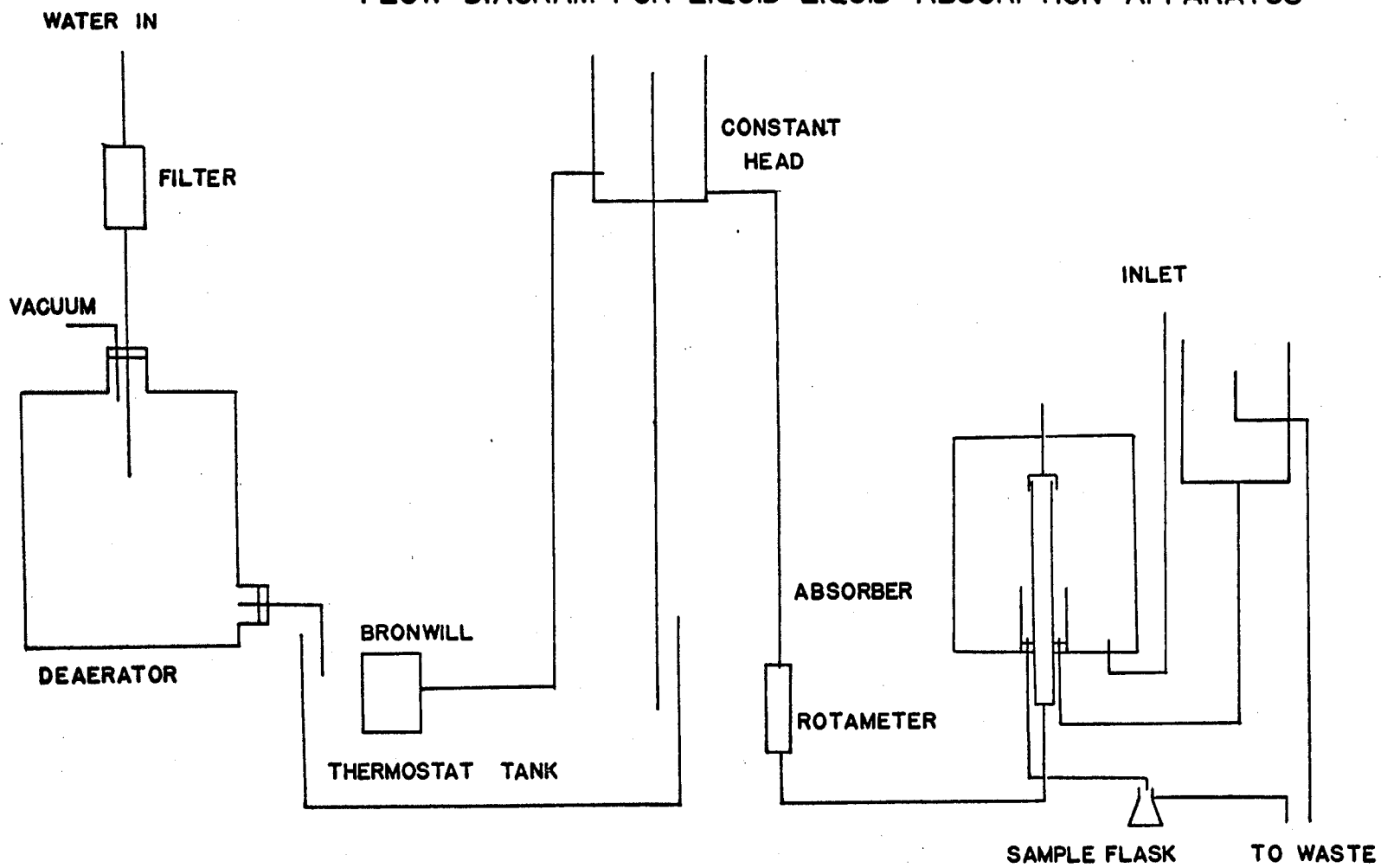
Apparatus

The flow diagram is shown in figure 3. Water from the mains was filtered through cotton and glass wool to remove impurities from the piping; and air was removed by a vacuum pump when the five gallon jar was filled. The deaerated water was then allowed to flow into the insulated fish tank. This tank held a Bronwill circulating system consisting of a pump and heater, which kept the water temperature constant to 0.1°C . The water was pumped overhead to a constant head device with a return to the tank. Water flowed through the rotameter into the bottom of the tube and around the outside of the cylinder. The interface between the water and the benzene was kept constant by means of a second constant head tank and a second outlet stream controlled by a valve. This second stream was used to obtain samples. The liquid film was very sensitive to vibrations and auxiliary equipment. To reduce this effect to a minimum the column or absorber (see fig. 4) was placed on three styrofoam pads.

Procedure

The introduction of the benzene or toluene was carried out in the following manner. The liquid flow rate of the water was adjusted to give the maximum flow obtainable on

FLOW DIAGRAM FOR LIQUID-LIQUID ABSORPTION APPARATUS

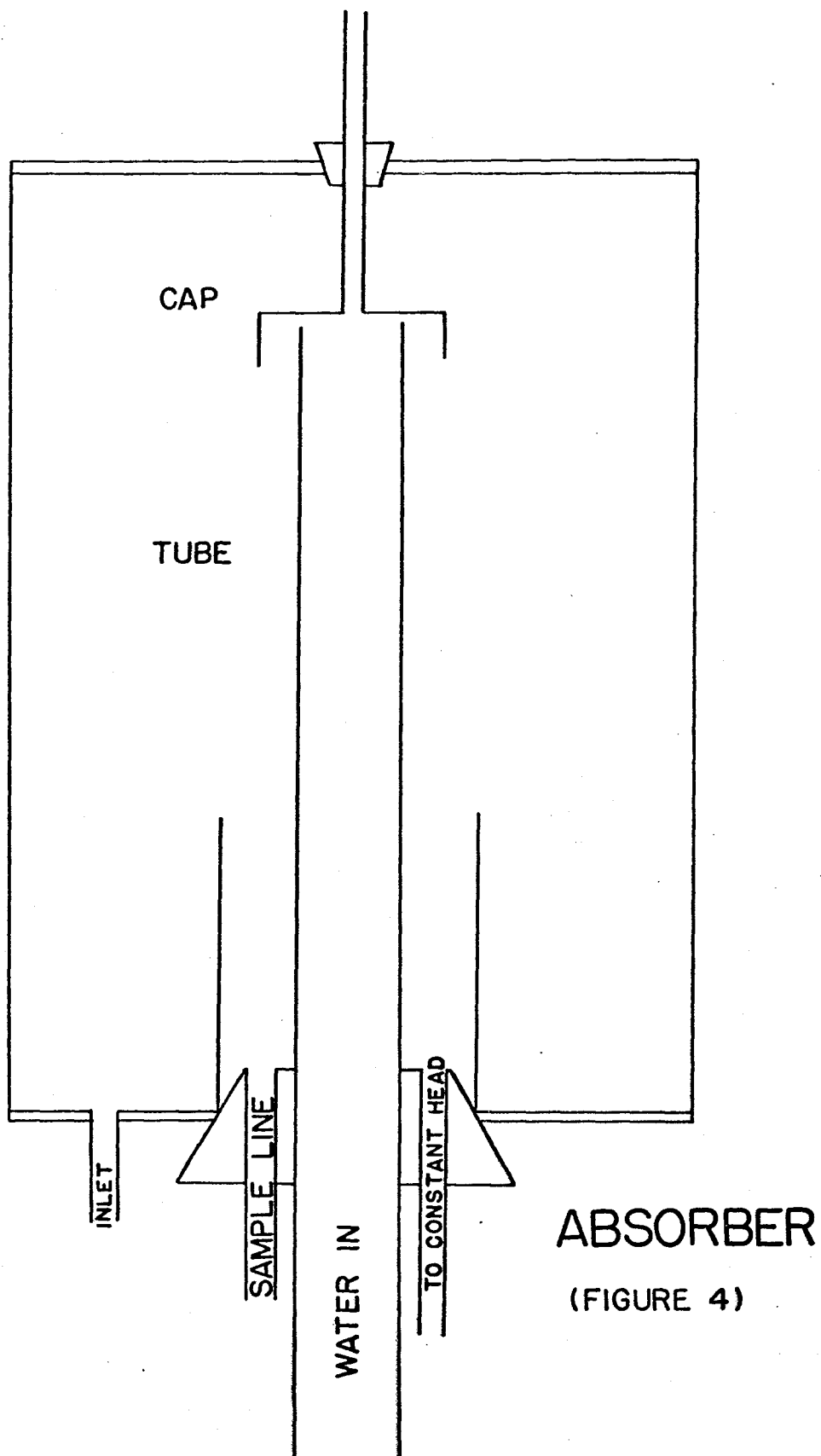


(FIGURE 3)

the rotameter scale. A cap was then placed on the top portion of the tube to produce a more even distribution of the film over the cylinder. This cap also served the purpose of eliminating the entrance effect of the liquid water appreciably. The valves to the constant head tank and the sampling line were then closed and water was allowed to overflow the take-off portion and pour into the column. When the water level reached approximately one inch from the top of the take-off portion the lines were opened again and benzene introduced through the bottom of the column through the water layer. The benzene was introduced slowly and the constant head tank raised as needed to keep the level in the take-off portion constant. The benzene was allowed to flow until it had completely covered the cap. The cap served the desirable purpose of trapping air, so that the water did not come in intimate contact with the liquid benzene until it reached the lip of the cap. This resulted in reducing the entrance effect of the water on the mass transfer. Consequently, the diffusion length was measured from the lip of the cap to the benzene-water interface in the take-off portion.

Analysis

The ultra-violet absorption spectrum of benzene in



aqueous solution has a peak value of 254 μ and that for (2) toluene has a peak value at 261 μ . Bohon and Claussen have determined the solubility of certain aromatic hydrocarbons in water and their work was utilized in determining the amount of aromatic in the water samples. The values of the extinction coefficients in their work were used in this thesis. Using the Beer-Lambert expression, the dimensions of their extinction coefficients produced a concentration unit expressed in grams per liter which was converted to weight percent by assuming the density of the solution to be the same as that of pure water. The same equipment was used in their studies as in this thesis, namely, a Beckman model DU spectrophotometer. Samples were taken after a minimum of ten minutes or after two liters of solution had passed through the take-off portion. At the lower flow rates the time between samples approached twenty and thirty minutes. The samples were collected from the second line leading from the take-off portion. The end of this line was a glass tapered tube. When steady-state conditions had been reached samples were taken by placing the end of the tapered glass tube into specially designed Beckman silica cells. These were rectangular, one centimeter light path cells of five cubic centimeters capacity with stoppers. The cells were rinsed with the particular sample to be taken a minimum of five

times then filled to overflowing and stoppered quickly to prevent any vapor loss. The sample was then placed in the spectrophotometer with deaerated water as the reference cell. At the low wavelengths slit-widths of from 0.05 mm. to 0.80 mm. were used with complete reproducibility of the data. After a run the cell was rinsed with acetone, allowed to dry and the same procedure followed at a different flow rate.

End Effects

The end effects observed with the liquid-liquid systems were similar in nature to those observed in the gas-liquid studies. ⁽³⁾ Wave formation was seen to occur at high flow rates. Slight vibrations and disturbances also caused wave formation. Single standing waves observed by Ratcliff and Reid were however not observed. A stagnant film of impurities did accumulate at the liquid-liquid interface and small dust particles were seen to follow a circular pattern at the base of the tube near the interface. These patterns became more pronounced at lower flow rates than at the higher flow rates. The diameter of some of these patterns reaching a value of almost one inch. It was observed that turbulence was present at flow rates above four cubic centimeters per second for the smaller radii tubes and as a consequence data above four cubic centimeters

per second flow shows increased mass transfer. The effect of turbulence at the interface was also markedly greater at the higher flow rates. This could be observed by seeing small particles of benzene liquid being forced below the interface for about an inch and then rising again.

METHOD OF CALCULATION

The data taken on any one run was the liquid flow rate in cubic centimeters per minute, and the percent transmission of the liquid samples by use of the Beckman DU spectrophotometer. From those two values and physical data obtained from various sources the diffusivity of the two organics benzene and toluene were calculated using equation eighteen which was derived in the theory section. This equation is given below.

$$G = 3.63 \left[\frac{\pi(\rho_w - \rho_o)g}{\mu_1} \right]^{1/6} R^{2/3} L^{1/2} D_{o/w}^{1/2} Q^{1/5} C_{o,s}$$

where,

G = absorption rate (g/s)

ρ_w = density of water (g/cm³)

ρ_o = density of organic (g/cm³)

R = outside radius of cylinder (cm)

L = height of transfer surface (cm)

$D_{o/w}$ = diffusivity (cm²/s)

$C_{o,s}$ = saturation concentration of organic in water at given temperature (g/cm³)

Q = liquid flow rate (cm³/s)

g = gravity constant 980cm/s²

μ_1 = viscosity of water (g/cm. s)

π = 3.1416

The data obtained on any run was plotted with G

(rate of mass transfer g/s) as ordinate versus flow rate (cm³/s) to the one third power and the best straight line drawn through the points, one point being the origin. Preference was given to the points lying between values of one to four cubic centimeters per second, values above being in error due to turbulence. The physical data such as viscosity and density were taken from the literature. C_{Ao}, the saturation concentration of the organic in water at any one particular temperature was taken from Bohon and Claussen's work and is plotted in the appendix as optical density as ordinate versus reciprocal temperature on semi-log paper. The corresponding concentration can be computed from the Beer-Lambert law as given below.

$$D_o = kcl$$

where,

D_o = saturation optical density

k = extinction coefficient (liters/g.cm.)

c = concentration (g/liter)

l = path length (cm)

This equation is the basis for the calculations of the concentrations of the organic in water from the transmission readings obtained from the various runs. For this application D_o is replaced by D the optical density of the particular sample. The optical density being computed from

the percent transmission of the liquid samples in that optical density is the logarithm to the base ten of the reciprocal of the percent transmission. Values of the absorption rate, G , were obtained by mass balance based on these analyses. The assumption was made for the viscosity term that the slight amount of benzene dissolved in the water did not alter its properties and the viscosity of the film could be taken as that for pure water at the temperature of the run. The diffusion length as has been previously mentioned was measured from the end of the glass cap to the liquid interface. The density equations used were taken from the International Critical Tables and are given below.

$$\rho_s = 0.90005 - 1.0636 \times 10^{-3} t - 0.0376 \times 10^{-6} t^2 - 2.213 \times 10^{-9} t^3$$

for benzene

$$\rho_L = 0.88448 - 0.9159 \times 10^{-3} t + 0.368 \times 10^{-6} t^2$$

for toluene t = °C

In order to calculate the mass transfer rate of the organic, the amount of material flowing was assumed to be whatever the pure liquid flow rate was; for example, two hundred and fifty cubic centimeters per minute of water was assumed to be a mass rate of two hundred and fifty grams per minute. This is justified when it is seen the percentage of the organic in the water is of the order of from 0.001 to 0.02 percent by weight. The error in-

herent in the water rotameter being much greater than any density correction for the very dilute solution. We now have all the information to place in the derived equation. Following is a sample calculation for run number five. From the plot on page twenty-seven the slope is 4.37 times ten to the minus fourth power or,

$$\frac{G}{Q^{1/3}} = 4.37 \times 10^{-4}$$

which term equals the rest of the equation or,

$$4.37 \times 10^{-4} = 3.63 \left[\frac{\pi(\rho_w - \rho_a)g}{\mu_1} \right]^{1/6} R^{2/3} L^{1/2} D_{r0}^{1/2} C_{r0}$$

Evaluating the density, viscosity and concentrations terms with the values for the radius and diffusion length gives for the diffusion coefficient a value of 0.95 times ten to the minus fifth power centimeters squared per second. The value for the toluene run is given in table eight.

Since data on these two systems is lacking in the literature, comparisons were made with two engineering empirical methods. One is the Wilke-Chang expression and the other is the Othmer-Thaker relation. Both are supposed to give results within a range of ten percent. The Othmer-Thaker relation giving a slightly better result coupled with simplicity. These expressions are given in the appendix.

DATA

Run 1

Diameter of Tube 10.0 mm.

Temperature 25.1°C

Material - Benzene

Diffusion Length 5.50 inches

Flow rate (cc/s)	Percent Trans.	Opt. Density	Flow rate (cc/s) ^{1/3}	Wt. Absorption % Rate(g/sx 10 ⁴)	
2.64	50.9	0.2933	1.38	0.01541	4.07
1.92	45.8	0.3391	1.24	0.01782	3.42
1.50	41.2	0.3851	1.14	0.02029	3.04
2.17	48.8	0.3116	1.29	0.01639	3.56
2.88	53.4	0.2725	1.42	0.01436	4.14
3.42	61.8	0.2090	1.51	0.0110	3.76
3.84	62.0	0.2076	1.57	0.01095	4.21
4.16	64.5	0.1904	1.61	0.0101	4.17
4.55	66.2	0.1791	1.66	0.00944	4.29
1.22	39.5	0.4034	1.07	0.0212	2.58
1.00	36.0	0.4437	1.00	0.02337	2.33
0.734	26.3	0.5800	0.90	0.0305	2.24
0.566	21.5	0.6676	0.83	0.0352	1.99
1.72	44.0	0.3565	1.20	0.0188	3.24
3.09	58.1	0.2358	1.46	0.0124	3.83

DATA

Run 2

Diameter of Tube 13mm.

Temperature 25.3°C

Material - Benzene

Diffusion Length 5.50 inches

Flow rate (cc/s)	Percent Trans.	Opt. Density	Flow rate (cc/s) ^{1/2}	Wt. %	Absorption Rate(g/s x10 ⁴)
6.55	63.7	0.1959	1.87	0.0103	6.74
5.75	62.6	0.2034	1.79	0.0107	6.15
5.20	59.8	0.2233	1.73	0.01175	6.11
4.52	59.0	0.2291	1.65	0.01206	5.44
3.84	56.1	0.2510	1.57	0.0132	5.07
3.17	51.6	0.2873	1.47	0.01511	4.79
2.67	47.2	0.3260	1.37	0.01718	4.58
2.13	40.8	0.3893	1.29	0.02048	4.36
1.75	37.7	0.4237	1.20	0.0223	3.90
1.28	32.6	0.4868	1.09	0.02562	3.28

DATA

Run 3

Diameter of Tube 13mm.

Temperature 25.3°C

Material - Benzene

Diffusion Length 4.50 inches

Flow rate (cc/s)	Percent Trans.	Opt. Density	Flow rate (cc/s) ^{1/3}	Wt. %	Absorption Rate(g/s x10 ⁴)
6.58	64.0	0.1938	1.87	0.0102	6.72
5.75	62.4	0.2048	1.79	0.01079	6.20
5.17	62.4	0.2048	1.73	0.01079	5.57
4.55	60.2	0.2204	1.66	0.01161	5.23
3.87	58.1	0.2358	1.57	0.01241	4.80
3.09	53.9	0.2684	1.46	0.01413	4.36
2.50	50.4	0.2975	1.36	0.01567	3.92
1.67	41.1	0.3862	1.19	0.02034	3.39
1.28	35.5	0.4498	1.08	0.02369	3.03
0.917	29.9	0.5243	0.97	0.0275	2.54

DATA

Run 4

Diameter of Tube 13mm.

Temperature 25.4°C

Material - Benzene

Diffusion Length 6.25 inches

Flow rate (cc/s)	Percent Trans.	Opt. Density	Flow rate (cc/s) ^{1/3}	Wt. %	Absorption Rate(g/s x10 ⁴)
3.34	50.1	0.3002	1.49	0.0158	5.27
2.87	47.2	0.3260	1.42	0.01715	4.92
2.40	42.4	0.3726	1.34	0.0196	4.70
1.92	35.5	0.4498	1.24	0.02365	4.54
1.67	33.6	0.4737	1.19	0.02490	4.15

DATA

Run 5

Diameter of Tube 20.3mm.

Temperature 25.4°C

Material - Benzene

Diffusion Length 5.50 inches

Flow rate (cc/s)	Percent Trans.	Opt. Density	Flow rate (cc/s) ^{1/3}	Wt. %	Absorption Rate(g/sx10 ⁴)
6.50	57.5	0.2403	1.87	0.01267	8.22
5.92	55.8	0.2534	1.81	0.01333	7.89
5.23	52.7	0.2782	1.74	0.01455	7.60
4.70	50.5	0.2967	1.67	0.01562	7.35
4.08	47.9	0.3197	1.60	0.01685	6.86

DATA

Run 1

Diameter of Tube 13mm.

Temperature 25.4°C

Material - Toluene

Diffusion Length 5.10 inches

Flow rate (cc/s)	Percent Trans.	Opt. Density	Flow rate (cc/s) ^{1/3}	Wt. %	Absorption Rate(g/sx10 ⁴)	
4.17	79.6	0.0991	1.62	0.00406	1.69	1.67*
3.72	79.0	0.1024	1.55	0.00420	1.56	1.54
3.28	76.6	0.1158	1.49	0.00474	1.54	1.52
2.84	75.8	0.1203	1.42	0.00494	1.40	1.38
2.38	71.2	0.1475	1.34	0.00605	1.44	1.42
1.90	68.0	0.1675	1.24	0.00686	1.31	1.29
1.50	65.1	0.1864	1.15	0.00764	1.14	1.13

* Corrected to a diffusion length of 5.00 inches.

DATA

Run 2

Diameter of Tube 13mm.

Temperature 25.4°C

Material - Toluene

Diffusion Length 5.00 inches

Flow rate (cc/s)	Percent Trans.	Opt. Density	Flow rate (cc/s) ^{1/2}	Wt. %	Absorption k ₁ Rate(g/sx10 ⁴)
4.00	78.3	0.1062	1.59	0.00435	1.74
3.00	76.8	0.1146	1.44	0.00470	1.41
2.72	75.0	0.1249	1.40	0.00512	1.40
2.37	72.9	0.1373	1.33	0.00564	1.34
1.95	70.1	0.1543	1.25	0.00633	1.23
1.67	65.3	0.1851	1.19	0.00761	1.26
1.38	65.0	0.1871	1.11	0.00769	1.06
1.03	59.8	0.2233	1.01	0.00915	0.96

RADIUS AS THE VARIABLE
AT CONSTANT TEMPERATURE

(FIGURE 5)

LEGEND

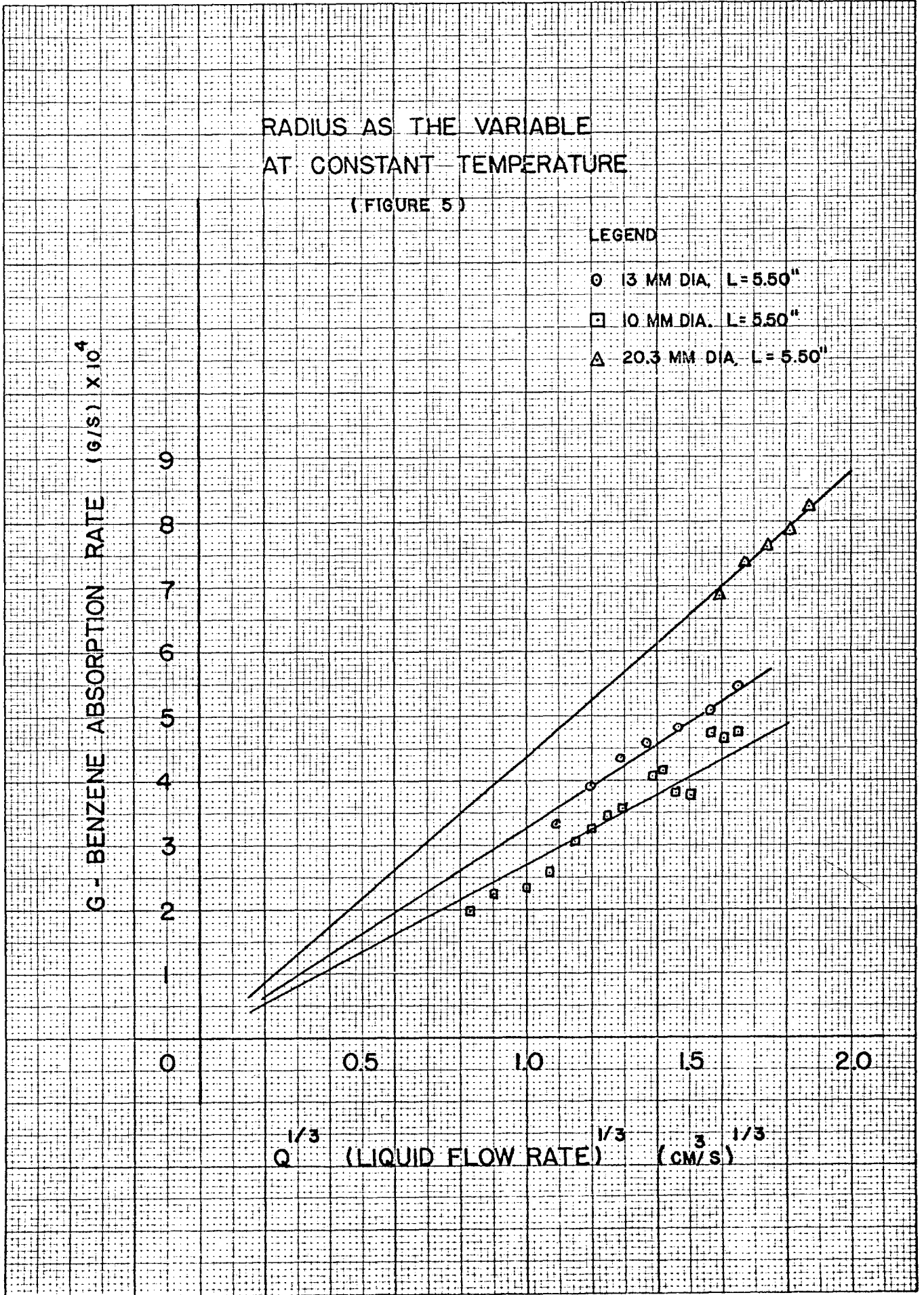
- 13 MM DIA. L = 5.50"
- 10 MM DIA. L = 5.50"
- △ 20.3 MM DIA. L = 5.50"

G - BENZENE ABSORPTION RATE (G/S) X 10⁴

9
8
7
6
5
4
3
2
1
0

$Q^{1/3}$ (LIQUID FLOW RATE)^{1/3} (CM/S)^{1/3}

0.5 1.0 1.5 2.0

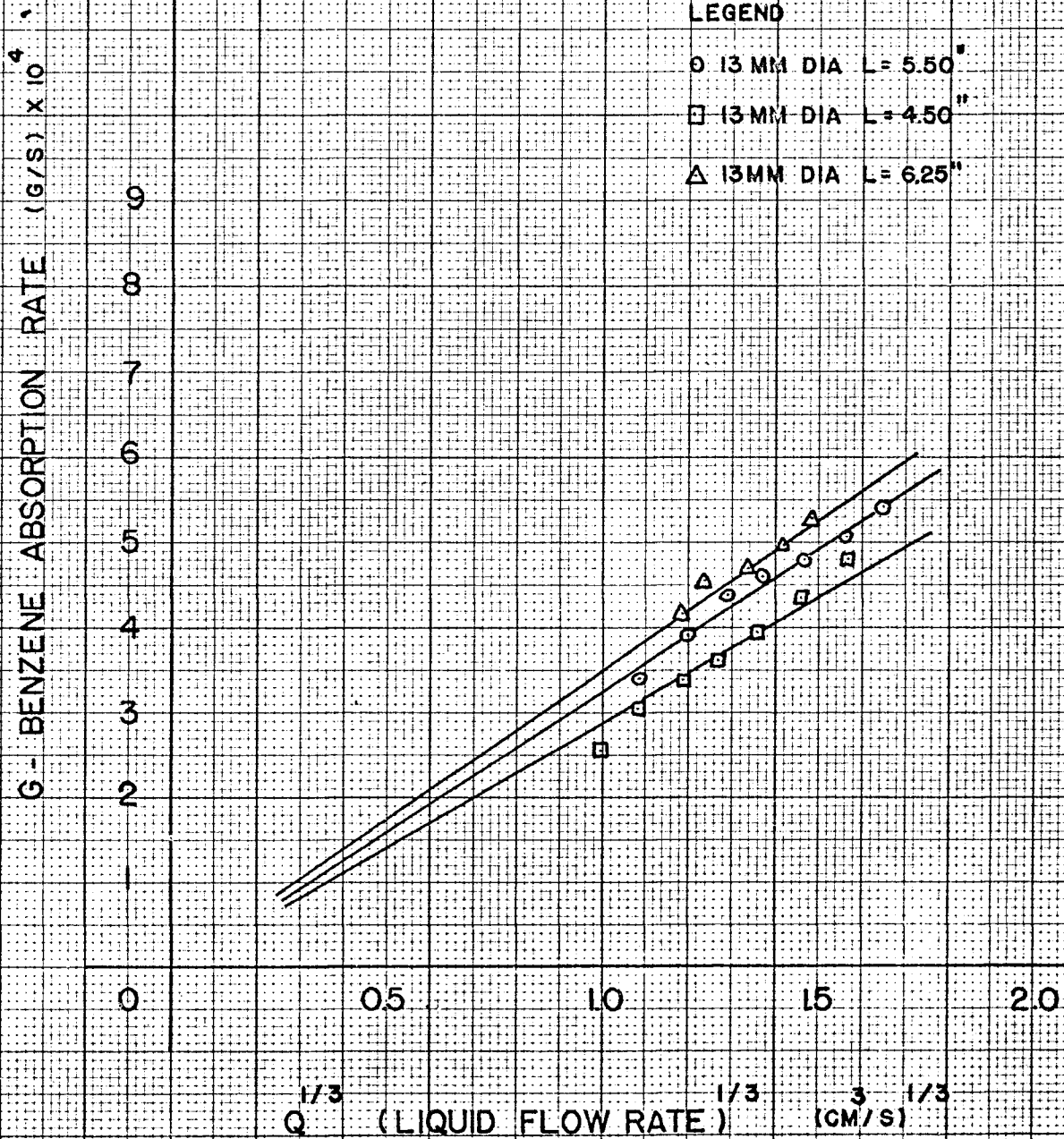


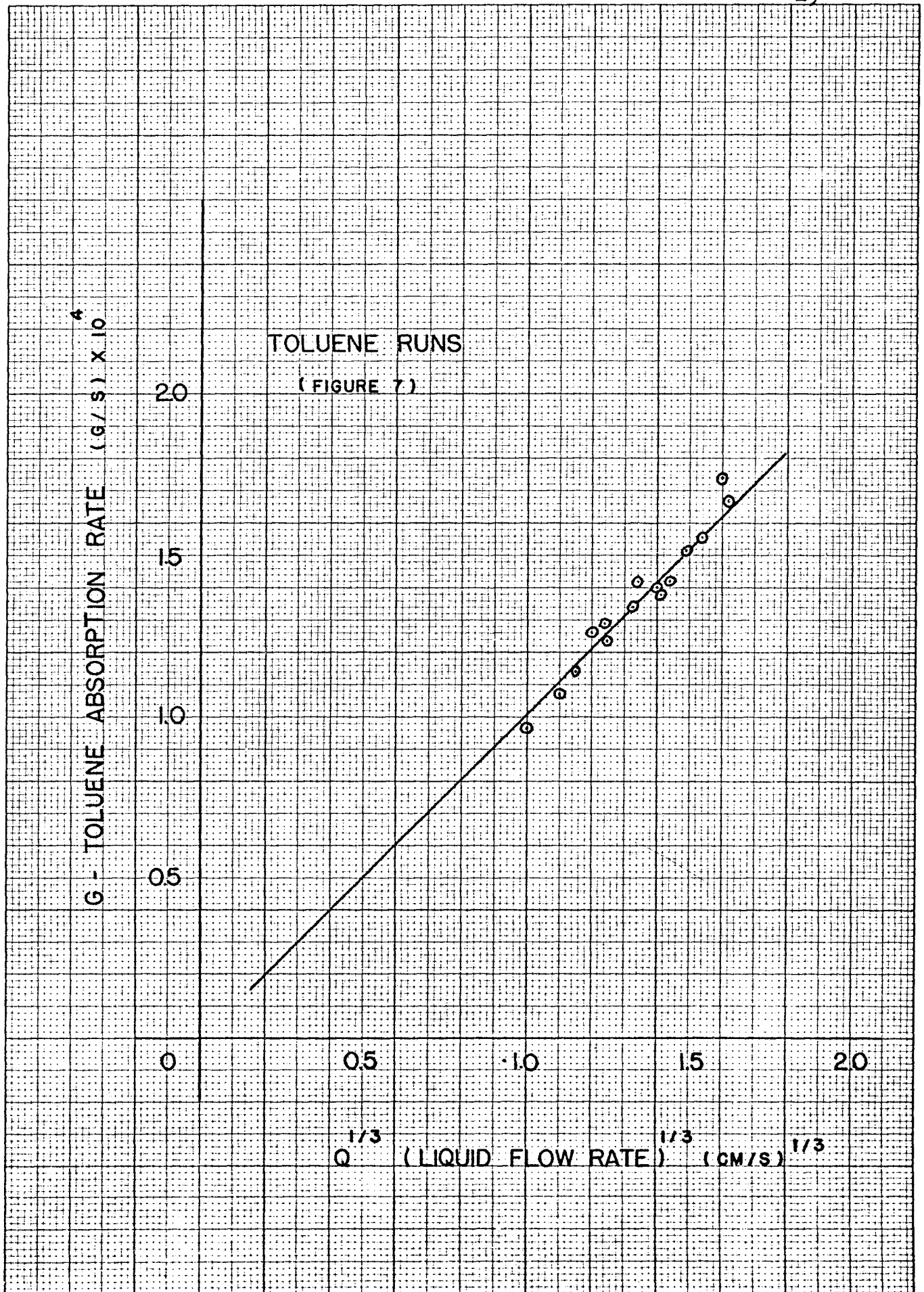
MADE IN U. S. A.

20 X 20 PER INCH

LENGTH AS THE VARIABLE
AT CONSTANT TEMPERATURE

(FIGURE 6)





CONCLUSION

Agreement between theory and results was excellent. The reproducibility was excellent, as in the case of the system benzene-water which was used to validate the equation derived in this thesis. Five runs at different radii and diffusion lengths produced agreement to within three percent. The exponents of the radius and length terms were validated by these results. The engineering empirical relation of Othmer-Thaker agreed to within eight percent while the Wilke-Chang expression was sixteen percent off. The comparison of the value of this work and that of Ratcliff and Reid is not as definite. Their published value of 1.09×10^{-5} cm²/s is fifteen percent greater than in this work. But this comparison is complicated because of the lack of any data given by these authors for the saturation concentration of benzene at twenty five degrees centigrade. In the authors equation and in the equation of Ratcliff and Reid (see appendix) the saturation concentration plays a big role in determining the value of the diffusion coefficient. A value for the saturation concentration of seven percent lower than the value used in this thesis would produce the result of Ratcliff and Reid. The uncertainty of the solubility data is shown by the fact that Bohon and Claussen⁽²⁾ show a value for the saturation concentration of toluene which is nineteen percent higher than that found in the literature previous to their

work. So it seems that an accurate determination of the diffusivity of a particular compound by steady state methods depends to a great extent on the accuracy of the solubility data. This plus the errors inherent in the experiment itself account for the discrepancy between the two values.

The two methods then provide a means of determining the diffusion coefficients of immiscible liquids. The easy way in which data can be taken once the equipment is assembled makes the method useful for rapid determination of diffusion coefficients. The only drawbacks being in the requirement that the two liquids be immiscible and accurate data on the solubility be available.

COMPARISON OF DIFFUSION COEFFICIENTS

Solute	T°C	Exp.	Wilke-Chang		Othmer-Thaker		R&R*
		Lovenguth	Calc.	%Dev.	Calc.	%Dev.	
D x 10 ⁵ cm ² /s							
Benzene	25.4	0.95	1.09	15	1.02	7	1.09
Toluene	25.4	0.83	0.97	17	0.91	9	-

* Ratcliff & Reid - data at 25.0°C

TABLE OF NOMENCLATURE

- a = film thickness cm.
 C = saturation concentration of organic in water at given temperature gm/cm³
 C = concentration of organic in water gm/liter
 D = diffusivity cm²/sec
 D_0 = saturation optical density
 D = optical density of sample
 G = absorption rate gm/sec
 g = gravity constant 980cm/sec²
 k = extinction coefficient liters/gm. cm.
 l = path length of transmission cell cm.
 L = height of transfer surface cm.
 Q = liquid flow rate cm³/sec
 R = outside radius of tube cm.
 ρ_B = density of benzene at given temperature gm/cm³
 μ_1 = viscosity of water at given temperature gm/cm.s.
 τ_{x2} = shear force per unit area dyne/cm or gm/cm.s²
 t, w = subscripts denoting toluene and water, respectively

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APPENDIX

(8)

Othmer-Thaker relation

$$D_{12} = \frac{14.0 \times 10^{-5}}{u_w V^{0.6}}$$

where

 u_w = viscosity of water at T_1 centipoise V = molal volume of solute as obtained from LeBas values cm^3/gmole D_{12} = diffusion coefficient at T_1 of 1 in dilute solution of 2 $\text{cm}^2/\text{sec.}$

(8)

Wilke-Chang expression

$$D_{12} = \frac{7.4 \times 10^{-8} (2.6M)^{\frac{1}{2}} T}{u_1 V^{0.6}}$$

where

 D_{12} = diffusion coefficient of solute 1 in dilute solution in solvent 2 at temperature T $\text{cm}^2/\text{sec.}$ M = molecular weight of solvent T = temperature $^{\circ}\text{K}$ u_1 = viscosity of solution centipoise V = molal volume of solute at normal boiling point cm^3/gmole 2.6 = "association" parameter of solvent
2.6 for water, benzene 1.0, etc.

Equation of Ratcliff & Reid

$$G = 4.21 \left[\frac{\pi(\rho_w - \rho_B)g}{\mu_1} \right]^{1/6} \sigma^{1/3} R^{7/6} L^{1/3} D_{AB}^{1/2} C^*$$

where

$$\sigma = 0.943$$

$$\pi = 3.1416$$

$$\rho_w = \text{density of water gm/cm}^3$$

$$\rho_B = \text{density of second fluid gm/cm}^3$$

$$g = 980 \text{ cm/sec}^2$$

$$\mu_1 = \text{viscosity of water (or solution) gm/cm.sec.}$$

$$R = \text{radius of sphere cm.}$$

$$L = \text{liquid flow rate cm}^3/\text{sec}$$

$$D_{AB} = \text{diffusion coefficient cm}^2/\text{sec.}$$

$$C^* = \text{equilibrium saturation concentration of organic in water at given temperature gm/cm}^3.$$

SOLUBILITY OF BENZENE AND TOLUENE WITH TEMPERATURE

(FIGURE 8)

○ BENZENE

△ TOLUENE

OPTICAL DENSITY

 RECIPROCAL ABSOLUTE TEMPERATURE
 $\times 10^4$ K
