

6-30-1964

## Interphase gas-liquid mass transfer study in a horizontal channel

Bruce R. Marx  
*New Jersey Institute of Technology*

Follow this and additional works at: <https://digitalcommons.njit.edu/theses>



Part of the [Chemical Engineering Commons](#)

---

### Recommended Citation

Marx, Bruce R., "Interphase gas-liquid mass transfer study in a horizontal channel" (1964). *Theses*. 2125.  
<https://digitalcommons.njit.edu/theses/2125>

This Thesis is brought to you for free and open access by the Electronic Theses and Dissertations at Digital Commons @ NJIT. It has been accepted for inclusion in Theses by an authorized administrator of Digital Commons @ NJIT. For more information, please contact [digitalcommons@njit.edu](mailto:digitalcommons@njit.edu).

## **Copyright Warning & Restrictions**

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be “used for any purpose other than private study, scholarship, or research.” If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of “fair use” that user may be liable for copyright infringement,

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

**Please Note: The author retains the copyright while the New Jersey Institute of Technology reserves the right to distribute this thesis or dissertation**

Printing note: If you do not wish to print this page, then select “Pages from: first page # to: last page #” on the print dialog screen

The Van Houten library has removed some of the personal information and all signatures from the approval page and biographical sketches of theses and dissertations in order to protect the identity of NJIT graduates and faculty.

INTERPHASE GAS-LIQUID MASS TRANSFER  
STUDY IN A HORIZONTAL CHANNEL

BY

BRUCE R. MARX

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

AT

NEWARK COLLEGE OF ENGINEERING

This thesis is to be used only with  
due regard to the rights of the author.  
Bibliographical references may be noted,  
but passages must not be copied without  
permission of the college and without  
credit being given in subsequent written  
or published work.

NEWARK, NEW JERSEY  
1964

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

NEWARK, NEW JERSEY

JUNE, 1964

### ACKNOWLEDGEMENT

The author is deeply indebted to Prof. George C. Keefe without whose guidance and encouragement this work could not have been completed.

The author would like to acknowledge his wife Ellen whose patientce and understanding aided this endeavor.

## ABSTRACT

The rate of transfer of hydrogen sulfide and of carbon dioxide from an atmosphere of the gas saturated with water to a flowing stream of water in a horizontal channel was investigated over a range of water flow velocities and absolute pressures.

Mathematical models describing the system in terms of the penetration and boundary layer theories were inadequate when used to calculate the diffusivity of each gas in water at various conditions. The results of the hydrogen sulfide-water system study shows a relationship between the diffusivity, the interfacial concentration and the liquid flow rate. The calculated diffusivity of the carbon dioxide-water system is independent of liquid velocity, but can be correlated as a function of pressure above one atmosphere. The diffusivity-flow rate relationship may be due to the presence of an interfacial resistance which prevents the liquid surface from becoming saturated with gas.

If the diffusivity is assumed constant, the interfacial concentration of the hydrogen sulfide-water system at 25.2°C and 1.23 atmospheres can be expressed by the following functional relationship.

$$C_1 = F (V_L) \cdot f (\bar{C}_L) = 23.0 (\bar{C}_L)^{0.455}$$

## TABLE OF CONTENTS

Introduction .....	1
Theoretical Background .....	5
Boundary Layer Theory .....	6
Penetration Theory .....	15
Experimental Equipment	
The Test Tray .....	16
The Gas Feed .....	18
The Liquid Feed .....	19
Analytical Methods	
Hydrogen Sulfide in Water .....	21
Carbon Dioxide in Water .....	22
Discussion of Results .....	24
Summary .....	42
Appendix	
Original Data .....	44
Physical Constants .....	47
Nomenclature .....	50
References .....	52



## LIST OF FIGURES

Figure 1.	Volume Element of Water .....	6
Figure 2.	Coordinate System for Mathematical Models .....	10
Figure 3.	Schematic Flow Diagram .....	20a
Figure 4.	Test Apparatus .....	20b
Figure 5.	The Apparent Boundary Layer Diffusivity of Hydrogen Sulfide in Water at 25.2°C and 1.23 Atmospheres as a Function of Flow Rate .....	27
Figure 6.	The Apparent Boundary Layer Diffusivity of Carbon Dioxide in Water at 25.2°C and 1.1 Atmospheres as a Function of Flow Rate .....	28
Figure 7.	The Effect of the Liquid Velocity on the Cup Mixing Concentration for a Hydrogen Sulfide-Water System at 25.2°C and 1.23 Atmospheres .....	32
Figure 8.	The Effect of Liquid Velocity on the Cup Mixing Concentration for a Carbon Dioxide-Water System at 25.2°C and 1.1 Atmospheres .....	33
Figure 9.	The Effect of Pressure on the Apparent Diffusivity of Hydrogen Sulfide in Water at 25.2°C and 300 cc/min Flow of Water .....	40
Figure 10.	The Effect of Pressure on the Apparent Diffusivity of Carbon Dioxide in Water at 25.2°C and Constant Volumetric Flow in the Liquid Film .....	41
Figure 11.	Viscosity of Hydrogen Sulfide as a Function of Temperature .....	48
Figure 12.	Equilibrium Concentration of Hydrogen Sulfide as a Function of Pressure .....	49

LIST OF TABLES

1.	The Effect of Flow Rate on the Apparent Diffusivity of Hydrogen Sulfide in Water at Constant Temperature and Pressure .....	26
2.	The Effect of Flow Rate on the Apparent Diffusivity of Carbon Dioxide in Water at Constant Temperature and Pressure .....	26
3.	The Effect of Liquid Velocity on the Cup Mixing Concentration for a Hydrogen Sulfide-Water System at 25.2°C .....	30
4.	The Effect of Liquid Velocity on the Cup Mixing Concentration for a Carbon Dioxide-Water System at 25.2°C .....	31
5.	Original Data - Hydrogen Sulfide (Saturated with Water Vapor)-Water Runs at 25.2°C .....	44
6.	Original Data - Carbon Dioxide (Saturated with Water Vapor)-Water Runs at 25.2°C .....	46

## INTRODUCTION

Physical absorption, a basic process in chemical engineering, has become an important engineering consideration in the proper treatment of a wide variety of equipment designs. Teller (1) considers that work in this field is necessary to obtain an accurate description of the physical situation existing in industrial equipment. The work done by Emmert and Pigford (2,3) indicates that it is a prerequisite that one understand the physical absorption process and the mechanisms governing it before kinetic studies are made on similar gas-liquid systems.

Despite the importance attached to physical absorption there is still wide disagreement as to the exact mechanism. Three theories; the two film, the boundary layer, and the penetration theories; are in varying degrees of use. Whitman's (4) two film theory, which is based on the assumption that there is a controlling stagnant film at the surface of the liquid layer, predicts that the rate of interphase mass transfer varies directly as the diffusivity. This theory is (5) the most widely used method at present for the interpretation of the mathematical model describing absorption in an industrial column. However, both Higbie's (6) penetration theory and the boundary layer theory as described by Schlichting (7) and Bird, Stewart,

and Lighfoot (8) differ radically from the two film theory in that they predict that the rate of mass transfer varies as the square root of the diffusivity. Higbie (9) in his penetration theory stated that the value of the liquid film coefficient,  $K_L$ , was equal to  $\sqrt{4D/(\pi\theta)}$ , where  $D$  is the diffusivity,  $\pi$  is 3.1415 and  $\theta$  is the contact time. Danckwerts (10) later modified this theory with the addition of a statistical surface renewal factor to the numerator of the previously given expression for the liquid film coefficient. The boundary layer theory, which was first applied to fluid flow problems by Schlichting (11) and was modified for mass transfer work, is based on the assumption that the boundary layer in the liquid film controls the rate of diffusion. The mathematical expression for this theory is similar to the one describing the penetration theory in that  $K_L = f\sqrt{D}$ . The relative validity and applicability of these theories is discussed by Toor and Marchello (12).

Studies examining the validity of these theories have utilized a wide variety of equipment. Originally diffusion cells such as the type used by Arnold (13) were the major means of studying diffusivity and mass transfer rates. Davidson and Cullen (14) point out that this steady state method has several disadvantages in that it relies upon the ability of the experimenter to calibrate the cell to the viscosity of the fluid being studied and it is based

upon extremely precise analytical procedures.

More recently several unsteady state methods for studying the various theories have been devised (15). These methods represent new mathematical models which can be solved by the application of the penetration or boundary layer theories. One of the most common of these devices is the wetted wall column. Investigators in this field including Davidson and Cullen (16) and others (17, 18, 19) have employed this type of model to determine diffusivities, mass transfer rates, and kinetics of gas-liquid reactions. Lynn, Straatemier, and Kramers (20) used the penetration theory to predict the rate of transfer of sulfur dioxide to a film of water flowing down a short glass column of lengths varying from one to five centimeters. Davidson and Cullen (21) used a variation of the wetted wall column when they studied the absorption of carbon dioxide in a film of water flowing over a spherical column. Still other pieces of apparatus including Dankwerts and Kennedy's (22) rotating cylindrical drum and Scriven and Pigford's (23) laminar jets have been used in absorption studies. Care must be taken in the design of all of these pieces of apparatus to insure laminar flow and to eliminate end effects.

The latest techniques in this field uses flat and inclined trays. Tailby and Portalski (24) and others (25) have investigated the fluid dynamics of water flowing on a

smooth plate. On the basis of the work of Tailby and Portalski (26) and J. J. van Rossum (27) it has been concluded that stratified laminar flow can be achieved when water flows through a horizontal channel. The ability to maintain laminar flow with no ripples is a necessity in the study of diffusion rates, since rippling increases the surface area, thus increasing the transfer of mass. Studies in a horizontal tray also eliminate errors that may be caused by end effects, since a slight increase in the rate of mass transfer due to turbulence in the liquid phase at the extremities of the equipment is negligible in comparison to the overall transfer throughout the length of the tray. Tang and Himmelblau (28) published an article on diffusional studies in a horizontal channel after work on the present study had commenced. These authors (29) studied the rate of diffusion of carbon dioxide in water in a piece of apparatus similar to the one used in the present study. However, their study was over a limited range of conditions and did not indicate the general applicability of this method for determining liquid-gas diffusivities.

## THEORETICAL BACKGROUND

At present three mathematical theories exist which may be used to describe two phase mass transfer in a horizontal channel. Of these the boundary layer and penetration theories are basic mathematical descriptions of the diffusion process. Depending upon the application of various assumptions, these models may be solved.

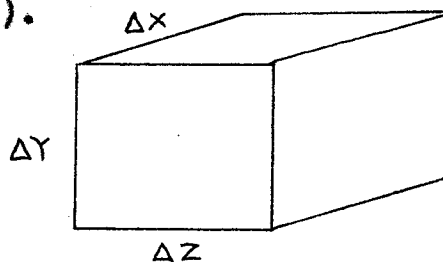
One solution of the mathematical model based on these theories assumes that laminar flow will exist in the liquid layer and that the diffusivity will remain constant. Other assumptions include the elimination of side wall effects which would occur only if the channel was of infinite width and the elimination of molecular diffusion in the direction of flow. Application of these theories also depends on the equality of the interfacial concentration and a theoretical equilibrium concentration. This supposition will be true if there is no interfacial resistance to interfere with saturation of the interface.

If no interfacial film resistance exists this concentration can be set equal to an equilibrium concentration. In previous studies considerable controversy has arisen over this assumption of interfacial equilibrium. Several investigators have found little or no indication of interfacial resistance in their studies (30, 31, 32). However,

other studies including one by Emmert and Pigford (33) and one by Chiang and Toor (34) have indicated the presence of an interfacial resistance associated with the liquid. Since the knowledge of the liquid interfacial concentration is necessary in the determination of diffusivities, it will be assumed that the liquid concentration at the interface is equal to an equilibrium concentration. If this assumption is false, the value of the diffusivity computed by the various theories will not be constant. The present work compares the apparent diffusivities based upon these various assumptions.

For this comparison the principal mathematical models will now be developed.

BOUNDARY LAYER THEORY: The general expression for mass transfer through an element of area such as a boundary layer may be obtained in the manner of Bird, Stewart, and Lightfoot(35).



Volume Element of Water

Figure I

Let the subscript "A" represent the diffusing substance, which in the existing problem is the gas. Using a volume



element of water as shown in Figure I as a basis, it can be seen that the time rate of change of mass of "A" in the element will be equal to the rate of change of density times the volume:

$$\frac{\partial \rho_A}{\partial t} \Delta x \Delta y \Delta z$$

There will be an input of substance across each of the faces of this volume element which can be described as follows:

Input of "A" across face at  $x = n_{Ax}|_x \Delta y \Delta z$

Input of "A" across face at  $x + \Delta x = n_{Ax}|_{x+\Delta x} \Delta y \Delta z$

Input of "A" across face at  $y = n_{Ay}|_y \Delta z \Delta x$

Input of "A" across face at  $y + \Delta y = n_{Ay}|_{y+\Delta y} \Delta z \Delta x$

Input of "A" across face at  $z = n_{Az}|_z \Delta x \Delta y$

Input of "A" across face at  $z + \Delta z = n_{Az}|_{z+\Delta z} \Delta x \Delta y$

Production of "A" in the volume element = 0

A mass balance on the system consisting of this volume element yields Equation 1.

$$\begin{aligned} \frac{\partial \rho_A}{\partial t} \Delta x \Delta y \Delta z = & ( n_{Ax}|_x - n_{Ax}|_{x+\Delta x} ) \Delta y \Delta z \\ & ( n_{Ay}|_y - n_{Ay}|_{y+\Delta y} ) \Delta x \Delta z \quad \text{Eq. (1)} \\ & ( n_{Az}|_z - n_{Az}|_{z+\Delta z} ) \Delta x \Delta y \end{aligned}$$

Dividing Equation 1 by  $\Delta x \Delta y \Delta z$  and taking the limit of all terms as  $\Delta x$ ,  $\Delta y$ , and  $\Delta z$  approaches zero yields the Equation of Continuity (Eq. 2).

$$\frac{\partial \rho_A}{\partial t} + \left( \frac{\partial n_{Ax}}{\partial x} + \frac{\partial n_{Ay}}{\partial y} + \frac{\partial n_{Az}}{\partial z} \right) = 0 \quad \text{Eq. (2)}$$

The equation of continuity may be expressed in terms of vector notation if the rectangular components of mass flux ( $n_{Ax}$ ,  $n_{Ay}$ ,  $n_{Az}$ ) are written as a single mass flux vector,  $n_A$ , which is equal to the product of the density and the velocity. Thus, in vector form the equation of continuity appears as Equation 3.

$$\frac{\partial \rho_A}{\partial t} + (\nabla \cdot n_A) = 0 \quad \text{Eq. (3)}$$

The same equation may be derived for component B in a two component system.

$$\frac{\partial \rho_B}{\partial t} + (\nabla \cdot n_B) = 0 \quad \text{Eq. (4)}$$

If equations 3 and 4 are added, the result is Equation 5 which is called the General Equation of Continuity.

$$\frac{\partial \rho}{\partial t} + (\nabla \cdot \rho v) = 0 \quad \text{Eq. (5)}$$

When these equations are referred to molar units they appear as equations 6 and 7.

$$\frac{\partial c_A}{\partial t} + (\nabla \cdot N_A) = 0 \quad \text{Eq. (6)}$$

$$\frac{\partial c_B}{\partial t} + (\nabla \cdot N_B) = 0 \quad \text{Eq. (7)}$$

Addition of equations 6 and 7 yields:

$$\frac{\partial c}{\partial t} + \nabla \cdot (N_A + N_B) = 0 \quad \text{Eq. (8)}$$

Since  $N_A + N_B = Cv^*$  :

$$\frac{\partial c}{\partial t} + (\nabla \cdot Cv^*) = 0 \quad \text{Eq. (9)}$$

For constant molar density (C) the preceding equation may be expressed as follows:

$$C (\nabla \cdot v^*) = 0 \quad \text{Eq. (10)}$$

Fick's Law is now introduced in the form:

$$N_A - X_A (N_A + N_B) = -CD_{AB} \nabla X_A \quad \text{Eq. (11)}$$

The term  $\nabla X_A$  is the concentration gradient in this expression. An equivalent expression is substituted for  $N_A + N_B$  to arrive at equation 12.

$$N_A = X_A C v^* - CD_{AB} \nabla X_A \quad \text{Eq. (12)}$$

If equation 12 is combined with equation 6, the following equation results.

$$\frac{\partial c_A}{\partial t} + \left[ \nabla \cdot (X_A C v^* - CD_{AB} \nabla X_A) \right] = 0 \quad \text{Eq. (13)}$$

In simplified form equation 13 becomes:

$$\frac{\partial c_A}{\partial t} + (\nabla \cdot X_A C v^*) = \nabla \cdot CD_{AB} \nabla X_A \quad \text{Eq. (14)}$$

Since  $X_A = C_A / C$  :

$$\frac{\partial C_A}{\partial t} + \nabla \cdot C_A v^* = \nabla \cdot CD_{AB} \nabla X_A \quad \text{Eq. (15)}$$

For the particular problem described in this instance it

will be assumed that the density and diffusivity remain constant. Thus, equation 15 reduces to the following form after application of the equation of continuity.

$$\frac{\partial C_A}{\partial t} + v \cdot \nabla C_A = D_{AB} \nabla^2 C_A \quad \text{Eq. (16)}$$

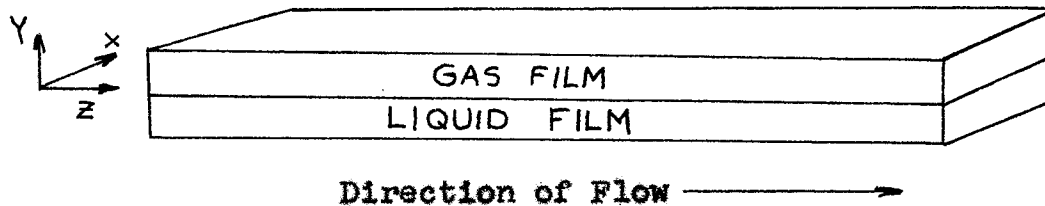
Since  $v \cdot \nabla C_A = DC_A/Dt - \partial C_A / \partial t$ , equation 16 may be written as:

$$\frac{DC_A}{Dt} = D_{AB} \nabla^2 C_A \quad \text{Eq. (17)}$$

When the previous equation is expanded it appears in the form of equation 18.

$$\begin{aligned} \frac{\partial C_A}{\partial t} + v_x \frac{\partial C_A}{\partial x} + v_y \frac{\partial C_A}{\partial y} + v_z \frac{\partial C_A}{\partial z} \\ = D_{AB} \left[ \frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right] \quad \text{Eq. (18)} \end{aligned}$$

It is now necessary to define a coordinate system that will enable further simplification of equation 18. The following diagram of the liquid film will serve this purpose in this and future derivations.



Coordinate System for Mathematical Models

Figure 2

The following assumptions will be used in the simplification of equation 18.

$$(a) v_x = v_y = 0$$

$$(b) \frac{\partial C_A}{\partial t} = 0 \quad (\text{steady - state condition})$$

$$(c) \frac{\partial C_A}{\partial x} = 0 = \frac{\partial^2 C_A}{\partial x^2}$$

$$(d) \frac{\partial^2 C_A}{\partial z^2} = 0$$

Application of these simplifications yields equation 19.

$$v_z \frac{\partial C_A}{\partial z} = -D_{AB} \frac{\partial^2 C_A}{\partial y^2} \quad \text{Eq. (19)}$$

The negative sign arises from the defined coordinate system. In an integrated form over the boundary layer thickness,  $\delta$ , equation 19 can be used to express the rate of diffusion through the thickness  $\delta$ . This boundary layer thickness is considered a finite volume of liquid which exhibits a concentration gradient. It is this concentration gradient that controls the rate of diffusion. If the subscripts are dropped in equation 19 and if the equation is expressed in a partially integrated form, the following expression will result.

$$\frac{d}{dz} \int_0^{\delta} vC \, dy = -D \left( \frac{\partial C}{\partial y} \right)_{y=0} \quad \text{Eq. (20)}$$

The solution of equation 20 is presented in the manner of

Tang and Himmelblau (36). It is now convenient to express the concentration term in a dimensionless group so as to facilitate the proceeding integration. An expression that is frequently used for this type of model is  $\theta = (C_1 - C)/(C_1 - C_0)$ . When this term is rearranged as an expression for the concentration it appears as  $C = (1 - \theta)(C_1 - C_0) + C_0$ . Upon substituting this value into equation 20, the following expression results.

$$C_0 \frac{d}{dz} \int_0^{\delta} v \, dy + (C_1 - C_0) \frac{d}{dz} \int_0^{\delta} (1 - \theta) v \, dy = D \left( \frac{\partial \theta}{\partial y} \right)_{y=0} \quad \text{Eq. (21)}$$

This equation can be simplified further if it is assumed that the velocity is not a function of the z-direction. This condition will be true only if there is a fully developed velocity profile such as one that would exist at steady state conditions. The simplification that results from the previously mentioned conditions is expressed in equation 22.

$$\frac{d}{dz} \int_0^{\delta} (1 - \theta) v \, dy = D \left( \frac{\partial \theta}{\partial y} \right)_{y=0} \quad \text{Eq. (22)}$$

Equation 22 can be solved only if suitable expressions for "v" and " $\theta$ " as functions of the y-distance are available. Russel and Charles (37) have derived an expression for the velocity distribution of a liquid-gas system. For cocurrent

horizontal flow in a channel that is half filled with gas the ratio of the point velocity to the average bulk velocity is given by equation 23.

$$\frac{u}{\bar{u}} = 6 \left( \frac{\mu_G + \mu_L}{\mu_G + 7\mu_L} \right) \left[ \left( \frac{2\mu_L}{\mu_G + \mu_L} \right) - \left( \frac{\mu_L + \mu_G}{\mu_G + \mu_L} \right) \left( \frac{y}{b} \right) - \left( \frac{y}{b} \right)^2 \right] \quad \text{Eq. (23)}$$

This expression can be simplified by using the following substitutions.

$$(a) \alpha = (12 \mu_L) / (\mu_G + 7 \mu_L)$$

$$(b) \beta = (\mu_L - \mu_G) / (2 \mu_L)$$

$$(c) \gamma = (\mu_L + \mu_G) / (2 \mu_L)$$

$$(d) \eta = \left( \frac{y}{b} \right)$$

$$\frac{u}{\bar{u}} = (1 - \beta\eta - \gamma\eta^2) \quad \text{Eq. (24)}$$

It is also necessary to choose a suitable function for the concentration function,  $\mathbb{D}$ . If a third degree polynomial in  $(y)/(\delta)$  is chosen as the expression, it will fill the necessary requirements that when  $y = 0$ ,  $\mathbb{D} = 0$  and  $(\partial^2 \mathbb{D})/(\partial y^2) = 0$  and when  $y = \delta$ ,  $\mathbb{D} = 1$  and  $(\partial \mathbb{D})/(\partial y) = 0$ . An expression that is frequently used in mass transfer and momentum transfer work (37) is the following:

$$\theta = \frac{3}{2} \left( \frac{y}{\delta} \right) - \frac{1}{2} \left( \frac{y}{\delta} \right)^3 \quad \text{Eq. (25)}$$

$$\left( \frac{\partial \theta}{\partial y} \right)_{y=0} = \frac{3}{2\delta} \quad \text{Eq. (26)}$$

When equations 22, 25, 23, and 26 are combined and the indicated operations are carried out equation 27 results.

$$\begin{aligned} 90 \left( \delta/b \right)^2 - 32 \left( \delta/b \right)^3 - 15 \left( \delta/b \right)^4 \\ = 720 D z / (\alpha b^2 \bar{u}) \end{aligned} \quad \text{Eq. (27)}$$

If  $(\delta/b)$  is small the last two terms in the left hand side of equation 27 can be neglected and the remaining equation can be solved for the boundary layer thickness.

$$\delta = 2.828 \sqrt{(Dz)/(\alpha \bar{u})} \quad \text{Eq. (28)}$$

The local mass flux  $q_z$  is usually given by the following:

$$q_z = -D \left( \frac{\partial C}{\partial y} \right)_{y=0} = D(C_1 - C_0) \left( \frac{\partial \theta}{\partial y} \right)_{y=0} \quad \text{Eq. (29)}$$

When this equation is combined with equations 26 and 28 the following expression arises.

$$q_z = 0.530 (C_1 - C_0) \sqrt{(D \alpha \bar{u}) / (z)} \quad \text{Eq. (30)}$$

The total mass transfer per unit of time,  $Q$ , may be arrived at by integrating this equation with respect to  $z$  from  $z=0$  to  $z=L$  and with respect to the width,  $W$ , from  $a=0$  to  $a=a$ .

$$Q = 1.060 (C_1 - C_0) W \sqrt{D \alpha \bar{u} L} \quad \text{Eq. (31)}$$



Since the rate of mass transfer,  $Q$ , is equal to the product of the average concentration,  $\bar{C}_L$ , and the volumetric flow rate, a final expression for concentration as a function of diffusivity and operating variables may be obtained.

$$\bar{C}_L = 1.060 (C_1 - C_0) \sqrt{(\propto DL)/(b^2 \bar{u})} \quad \text{Eq. (32)}$$

The Penetration Theory: The penetration theory was originated by Higbie (39) in an attempt to simplify calculations of interphase mass transfer. He assumed a constant velocity in the boundary layer. The result of his theory may be expressed by the following equation.

$$q_z = (C_1 - C_0) \sqrt{D/(\pi t)} \quad \text{Eq. (33)}$$

Since his theory is based on the assumption of constant velocity with respect to the  $z$ -direction, it is necessary to omit the last two terms in equation 24 (velocity profile). When the value for the contact time,  $t$ , is expressed in terms of  $z$ ,  $\bar{u}$ , and equation 33 can be written as follows:

$$q_z = (C_1 - C_0) \sqrt{(\bar{u} \propto D)/(\pi z)} \quad \text{Eq. (34)}$$

This equation must be integrated over the surface area from  $a=0$  to  $a=a$  and from  $z=0$  to  $z=L$  in order to obtain the final expression relating the average concentration to the diffusivity.

$$\bar{C}_L = 1.129 (C_1 - C_0) \sqrt{(\propto DL)/(\bar{u} b^2)} \quad \text{Eq. (35)}$$

## THE EXPERIMENTAL EQUIPMENT

THE TEST TRAY: The experimental equipment upon which the mathematical model was based consisted of a long horizontal plexiglass tray which contained the flow of the cocurrent gas and liquid streams. This tray had a rectangular cross section which was divided into two sections of equal area. The upper section was for gas flow and the lower one for liquid flow. The inside cross-sectional dimensions of the apparatus were five and one half inches wide by seven-eighths inch high. The length of the tray consisted of three sections; an entrance calming area, the main test section, and the exit area. The tray was similar to that used by Y. P. Tang and D. M. Himmelblau (40) in their absorption studies of carbon dioxide and water. One major difference between the two designs existed in the entrance calming section. Tang's section consisted of a one foot length in which the cross-sectional area was increased from one square inch to the final test area dimensions. This section was followed by a one foot length in which the liquid and gas layers remained separated and were allowed to reach a steady state velocity distribution. The entrance section used in this study had an additional six inch length which was one inch wide and seven-eighths inch deep at the beginning of the apparatus. This additional length was added to

enhance the chances of providing streamline flow in the main test section by adding an extra calming area in which the initial turbulent flow would vanish. Both the gas and the liquid entered the tray through four evenly spaced one-eighth inch 304 stainless steel tubes.

The six foot long test section followed the two and one half feet of calming length. In this section the gas and liquid came into contact in cocurrent laminar flow. The test area was followed by an exit section which was one foot long. In this region the gas and liquid layers were separated by a wedged shape plexiglass divider. This wedge shape permitted the gas film to leave the apparatus at an inclined position. This type of design prevents the liquid from entering the gas section since it would in effect have to flow uphill. The gas and liquid streams were reduced in cross-sectional area in a manner similar to that in the entrance section. The original test section dimensions were reduced to one inch wide by seven sixteenths of an inch high per phase. Both streams were removed from the plexiglass through four evenly spaced one eighth inch 304 stainless steel tubes.

The entire tray was constructed of one quarter inch clear plexiglass sheets. The sides and top of the trough were held together by a cement designed for use with plexiglass. The front of the entrance and exit ends were

strengthened by replacing the quarter inch plexiglass with one half inch stock. This additional thickness was necessary to support the fluid entrance and exit steel tubes.

THE GAS FEED: The gas was fed from a Matheson number one cylinder through a regulating valve which restricted the pressure to a maximum of six and one quarter pounds per square inch guage. From this regulator the gas flowed through a surge tank which was constructed of four inch steel pipe. The purpose of this piece of apparatus was to enhance continuous smooth flow of gas. The surge tank along with the proceeding coils immersed in a constant temperature bath brought the gas temperature up to the temperature of the system. The gas was than saturated with water by passing it through a glass scrubber. The scrubber was also immersed in the same constant temperature bath to maintain the final gas stream at the temperature of the system. The gas stream rate was measured in a Fisher-Porter gas flowrater calibrated for gas flow from 0.09 cubic feet per minute, to 1.00 cubic feet per minute. A micrometer adjusting needle valve following the flowrater was used to control the gas flow at a previously determined ratio. This ratio was chosen so as to permit a continuous velocity profile through the system. The ratio is given in the following expression (41).

$$\frac{V_G}{V_L} = \frac{\mu_L (7\mu_G + \mu_L)}{\mu_G (\mu_G + 7\mu_L)}$$

Thus, once the temperature and the liquid flow rate are decided upon, the gas flowrate is set. The gas stream leaving the micrometer valve is split into four equal streams, and then enters the reaction tray.

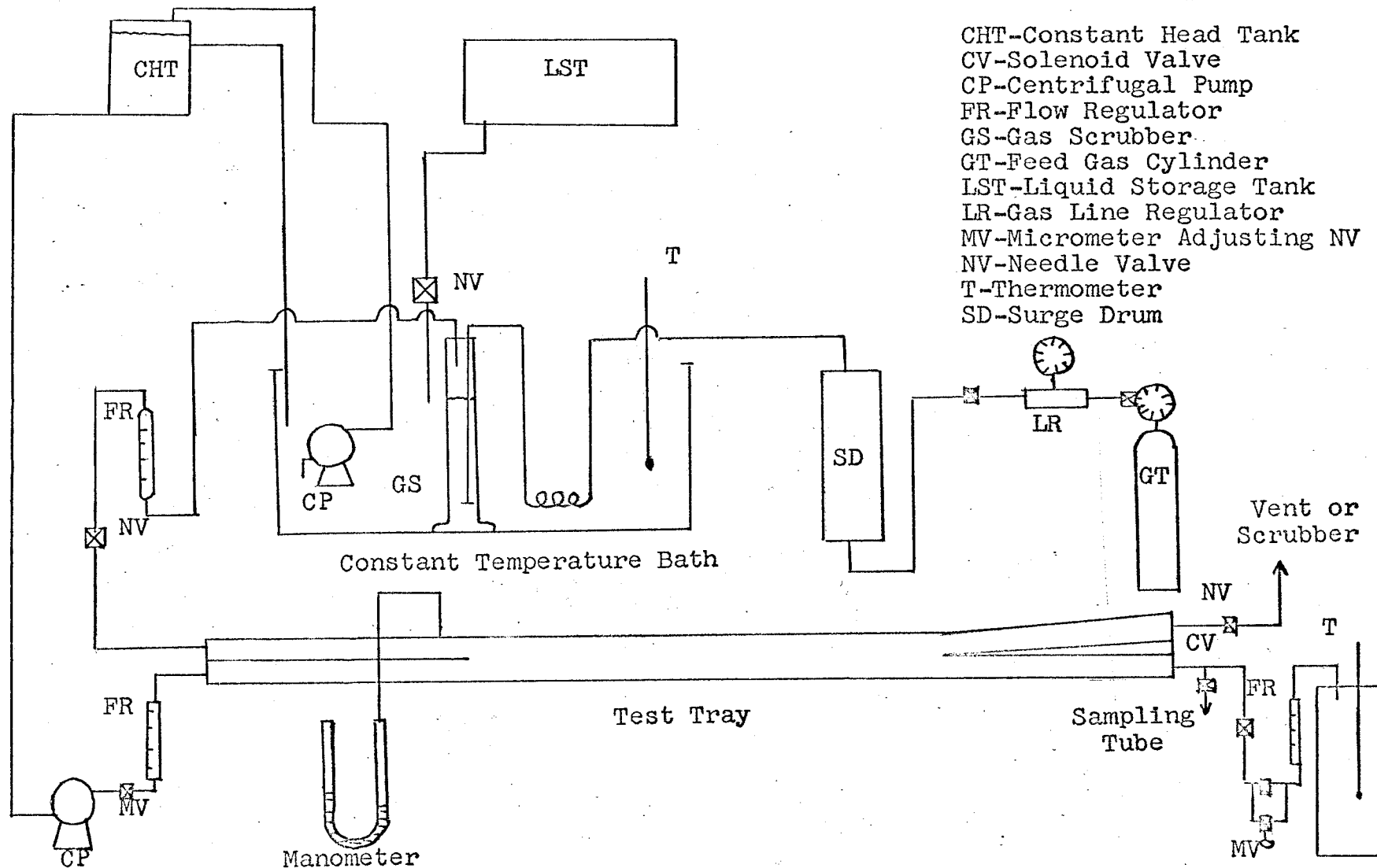
The gases leaving the experimental apparatus were treated in different manners depending on their toxicity. The hydrogen sulfide was passed through a needle valve after leaving the tray. This needle valve was utilized to set and control the gas pressure within the system. From this point the gas was absorbed by monoethanolamine solutions contained in a series of two liter flasks through which the gas stream was passed. When carbon dioxide was used as the solute gas fewer precautions had to be taken. For this solute the stream leaving the pressure adjusting needle valve was vented to the atmosphere outside of the building.

THE LIQUID FEED: The deionized water was fed by gravity flow from twelve gallon storage tanks to the same constant temperature both used to heat the gas stream. From this point it was circulated through a constant head device maintained ten feet above the test tray. The water leaving this piece of equipment was fed to a centrifugal pump that increased the pressure so as to maintain higher flow rates and compensate for the pressure drop

in the tray. The water leaving the pump was passed through a micrometer adjusting needle valve and through a Fisher Porter Flowrater. The valve was used to control the flow rate of water. The water then passed through the test tray. At the exit of the test tray the liquid passed through a series of two needle valves followed by one micrometer adjusting needle valve set in parallel with the other valves. This micrometer valve is used to insure that the liquid height in the test section remains at exactly one half the height of the tray. A by-pass line controlled by a solenoid valve was placed immediately following the exit from the tray. This line was used for the liquid sampling procedure.

The liquid stream containing dissolved gas was disposed of in a manner that was determined on the basis of the nature of the gas used. Water containing dissolved hydrogen sulfide was run from the adjusting valves through a Fisher and Porter Flowrater which was used to compare the entrance and exit flow rates. After leaving this apparatus the stream ran into a twelve gallon bottle containing cupric sulfate. This substance reacted with the hydrogen sulfide and formed a solution containing a cupric sulfide precipitate in water. When carbon dioxide was used as the solute gas the exit water stream was permitted to go directly from the flowrater to the drain.

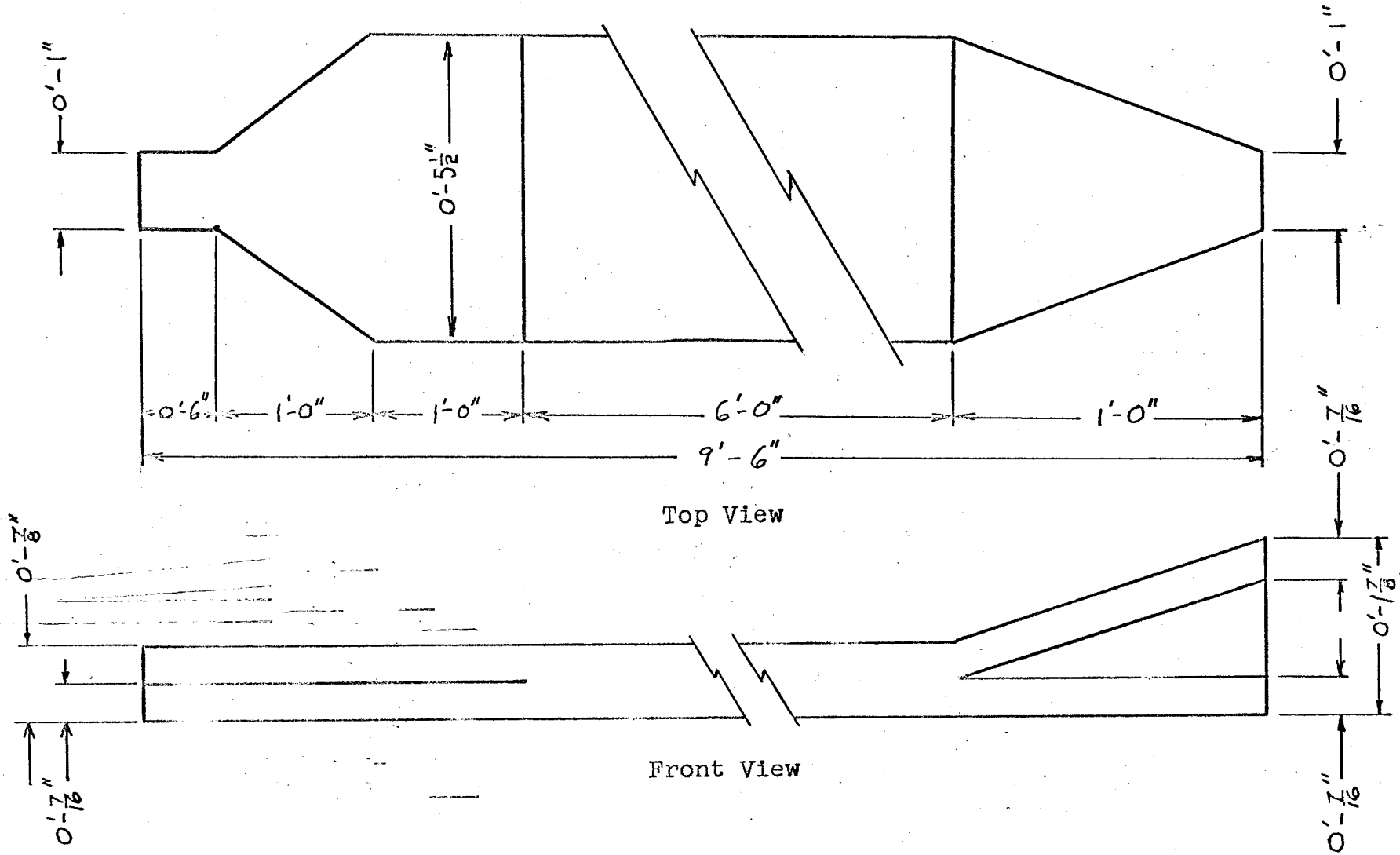
Figure 3- Schematic Flow Diagram



Key

- CHT-Constant Head Tank
- CV-Solenoid Valve
- CP-Centrifugal Pump
- FR-Flow Regulator
- GS-Gas Scrubber
- GT-Feed Gas Cylinder
- LST-Liquid Storage Tank
- LR-Gas Line Regulator
- MV-Micrometer Adjusting NV
- NV-Needle Valve
- T-Thermometer
- SD-Surge Drum

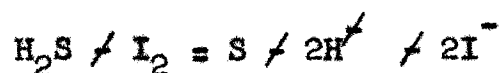
Figure 4- TEST APPARATUS SCHEMATIC  
 GIVING INSIDE DIMENSIONS





ANALYTICAL METHODS

HYDROGEN SULFIDE IN WATER: The hydrogen sulfide dissolved in the water was analyzed by treating it with an excess of standard iodine solution. The remaining iodine was back titrated with a standard sodium thiosulfate solution until the blue color of a starch indicator disappeared. The general method is discussed by Scott (42) in his book on standard analytical procedures. The main reactions for these two procedures are as follows.

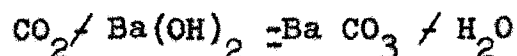


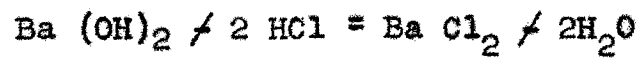
There are several disadvantages with this method of analysis and some disagreement as to its accuracy has arisen. However, it has been pointed out that the error is caused by the failure to maintain the iodine reagent slightly acidic. It has been shown that the error in this method is proportional to the amount of basic salts present. To insure acidic conditions the pH of the iodine solution was reduced to 6.0 by the addition of hydriodic acid. Thus, much of the error arising in previous work was eliminated.

The sample of water to be tested was removed directly from the system to the iodine reagent by allowing the gas containing water to run through the by-pass

line into a flask containing twenty-five milliliters of 0.05 normal iodine solution and one hundred milliliters of distilled water. By this method the water to be tested was not permitted to come into contact with the surrounding air and the gas contained in the water was immediately reacted with the iodine. Thus, any possibility of gas escaping from the liquid was eliminated. Before the liquid sample was taken, the by-pass line was opened and drained to prevent any stagnant solution from mixing with the sample. These samples were taken after thirty minutes of operation and at ten minute intervals until it was assured that steady state conditions had been reached.

CARBON DIOXIDE IN WATER: The amount of carbon dioxide dissolved in water was determined by reacting the sample with a solution containing an excess of barium hydroxide. The carbon dioxide reacts with the barium hydroxide and forms a precipitate of barium carbonate. This precipitate is filtered off and the remaining solution is backtitrated with 0.1 normal hydrochloric acid to determine the excess barium hydroxide. The entire procedure has been described by Starck (43) in his book on chemical analysis. The following reactions describe the operation.





The same general sampling procedure was used for the carbon dioxide runs as was used for the hydrogen sulfide runs. The water sample in this case was run directly from the tray to the flask containing twenty-five milliliters of 0.10 normal barium hydroxide.

## DISCUSSION OF RESULTS

The purpose of this study was to investigate the rate of mass transfer of hydrogen sulfide and of carbon dioxide to water moving in a horizontal film. The penetration and boundary layer theories were used as a basis in the solution of the mathematical model describing the physical situation. The validity of this model as a means of predicting diffusivity from measured variables was investigated. This study also attempted to extend and confirm the work of Tang and Himmelblau (44) who used similar physical and mathematical techniques in their study of mass transfer in a carbon dioxide-water system.

Application of the boundary layer and penetration theories gives similar equations relating the diffusivity to the interfacial concentration, the exit (cup mixing) concentration, the average liquid velocity, and the liquid film thickness. The resulting equations for the cup mixing concentration using either theory are the same differing only in the constant.

$$\bar{C}_L = K (C_1 - C_0) \sqrt{(\alpha DL)/(b^2 \bar{u})}$$

Boundary layer  $K = 1.060$

Penetration Theory  $K = 1.129$

These equations were derived under the premise that the diffusivity will be independent of the measured variables

$\bar{C}_L$  and  $\bar{V}_L$  ( $\bar{u}$ ). This relationship must hold because of the preliminary assumption that  $(\partial D) / (\partial V) = (\partial D) / (\partial C) = 0$ . Thus, if the theories and assumptions used in their employment are correct, the diffusivity will be a function of temperature alone.

The calculated diffusivity of hydrogen sulfide and of carbon dioxide in water based on this equation is given in Tables I and II and Figures 5 and 6. In addition to the 12 per cent difference between the diffusivities computed by the two theories, the results indicate that the diffusivity varies with the liquid flow rate. This latter occurrence is contrary to one of the basic assumptions upon which the equations were developed.

Although the diffusivity computed by the boundary layer theory should differ by 12 per cent from that computed by the penetration theory, it should be independent of the velocity of the liquid phase at constant temperature. This independence of liquid velocity was not indicated by the results of Tables I and II. If the diffusivity really does remain constant some other term in the equation describing the diffusivity was improperly used. Simplification of the general boundary layer and penetration theory equations yields the following relationship between the diffusivity, the average exit concentration ( $\bar{C}_L$ ), the liquid velocity, and the interfacial concentration.

TABLE I

The Effect of Flow Rate on the Apparent Diffusivity of H<sub>2</sub>S  
in Water at Constant Temperature and Pressure:

$V_L$ (cc/min)	$C_L$ (mg of H <sub>2</sub> S) cc	Boundary Layer Diffusivity $\times 10^5$ D (cm <sup>2</sup> /sec)	Penetration Theory Diffu- sivity $\times 10^5$ D (cm <sup>2</sup> /sec)
800	0.131	0.306	0.271
755	0.152	0.355	0.314
700	0.155	0.363	0.321
500	0.212	0.480	0.424
500	0.208	0.470	0.416
300	0.348	0.794	0.702
300	0.351	0.800	0.706
50	1.95	4.18	3.69

$P_G = 1.23 \text{ atm}; T = 25.2^\circ\text{C}$

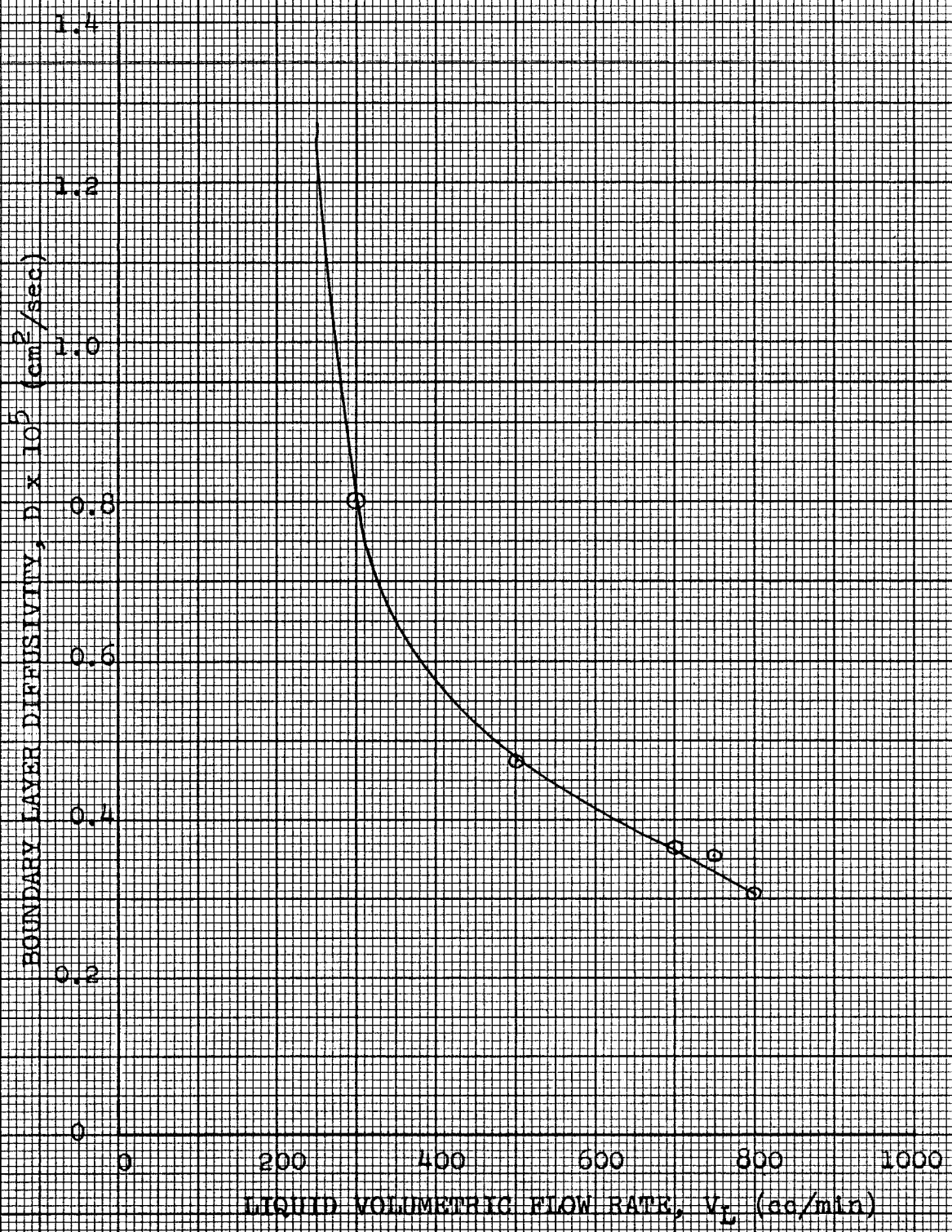
TABLE II

The Effect of Flow Rate on the Apparent Diffusivity of CO<sub>2</sub>  
in Water at Constant Temperature and Pressure:

$V_L$ (cc/min)	$C_L$ (mg of CO <sub>2</sub> ) (cc)	Boundary Layer Diffusivity $\times 10^5$ D (cm <sup>2</sup> /sec)	Penetration Theory Diffu- sivity $\times 10^5$ D (cm <sup>2</sup> /sec)
700	0.166	2.71	2.49
500	0.214	3.29	2.91

$P_G = 1.10 \text{ atm}; T = 25.2^\circ\text{C}$

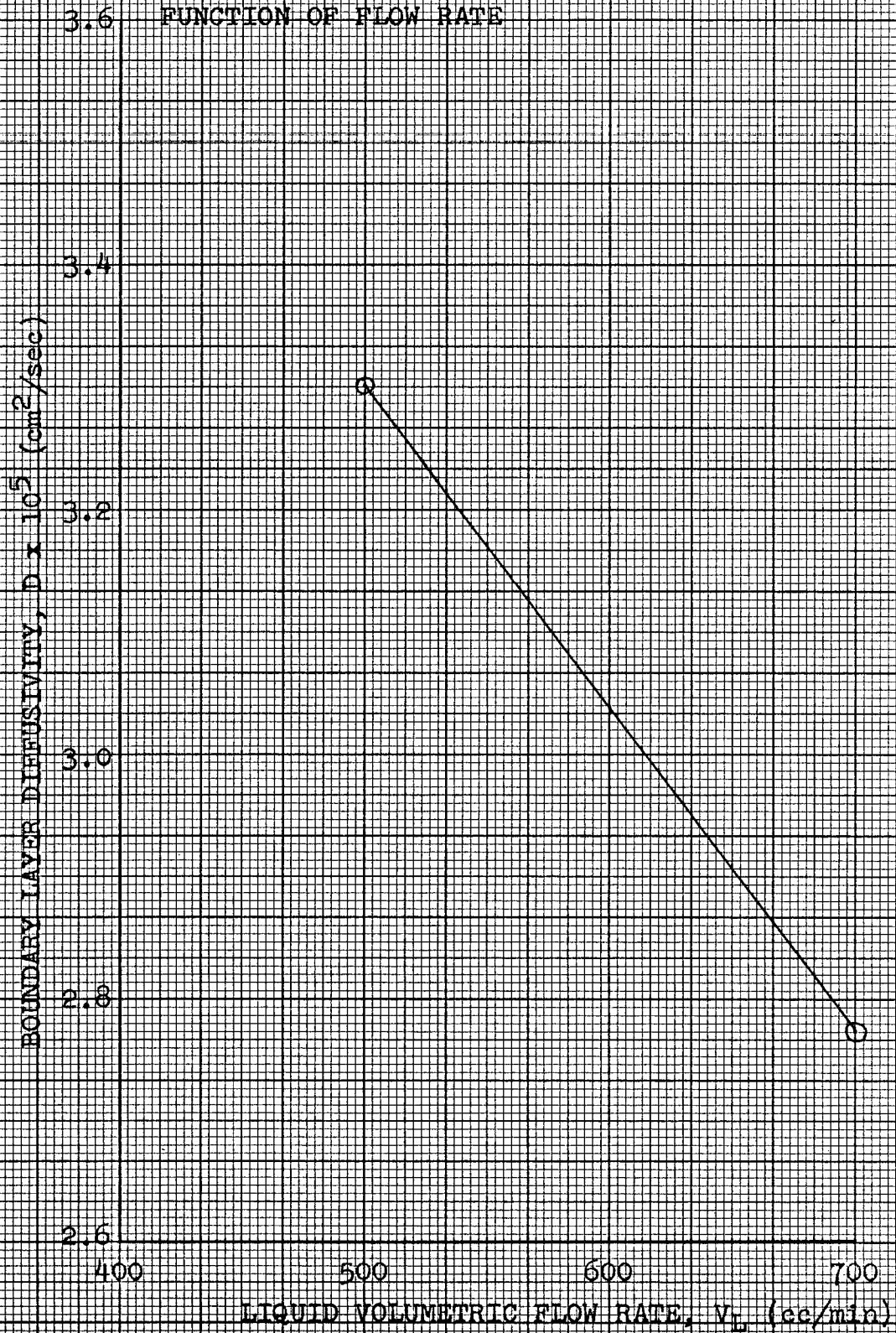
Figure 5 - THE APPARENT BOUNDARY LAYER  
DIFFUSIVITY OF HYDROGEN SULFIDE IN WATER  
AT 25.2°C AND 1.23 ATMOSPHERES AS A FUNCTION  
OF FLOW RATE



10 X 10 TO THE 1/2 INCH  
KEUFFEL & ESSER CO.  
358-11  
MADE IN U.S.A.



Figure 6 - THE APPARENT BOUNDARY LAYER  
DIFFUSIVITY OF CARBON DIOXIDE IN WATER  
AT 25.2°C AND 1.1 ATMOSPHERES AS A  
FUNCTION OF FLOW RATE





$$D = K' (\bar{C}_L / c_1)^2 \bar{V}_L$$

The constant "K'" includes all constant terms appearing in the two theoretical equations describing the diffusivity. If the diffusivity is considered constant at a given temperature as is indicated by other investigators, the preceding equation can be treated as follows.

$$K' = (DC_1^2)/K = \bar{C}_L \bar{V}_L$$

$$K'' = \log K' = 2 \log \bar{C}_L + \log \bar{V}_L$$

This equation would indicate that the slope of a plot of  $\bar{C}_L$  vs.  $1/\bar{V}_L$  on log-log coordinates should give a straight line with a slope of 0.5 or 2.0 depending on the choice of axis. Tables III and IV and Figures 7 and 8 show the relationship between the exit concentration ( $\bar{C}_L$ ) and the liquid velocity ( $\bar{V}_L$ ). However, the plot of  $\log \bar{C}_L$  vs.  $(1/\bar{V}_L)$  (Figures 7 and 8) does not yield a slope of 2.0 as would be expected from the preceding expression relating the liquid flow and the bulk concentration. Thus, one of the terms in the constant, K', must have varied in such a manner as to cause the variance in slope. The constant under consideration took into account the diffusivity, the interfacial concentration, and the geometric factors of the system. Of these terms a variance was possible only in the diffusivity or the interfacial concentration.

TABLE III

The Effect of Liquid Velocity On the Cup Mixing Concentration  
for a Hydrogen Sulfide-Water System at 25.2°C:

Run Number	$\bar{V}_L$ (cc/min)	$P_G$ (atm)	$\bar{C}_L$ (mg H <sub>2</sub> S/cc)	$\log \bar{C}_L$	$\log (1/\bar{V}_L)$
13a	800	1.23	0.131	-0.8825	-2.9030
7	755	1.28	0.152	-0.8185	-2.8785
9	700	1.23	0.155	-0.8100	-2.8455
10	500	1.23	0.212	-0.674	-2.6990
11a	500	1.23	0.208	-0.682	-2.6990
11b	300	1.23	0.348	-0.452	-2.4780
12a	300	1.23	0.351	-0.454	-2.4780
16	50	1.23	1.95	-0.290	-1.6990

TABLE IV

The Effect of Liquid Velocity on the Cup Mixing Concentration  
for a Carbon Dioxide-Water System at 25.2°C:

Run Number	$\bar{v}_L$ (cc/min)	$P_G$ (atm)	$\bar{c}_L$ (mg CO <sub>2</sub> /cc)	log $\bar{c}_L$	log (1/ $\bar{v}_L$ )
19	700	1.10	0.166	-0.780	-2.8455
20	500	1.10	0.214	-0.670	-2.6990

Figure 7 - THE EFFECT OF THE LIQUID VELOCITY  
ON THE CUP MIXING CONCENTRATION FOR A  
HYDROGEN SULFIDE-WATER SYSTEM AT 25.2°C  
AND 1.23 ATMOSPHERES

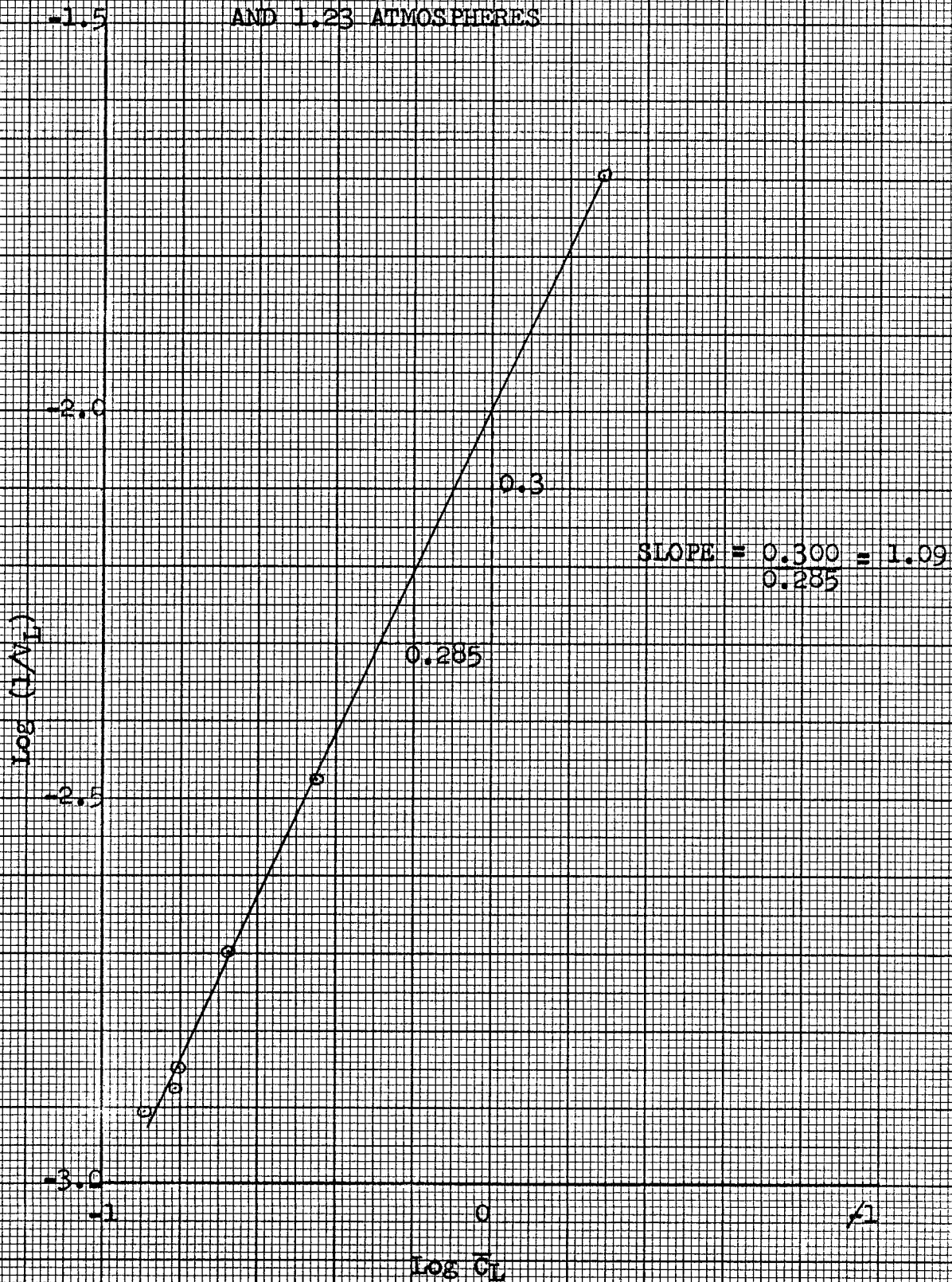
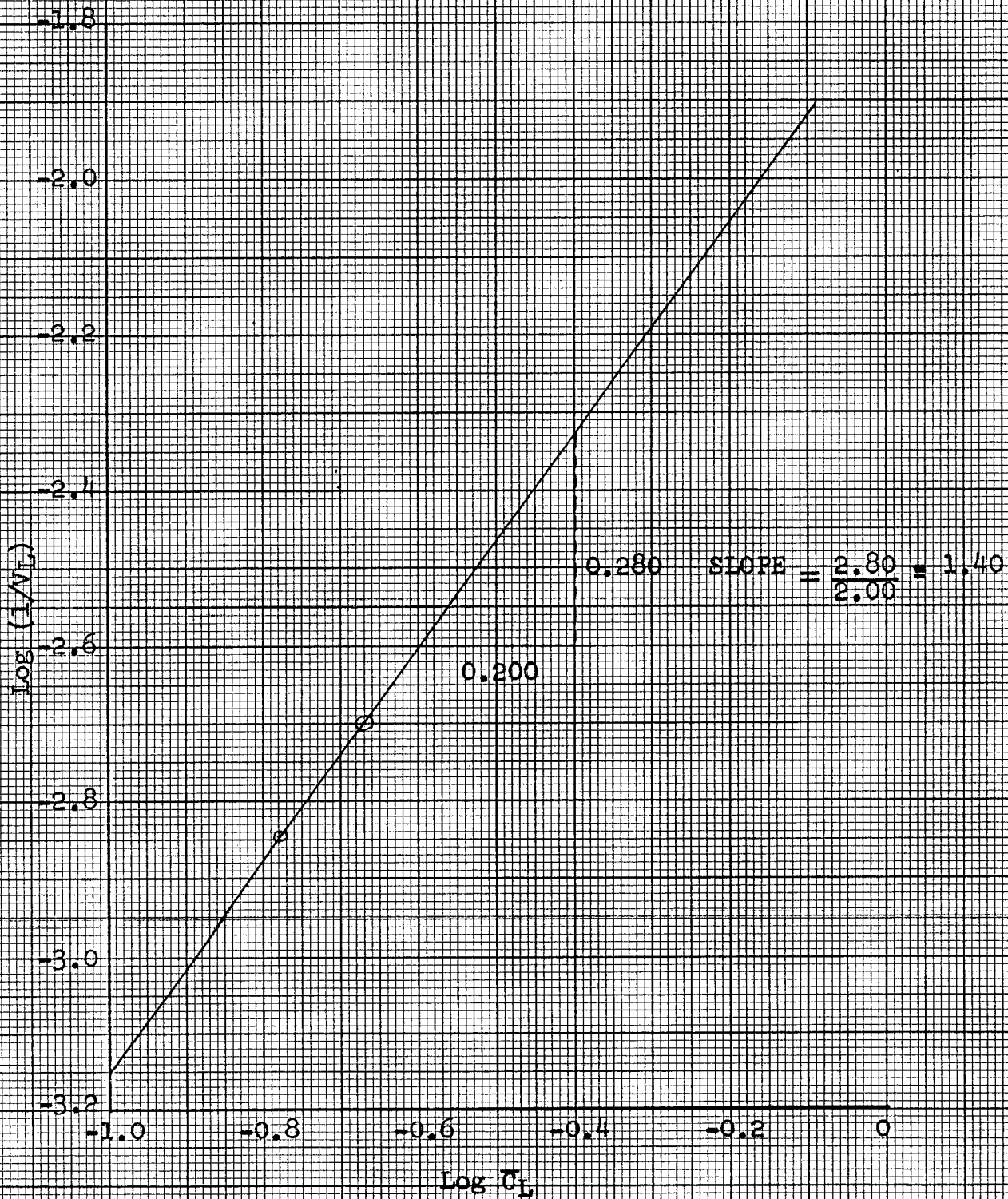


Figure 8- THE EFFECT OF LIQUID VELOCITY  
ON THE CUP MIXING CONCENTRATION FOR A  
CARBON DIOXIDE - WATER SYSTEM AT 25.2°C  
AND 1.1 ATMOSPHERES



Since all previous workers in this field have found the diffusivity to be a function of temperature alone, it seems likely that one of the basic assumptions, other than constant diffusivity is not valid. Thus, an actual variance in a quantity previously assumed to be constant would account for apparent deviations in diffusivity.

The most controversial assumption used in the derivation of the equations based on the penetration and boundary layer theories is the equivalence of the gas-liquid interfacial concentration and the hypothetical equilibrium concentration. This assumption, although often questioned, has been used extensively because of the lack of any quantitative method for determining the true value of the concentration at the liquid surface. The interfacial or equilibrium concentration was originally introduced into the mathematical relationship defining the diffusivity in the form of a constant value at a given temperature and pressure. It was originally assumed the following relationship was valid.

$$D = A (\bar{V}_L) (\bar{C}_L/C_1)^2 = A' (\bar{V}_L) (\bar{C}_L)^2$$

In this equation A is a constant including values for the geometry of the liquid film. If the diffusivity described by this equation is constant  $\bar{V}_L = k (1/\bar{C}_L)^2$ . However, if  $C_1$  varies with  $\bar{V}_L$  than the liquid film velocity is no longer a function of  $(1/\bar{C}_L)^2$  alone and the above equation will

indicate a false variation in the diffusivity.

Divergence of the interfacial concentration from the equilibrium concentration is thought to be a result of the presence of an interfacial resistance. Emmert and Pigford (45) discuss the possibility of an interfacial resistance decreasing the rate of absorption. These same authors (46) explain that this resistance is caused by the formation of an activated state of gas molecule that strikes the liquid surface. The fraction of these molecules that possess enough energy to form this state is called the accommodation coefficient. This term was found to equal  $(\sqrt{6\pi} k_1)/(\bar{u})$ , where  $k_1$  is the mass transfer coefficient for interfacial resistance and  $\bar{u}$  is the velocity of the gas molecules. It has been found that the accommodation coefficient increases in a manner directly proportional to the liquid flow rate. Thus, if an interfacial film resistance exists, it will decrease the rate of mass transfer as the liquid velocity ( $V_L$ ) increases. Pigford (47) found that the interfacial resistance resulted in an interfacial concentration that was not equal to an equilibrium concentration. It should be noted that the interfacial concentration was taken as equal to the equilibrium concentration in previous calculations in this thesis.

It is necessary to determine a value of the interfacial concentration to properly apply the existing equations.

Pigford solved a differential equation describing the mathematical model of a short wetted wall column and arrived at a solution of the form:

$$C_1 = \left[ K_1 e^{-K_2 P} + K_3 e^{-K_4 P} + \dots \right] \bar{C}_L$$

where  $C_1$  is the true interfacial concentration of gas in the liquid and  $P$  is a quantity dependent upon the temperature, the contact time, the diffusivity, and the pressure. Thus if this expression for concentration is used in either of the previously derived expressions for the diffusivity, the following equations will result.

Boundary Layer Theory:

$$D = \frac{(b^2 \bar{u})}{L (1.060)^2} \left[ \frac{\bar{C}_L}{f(\bar{C}_L)} \right]^2 = K \bar{V}_L \left[ \frac{\bar{C}_L}{f(\bar{C}_L)} \right]^2$$

Penetration Theory:

$$D = K'' \left[ \bar{V}_L \left\{ \frac{\bar{C}_L}{f(\bar{C}_L)} \right\}^2 \right]$$

From the logarithmic plot of  $1/\bar{V}_L$  versus  $\bar{C}_L$  at constant pressure and temperature, the functional relationship between  $\bar{C}_L$  and  $C_1$  for hydrogen sulfide and water can be determined. This plot has a slope of 1.09. If the diffusivity remains constant these equations can be rewritten in the following form.



$$\frac{D}{K} = K' = V_L \left[ \frac{\bar{C}_L}{f(\bar{C}_L)} \right]^2$$

$$K'' = \log K' = \log V_L + 2 \log \frac{\bar{C}_L}{f(\bar{C}_L)}$$

Rewriting the expression,  $f(\bar{C}_L)$ , as  $J(\bar{C}_L)^x$ , the above equation can be expressed in the form of a straight line relation,  $y = a/bz$ , where  $y$  is the  $\log (1/V_L)$  and  $z$  is the  $\log \bar{C}_L$ .

$$\log (1/V_L) = [K'' - (2-2x)\log J] / (2-2x)\log \bar{C}_L$$

For the hydrogen sulfide-water system the slope  $(2-2x)$  equals 1.09 and  $x$  is found to be equal to 0.455.

$$\frac{D}{K} = V_L \frac{\bar{C}_L}{J (\bar{C}_L)^{0.455}}$$

Based on a value of  $1.61 \times 10^{-5}$  cm<sup>2</sup>/sec (48) for the diffusivity of hydrogen sulfide in water at 25°C, the value of  $J$  in the previous equation becomes 23.0. Thus, an expression for the interfacial concentration of hydrogen sulfide in water at 25.2°C and 1.23 atmospheres has been empirically derived.

$$C_1 = 23.0 (\bar{C}_L)^{0.455}$$

This expression may be compared to the original assumption that the interfacial concentration ( $C_1$ ) is equal to the equilibrium concentration, which for the given system and conditions yields a constant value for  $C_1$  of 0.125 gram

moles of hydrogen sulfide per liter of solution. It should be remembered that the final empirical expression relating the interfacial and exit concentrations was derived for the particular equipment under consideration and for a specified pressure of 1.23 atmospheres and a temperature of 25.2°C.

The effect of the interfacial concentration on the carbon dioxide-water system was less pronounced than it was in the hydrogen sulfide-water system. The plot of  $\log (1/\sqrt{V_L})$  versus  $\log \bar{C}_L$  for the carbon dioxide runs yields a slope of 1.40 as compared with a value of 1.09 for the hydrogen sulfide runs. These values may be compared with a value of 2.0 for the slope of a system in which there is no interfacial resistance.

The exact nature of the interfacial resistance has been difficult to determine because of the occurrence of effects due to surface active materials. Emmert and Pigford (49) in a study of interfacial resistance in a falling liquid film noted the occurrence of a decrease in the rate of mass transfer when surface active materials were applied. They found an eleven per cent decrease in the rate of absorption when an organic wetting agent was added. Dust is another form of wetting agent in that it can create a stagnant film at the surface of the liquid layer that would offer resistance to diffusion. The mechanical liquid feed system, which consisted of an open tank, could not be properly shielded against foreign particles from the atmosphere.

It was also found that the diffusivity may become a function of the pressure of the system. Although the diffusivity was independent of the pressure in the hydrogen sulfide system, it was directly proportional to the pressure above an absolute value of 1.1 atmospheres in the carbon dioxide-water system. The plot of diffusivity versus pressure for a carbon dioxide-water system at 25.2°C shows that the diffusivity is proportional to pressure above 1.1 atmospheres and this dependence becomes more pronounced at lower flow rates. If the curve resulting from this plot is extrapolated to a pressure of one atmosphere, a value of  $2.0 \times 10^{-5}$  cm<sup>2</sup>/sec for the diffusivity of carbon dioxide in water at 25.2°C can be obtained. This value agrees favorably with the value of  $1.96 \times 10^{-5}$  cm<sup>2</sup>/sec frequently listed in the literature (50).

ERRORS: The errors in the mathematical model have already been discussed. Any additional errors in the experimental values of diffusivity were results of instrumental precision. The flow rate was determined by a Fisher and Porter flow-rater with an accuracy of  $\pm 2$  per cent of full scale. These flowraters were used to monitor the liquid and gas streams.

The other source of instrumental error is found in the chemical analysis used to determine the cup mixing concentration. The liquid sample was transferred directly from the test tray to the reagent to avoid any loss of gas. The buret used in the analytical titrations described previously were accurate to within  $\pm 2$  per cent of full scale.

Figure 9- THE EFFECT OF PRESSURE ON THE  
 APPARENT DIFFUSIVITY OF HYDROGEN SULFIDE  
 IN WATER AT 25.2 °C AND 300 cc/min FLOW  
 OF WATER

2.0

1.6

1.2

0.8

0.4

0

DIFFUSIVITY,  $D \times 10^5$  (cm<sup>2</sup>/sec)

1.00

1.04

1.08

1.12

1.16

1.20

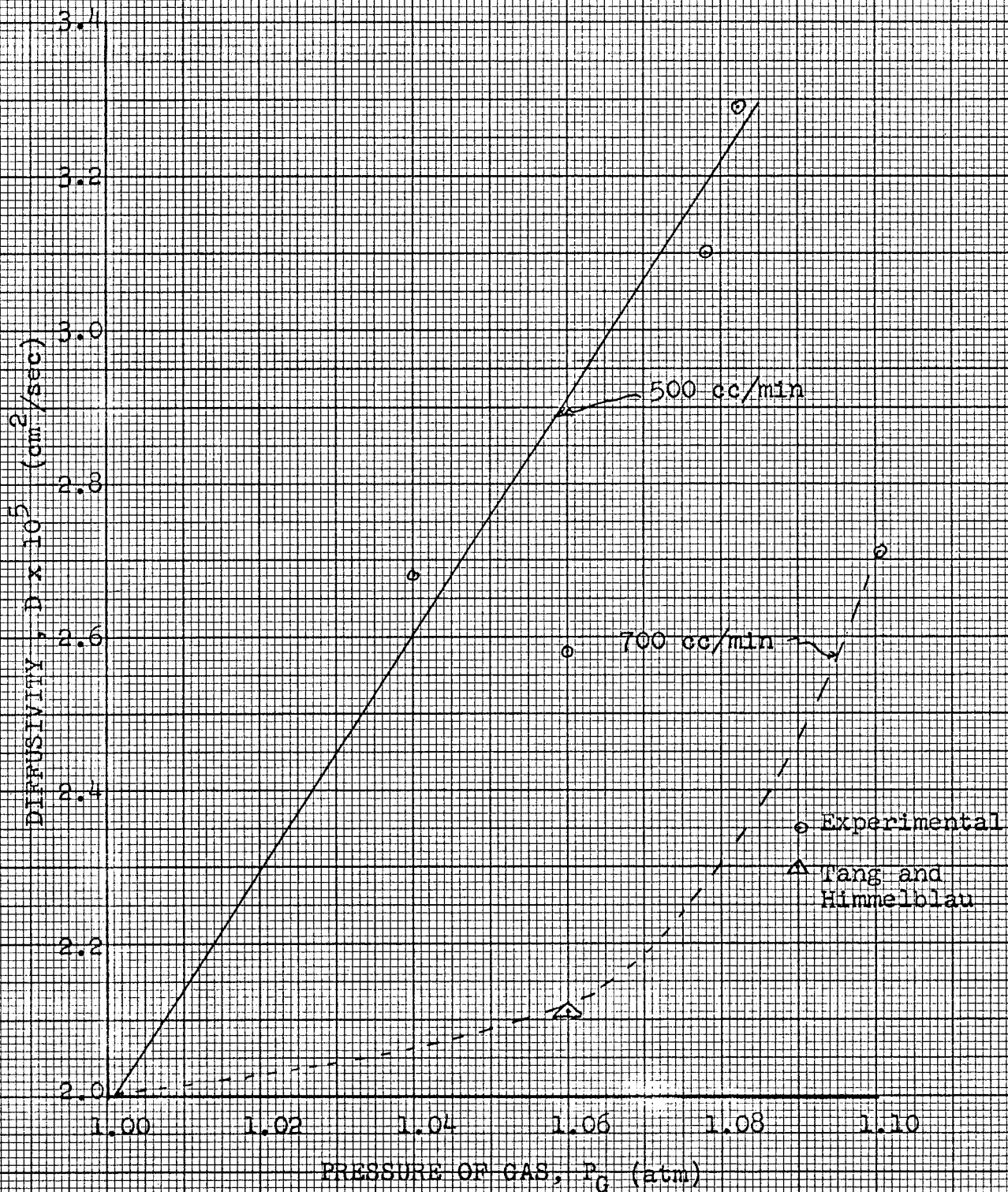
1.24

1.28

1.32

PRESSURE OF THE GAS STREAM,  $P_G$  (atm)

Figure 10 - THE EFFECT OF PRESSURE ON THE APPARENT DIFFUSIVITY OF CARBON DIOXIDE IN WATER AT 25.2 °C AND AT CONSTANT VOLUMETRIC FLOW IN THE LIQUID FILM



### SUMMARY

The results of the application of the boundary layer and the penetration theories to the mathematical model describing mass transfer between cocurrently flowing gas and liquid streams in a horizontal channel indicates that the diffusivity may be dependent on the pressure of the system and on the degree of interfacial resistance present. The effect of interfacial resistance on the diffusivity is more pronounced with more soluble gases such as hydrogen sulfide. The decreased interfacial concentration of hydrogen sulfide in water at 25.2°C and 1.23 atmospheres resulting from interfacial resistance is given by:

$$C_i = 23.0 (\bar{C}_L)^{0.455}$$

Highly soluble gases yield interfacial resistances resulting in variations in the apparent or computed diffusivity. Thus, solubility becomes one limiting factor in the application of the boundary layer and the penetration theories.

The effect of pressure on the diffusivity is more pronounced in less soluble systems. In the carbon dioxide-water system the diffusivity increases in a manner directly proportional to the pressure above absolute values of 1.1 atmospheres.

APPENDIX

ORIGINAL DATAHYDROGEN SULFIDE (SATURATED WITH WATER) - WATER RUNS AT 25.2°CTable V

Run Number	Flow Rate (Liquid) $V_L$ (cc/min)	Gas Pressure $P_G$ (atm)	Exit Conc. $C_L$ (mg/cc)	Comments
1	400	1.11	0.1921	Void;1,2
2	395	1.11	0.2409	Void;1,2
3	400	1.11	0.2389	Void;1,2
4	---	---	-----	Void;1,2 3,4
5	800	1.22	0.1187	Void;1,2
6	400	1.12	0.3066	Void;1,2
7	755	1.28	0.152	
8	700	1.15	0.152	
9	700	1.23	0.155	
10	500	1.23	0.212	
11a	500	1.23	0.208	
11b	300	1.23	0.348	
12a	300	1.23	0.351	



TABLE V (cont.)

Run Number	Flow Rate (Liquid) $V_L$ (cc/min)	Gas Pressure $P_G$ (atm)	Exit Conc. $\bar{C}_L$ (mg/cc)	Comments
12b	300	1.04	0.319	
13a	800	1.23	0.131	
13b	300	1.02	0.308	
14a	300	1.08	0.298	
14b	300	1.14	0.314	
15a	300	1.08	0.228	Void; 2
15b	300	1.14	0.254	Void; 2
16	50	1.23	1.950	

## Reasons For Voiding Runs:

1. Poor Pressure Control
2. Poor Temperature Control
3. Poor Control of Liquid Film Height
4. Steady State Conditions Not Reached

TABLE VICarbon Dioxide (Saturated with Water Vapor)-Water Runs at 25.2°C

Run Number	Flow Rate (Liquid) $V_L$ (cc/min)	Gas Pressure $P_G$ (atm)	Exit Conc. $\bar{C}_L$ (mg/cc)
17	500	1.041	0.182
18a	500	1.052	0.182
18b	500	1.064	0.198
19	700	1.100	0.166
20	500	1.100	0.214

### PHYSICAL CONSTANTS USED IN CALCULATING DIFFUSIVITY

Data for variables not directly measured and appearing in the general equation for diffusivity has been obtained from several standard sources. It was assumed in this study that the initial concentration of gas in the feed water was zero. The viscosity of the gases tested was determined from The International Critical Tables (51). The resulting viscosity of hydrogen sulfide as a function of temperature is presented in Figure 11. The value of the concentration of the gas in the liquid at the gas-liquid interface ( $C_1$ ) was assumed to be the equilibrium concentration. This assumption was tested by examining the consistency of the diffusivity. Values of " $C_1$ " were obtained from Linke's Solubilities of Inorganic and Metal Organic Compounds (52). Figure 12 shows the solubility of  $H_2S$  and water as a function of temperature and pressure.

Figure 11 - VISCOSITY OF HYDROGEN SULFIDE  
AS A FUNCTION OF TEMPERATURE

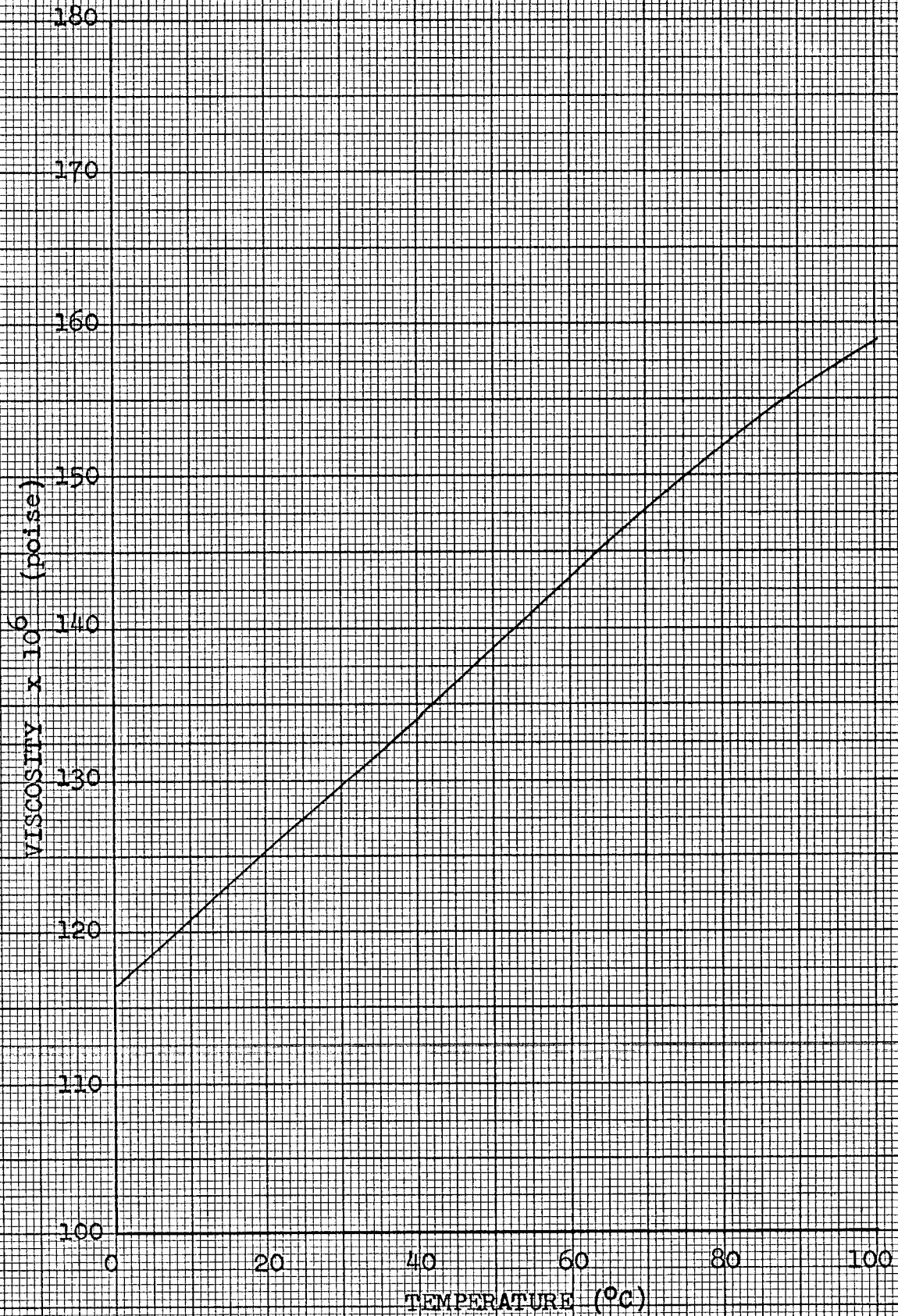
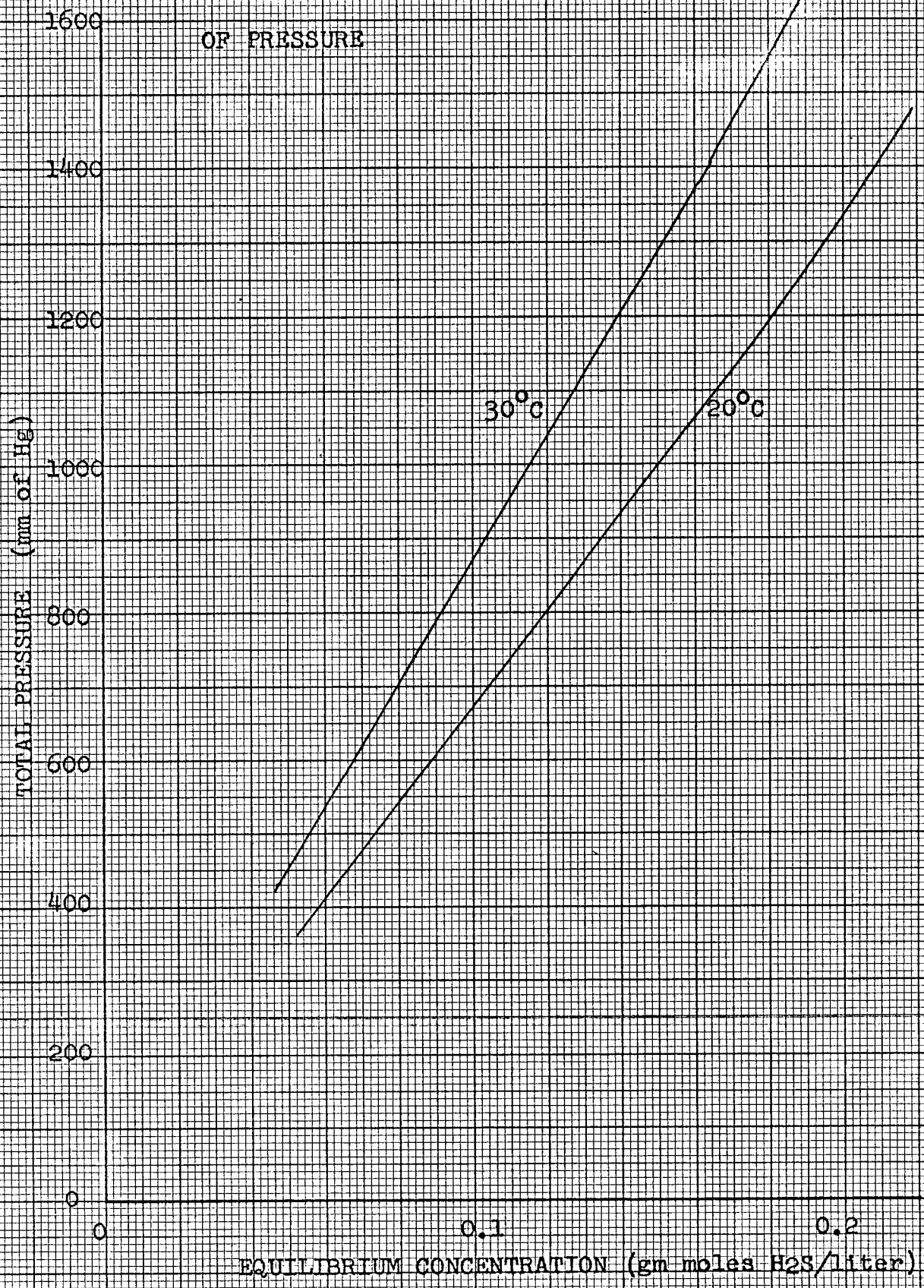


Figure 12 - EQUILIBRIUM CONCENTRATION OF HYDROGEN SULFIDE IN WATER AS A FUNCTION OF PRESSURE



KEUFFEL & ESSER CO. MADE IN U.S.A.

NOMENCLATURE

- a- Accommodation coefficient
- b- Depth of liquid film; one half depth of channel, cm
- C- Concentration, mg lcc
- $C_1$ - Concentration of gas in liquid film
- $C_0$ - Concentration of gas in liquid at  $t = 0$ , mg/cc
- $\bar{C}_L$ - Concentration of gas in liquid at exit, mg/cc
- D- Molecular diffusivity,  $\text{cm}^2/\text{sec}$ .
- $k_i$ - Interfacial film resistance coefficient
- L- Length of test section of channel (cm)
- n- Mass flux with respect to stationary coordinates,  $\text{mg}/\text{cm}^2 \text{ sec}$ .
- N- Molecular flux with respect to stationary coordinates,  $\text{moles}/\text{cm}^2 \text{ sec}$ .
- $P_g$ - Pressure of gas, atm or mm of Hg
- Q- Total mass transfer per unit time, mg/sec.
- $q_z$ - Local mass flux,  $\text{mg}/\text{cm}^2 \text{ sec}$ .
- u- Point velocity in the direction of flow in the liquid film at some distance y from the axis or interphase, cm/sec.
- $\bar{u}$ - Average velocity of liquid, cm/sec.
- T- Temperature ( $^{\circ}\text{C}$ )
- t- Time (sec)
- v- Mass average velocity
- $v^*$ - Molar average velocity-cm/sec.
- $\bar{V}_L$ - Volumetric liquid flow rate, cc/min.
- $\bar{V}_G$ - Volumetric gas flow rate, cc/min.
- W- Width of test section of channel, cm
- $x_A$ - Mole fraction of A,  $C_A/C$

Greek Letters

$$\alpha - \text{Dimensionless group} - \frac{12 \mu_L}{\mu_G + 7 \mu_L}$$

$$\beta - \text{Dimensionless group} - \frac{\mu_L - \mu_G}{2 \mu_L}$$

$$\gamma - \text{Dimensionless group} - \frac{\mu_L + \mu_G}{2 \mu_L}$$

$\delta$  - Liquid film thickness controlling diffusion cm.

$\rho$  - Density, mg/cc

$\mu_L$  - Viscosity of liquid,  $C_p$

$\mu_G$  - Viscosity of gas

$\pi$  - 3.1415

$$\phi - \text{Dimensionless group} - \frac{C_L - C}{C_L - C_0}$$

Subscripts

A- Gas

B- Liquid

x- Direction corresponding to width of channel

y- Direction corresponding to depth of channel

z- Direction corresponding to that of flow or length of channel

REFERENCES

1. Teller, Aaron J., "Absorption with Chemical Reaction," Chemical Engineering, Vol. 67, No. 14 (July 11, 1960) p. 111.
2. Emmert, R. E. and R. L. Pigford, "A Study of Gas Absorption in Falling Liquid Films," Chemical Engineering Progress, Vol. 50, No. 2 (February, 1954) pp. 87-93.
3. Emmert, R. E. and R. L. Pigford, "Gas Absorption Accompanied by a Chemical Reaction," A. I. Ch. E. Journal, Vol. 8, No. 2 (May, 1962) p. 171.
4. Whitman, W. G., Chemical and Metallurgical Engineering (July 23, 1923) p. 146.
5. Teller, loc. cit., p. 111.
6. Higbie, Ralph, "The Rate of Absorption of a Pure Gas Into a Still Liquid During Short Periods of Exposure," Transactions of the American Institute of Chemical Engineers, Vol. 31 (1935) p. 365.
7. Schlichting, Herman, Boundary Layer Theory, (McGraw Hill, 1960)
8. Bird, R. Byron, Warren E. Stewart, and Edwin N. Lightfoot, Transport Phenomena (John Wiley and Sons, Inc., 1960) pp. 601-619.
9. Higbie, Ibid, p. 365.
10. Dankwerts, P. V., "Gas Absorption Accompanied by Chemical Reaction," A. I. Ch. E. Journal, Vol. 1, No. 4 (December, 1955) p. 456.
11. Schlichting, op. cit., p. 239.
12. Toor, H. L. and J. M. Marchello, "Film-Penetration Model for Mass and Heat Transfer," A. I. Ch. E. Journal, Vol. 4, No. 1 (March, 1958) p. 97.
13. Arnold, Journal of the American Chemical Society, Vol. 52 (1930) p. 3937.
14. Davidson, J. F. and E. J. Cullen, "The Determination of Diffusion Coefficients for Sparingly Soluble Gases in Liquids," Transcripts Instn. Chem. Engrs., Vol. 35 (1957) p. 51.



15. Davidson and Cullen, Ibid, p. 51.
16. Davidson and Cullen, Ibid, p. 51.
17. Lynn, S., J. R. Straatemeier, and H. Kramers, "Absorption Studies in the Light of the Penetration Theory," Chemical Engineering Science, Vol. 4, No. 8 (April, 1955) p. 49.
18. Emmert and Pigford, loc. cit., p. 171.
19. Vivian, J. E. and D. W. Peaceman, "Liquid-Side Resistance in Gas Absorption," A. I. Ch. E. Journal, Vol. 2, No. 4 (December, 1956) p. 439.
20. Lynn, Straatemeier, and Kramers, loc. cit., p. 49.
21. Davidson and Cullen, loc. cit., p. 51.
22. Dankwerts, P. V. and A. M. Kennedy, "The Kinetics of Absorption of CO<sub>2</sub> Into Neutral and Alkaline Solutions," Chemical Engineering Science, Vol. 8, No. 3 (1958) p. 201.
23. Scriven, L. E. and R. L. Pigford, "Fluid Dynamics and Diffusion Calculations for Laminar Liquid Jets," A. I. Ch. E. Journal, Vol. 5, No. 3 (September, 1959) p. 397.
24. Tailby, S. R. and S. Portalski, "Wave Inception on a Liquid Flowing Down a Hydrodynamically Smooth Plate," Chemical Engineering Science, Vol. 17 (1962) p. 283.
25. van Rossum, J. J., "Experimental Investigation of Horizontal Liquid Films," Chemical Engineering Science, Vol. 11, No. 1 (1959) p. 35.
26. Tailby and Portalski, loc. cit., pp. 283-290.
27. van Rossum, J. J., loc. cit., p. 35.
28. Tang, Y. P. and D. Himmelblau, "Interphase Mass Transfer for Laminar Cocurrent Flow of Carbon Dioxide and Water Between Two Parallel Plates," A. I. Ch. E. Journal, Vol. 9, No. 5 (September, 1963) pp. 630-635.  
Also Tang, Y. P., Thesis, University of Texas (January, 1962)
29. Tang and Himmelblau, loc. cit., pp. 630-635.
30. Raimondi, Pietro and H. L. Toor, "Interfacial Resistance in Gas Absorption," A. I. Ch. E. Journal, Vol. 5, No. 1 (March, 1959) p. 86.
31. Scriven, L. E. and R. L. Pigford, loc. cit., p. 397.

32. Harvey, E. A. and W. Smith, "The Absorption of Carbon Dioxide by a Quiescent Liquid," Chemical Engineering Science, Vol. 10, No. 4 (1959) p. 274.
33. Emmert, R. E. and R. L. Pigford, "A Study of Gas Absorption in Falling Liquid Films," Chemical Engineering Progress, Vol. 50, No. 2 (February, 1954) pp. 87-93.
34. Chiang, S. H. and H. L. Toor, "Interfacial Resistance in the Absorption of Oxygen by Water," A. I. Ch. E. Journal, Vol. 5, No. 2 (June, 1959) p. 165.
35. Bird, Stewart, and Lightfoot, op. cit., p. 554.
36. Tang and Himmelblau, loc. cit., p. 630.
37. Russell, T. P. and M. E. Charles, Canadian Journal of Chemical Engineering, Vol. 37 (1959) p. 18.
38. Schlichting, op. cit., p. 237.
39. Higbie, loc. cit., p. 365.
40. Tang and Himmelblau, loc. cit., p. 630.
41. Tang and Himmelblau, Ibid, p. 630.
42. Furman, N. H., Scott's Standard Methods of Chemical Analysis, Vol. II, Fifth Edition (D. Van Nostrand Company, Inc., 1939) p. 2070.
43. Starok, H. P., Volumetric Analysis (William Wood and Co., 1934) p. 60.
44. Tang and Himmelblau, loc. cit., p. 630.
45. Emmert and Pigford, loc. cit., p. 87.
46. Emmert and Pigford, Ibid, p. 87.
47. Pigford, R. L., Ph. D. Thesis, University of Illinois (1941)  
Also in Emmert and Pigford, Ibid, p. 87.
48. Arnold, Journal of the American Chemical Society, Vol. 52 (1930) p. 3937.
49. Emmert and Pigford, loc. cit., p. 90.
50. Arnold, loc. cit., p. 3937.

51. West, Clarence J., International Critical Tables of Numerical Data, Physics, Chemistry, and Technology, Vol. V (Mc Graw Hill Co., Inc., 1933) p. 3.
52. Seidell, A. and W. F. Linke, Solubilities of Inorganic and Metal Organic Compounds, Vol. I, Edition 4 (Van Nostrand, 1958) p. 470.