

A STUDY OF DIFFUSION IN POROUS MEDIA

A THESIS

Presented to
the Faculty of the Graduate Division

by





Robert Fulton Dye

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
in the School of Chemical Engineering

Georgia Institute of Technology

March 1953

A STUDY OF DIFFUSION IN POROUS MEDIA

Approved: 

Date Approved by Chairman: April 25, 1954

ACKNOWLEDGEMENTS

The author is pleased to acknowledge his indebtedness to Dr. J. M. DallaValle, who suggested the problem, for his aid and guidance in the definition and prosecution of this work. He is deeply grateful to Drs. M. J. Goglia and W. M. Newton for suggestions and counsel. Appreciation is expressed to the Shell Oil Company, for sponsoring a fellowship, which has provided material assistance during the major portion of the time devoted to this work.

And in no small, single way did the assistance and efforts of my wife, Rebecca Gaston Dye, make this work possible.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS.ii
LIST OF TABLES.	v
LIST OF FIGURESvi
ABSTRACT.viii
Chapter	
I. INTRODUCTION	1
II. THEORY OF DIFFUSION IN GASES	4
The Differential Diffusion Equation	
The Diffusion Coefficient	
Diffusion in Porous Media	
III. STATEMENT AND GENERAL SOLUTION OF THE PROBLEM.	14
IV. EXPERIMENTAL EQUIPMENT AND PROCEDURE	24
Equipment	
Material	
Procedure	
V. DATA AND RESULTS	38
Application of the General Solution	
Experimental Results and Calculations	
Discussion of Results	
VI. CONCLUSIONS	58
Appendix	59
I. CALIBRATION OF EQUIPMENT	60
II. EXPERIMENTAL DATA.	64
III. MISCELLANEOUS CALCULATIONS	72

	Page
IV. NOMENCLATURE	75
BIBLIOGRAPHY	79
VITA	82

LIST OF TABLES

Table	Page
1. Calculated Diffusion Coefficients- CO_2 Sat'd.Plugs.	52
2. Calculated Diffusion Coefficients- N_2 Sat'd. Plugs.	53
3-A. Diffusion Data. 1 inch Plugs- CO_2 Sat'd.	64
3-B. Diffusion Data. 2 inch Plugs- CO_2 Sat'd.	65
3-C. Diffusion Data. 4 inch Plugs- CO_2 Sat'd.	65
3-D. Diffusion Data. 8 inch Plugs- CO_2 Sat'd.	66
4-A. Diffusion Data. 1 inch Plugs- N_2 Sat'd	67
4-B. Diffusion Data. 2 inch Plugs- N_2 Sat'd	68
4-C. Diffusion Data. 4 inch Plugs- N_2 Sat'd	68
4-D. Diffusion Data. 8 inch Plugs- N_2 Sat'd	69

LIST OF FIGURES

Figure	Page
1. A Typical Diffusion Rate Curve of $\log (C - C_{\infty})$ vs Time	22
2. Overall View of Equipment	25
3. View of Equipment Arrangement in Constant Temperature Bath.	26
4. Control Panel and Associated Equipment.	27
5. Schematic Diagram of Diffusion Equipment.	28
6. Sketch of Diffusion Cell Construction	30
7. Analyzer Schematic Electrical Circuit	31
8. Plug Holders and Filling Equipment.	34
9. Diffusion Data. CO_2 -Sat'd. Plugs: $\epsilon = 0.20$	42
10. Diffusion Data. CO_2 -Sat'd. Plugs: $\epsilon = 0.25$	43
11. Diffusion Data. CO_2 -Sat'd. Plugs: $\epsilon = 0.30$	44
12. Diffusion Data. CO_2 -Sat'd. Plugs: $\epsilon = 0.35$	45
13. Diffusion Data. CO_2 -Sat'd. Plug: $\epsilon = 0.40$	46
14. Diffusion Data. N_2 -Sat'd. Plugs: $\epsilon = 0.20$	47
15. Diffusion Data. N_2 -Sat'd. Plugs: $\epsilon = 0.25$	48
16. Diffusion Data. N_2 -Sat'd. Plugs: $\epsilon = 0.30$	49
17. Diffusion Data. N_2 -Sat'd. Plugs: $\epsilon = 0.35$	50
18. Diffusion Data. N_2 -Sat'd. Plug: $\epsilon = 0.40$	51
19. Diffusion Coefficient vs Porosity- CO_2 Sat'd. Plugs.	53

Figure	Page
20. Diffusion Coefficient vs Porosity- N_2 Sat'd. Plugs.	54
21. Diffusivity Ratio D/D_0 vs Porosity CO_2 -Sat'd. Plugs.	57
22. Calibration Curves. Thermal Conductivity Units.	62
23. Diffusion Data Log Sheet	71

A STUDY OF DIFFUSION IN POROUS MEDIA

Robert Fulton Dye

ABSTRACT

Frequently, in chemical engineering practice, information and data pertaining to diffusion rates in porous materials is of great importance. In some fields, even though the importance of diffusion has long been recognized, very little information has been offered about the controlling factors involved. This thesis is concerned with the study of some of these factors.

An experimental investigation was made of one-dimensional counter-current gas diffusion in porous media. Cylindrical plugs 1 1/2" in diameter pressed from powdered potassium perchlorate in lengths of 1, 2, 4, and 8 inches and of known porosity (fractional void volume), were used. Plugs were mounted for study in a diffusion cell in such a manner that they separated two gas volumes. Diffusion runs were made using carbon dioxide and nitrogen gases under unsteady-state conditions. Preliminary to starting a diffusion run, plugs were given a treatment such that some statement could be made as to the initial concentration distribution in them. During the diffusion period the change of concentration with time was observed on each side of the porous medium. Experiments were conducted at 104° F (40° C) and barometric pressure.

From the data, diffusion coefficients were calculated based on the exact mathematical treatment of the problem and no assumptions are made as to

linearity of concentration distribution in the plug during the diffusion.

A correlation of diffusivity with porosity shows, (1) the diffusivity is independent of the geometric length of path or medium thickness; and (2) the diffusivity changes little with decreasing porosity until a porosity value of approximately 0.5 is reached. From this value of 0.5, further decrease of porosity indicates a decided increase in rate of change of slope in the range 0.4 to 0.2 (range covered in this study) which becomes increasingly larger as the origin is approached. Initially, the slope is zero.

The mean values (average of all determinations for a given porosity) of the diffusion coefficient vs porosity for the counter-current diffusion of the two gases as determined experimentally are:

Porosity:	0.20	0.25	0.30	0.35	0.40
D	: 0.123	0.129	0.143	0.155	0.165

The calculated free diffusion coefficient is 0.169. This value corresponds to a porosity of 1.0.

CHAPTER I

INTRODUCTION

World War II provided the impetus for intensive investigations directed toward the separation of gaseous mixtures. Resulting from these investigations were many contributions of great importance in the field of diffusional operations. Gaseous effusion, thermal diffusion, and mass diffusion received much attention and interest.¹ Advances made in these fields have almost overshadowed completely the advancements of the past fifty years in other fields where gas diffusion has found application.

Diffusional principles underly many chemical engineering operations. Perhaps the first major contribution in diffusion in this branch of engineering was that of Lewis and Chang,² who applied the basic theories of Maxwell and Stefan to rectification, absorption and other operations. Sherwood,³ following the treatment of Lewis and Chang, gave a brief survey of diffusion theory and derived the diffusion equations for several steady-state and under-steady state cases. The transfer of

¹M. Benedict, Chem. Eng. Prog. 43, 2, 41 (1947).

²W. K. Lewis and K. C. Chang, Trans. Am. Inst. of Chem. Engrs., 21, 127 (1928).

³T. K. Sherwood, Absorption and Extraction, 1st ed., (McGraw-Hill Book Co., 1937) p. 5.

material between phases as related to the diffusional characteristics of the materials involved was treated extensively.

In chemical engineering practice, information and data pertaining to the rates of diffusion of gases in porous materials is frequently of great importance. This is particularly true in the fields of catalysis and adsorption. These factors are of much import in such unique operations as underground storage of gases.⁴ In many cases, the overall kinetics or adsorption rates may be entirely controlled by the diffusional characteristics of the system.⁵ The importance of diffusion as related to these two particular cases has long been recognized, but only meager information as to the controlling factors has been advanced.

That the porosity and length of diffusion path are significant factors influencing the diffusional characteristics of a porous material was perhaps first recognized by Buckingham⁶ in 1904. In an experimental study of diffusion in soils, Buckingham concluded that the rate of diffusion of a gas through a porous soil is approximately proportional to the square of the porosity (fractional void volume). Later, Penman⁷ examined Buckingham's data and conducted similar experiments without agreement. For a limited range of porosity values ($0.0 < \epsilon < 0.7$), Penman suggested as a good approximation, $\frac{D}{D_0} = 0.66 \epsilon$ where D_0 designates the free diffusion

⁴K. Toler, The Atlanta Journal-Constitution, p. 4-F, Mar. 8, (1953).

⁵F. J. Lavacot, Doctor of Science Thesis in Chemical Engineering, Washington University, St. Louis, (1951).

⁶E. Buckingham, Bull. U. S. Dep. Agric. no. 25, (1904).

⁷H. L. Penman, J. of Agric. Science, 30, 437 (1940).

coefficient and D the coefficient for diffusion in a porous medium. Consideration was not given to the effect of material thickness on the diffusivity in either of these investigations.

It was thus felt that a study of some of the factors controlling rates of diffusion such as area, medium thickness, and porosity would be helpful in the evaluation of porous materials as used in some of the applications discussed here.

Essentially, the investigation pursued was the experimental determination of diffusion coefficients connected with an unsteady-state counter-current diffusion process in a porous medium of predetermined characteristics.

CHAPTER II

THEORY OF DIFFUSION IN GASES

True diffusion is defined by Sherwood¹ as the spontaneous intermingling of miscible fluids placed in mutual contact without the aid of mechanical mixing. He notes, however, that convection currents due to temperature differences, or due to residual or undamped mechanical motion, make it very difficult to attain true diffusion conditions.

According to the kinetic theory,² a gas consists of a large number of molecules which move rapidly about in random fashion suffering frequent collisions with one another. Although molecular velocities are in the order of several hundred meters per second, the interdiffusion of gases is extremely slow due to the large number of collisions which the molecules undergo. Diffusion is more rapid at high temperatures because of increased molecular speeds. It is similarly more rapid at low pressures because average intermolecular distances are greater and collisions are less frequent. In addition small molecules diffuse rapidly, principally because of their greater molecular speeds and because the chance for collisions is less than for large molecules.

¹Sherwood, op. cit., p. 1.

²J. Jeans, Introduction to the Kinetic Theory of Gases, (Cambridge University Press, 1940) p. 9.

The theoretical work of Adolf Fick,³ published in 1855, precedes that of any quantitative experimental work and is regarded as the phenomenological or descriptive basis of the diffusion theory of today. The principal contributions to the theory of diffusion in gases were made by Maxwell⁴ and Stefan.^{5,6} Others, such as Enskog, Jeans, Chapman, and Meyer have made important additions to the theory.

The Differential Diffusion Equation.--- Following the derivations of Lewis and Chang,⁷ and Sherwood⁸ the diffusion equation most frequently encountered in discussions of the theory of diffusion in gases will be developed.

Consider the case of a countercurrent diffusion process taking place in a binary system of gas molecules A and B. Maxwell's basic concept is that the resistance to diffusion is proportional to the number of molecules of A and of B, proportional to the relative velocity of the diffusing component past the interfering one, and to the length of path in the direction of diffusion. Denoting the velocities of the two components as u_A and u_B , the frictional resistance will be proportional to the difference of these ($u_A - u_B$) and to the distance of travel

³A. Fick, Phil. Mag., (4) 10, 30 (1855).

⁴J. C. Maxwell, Scientific Papers, 2, 57 (1890).

⁵J. Stefan, Sitz. Akad. Wiss. Wien 63, (2), 63 (1871).

⁶J. Stefan, Sitz. Akad. Wiss. Wien 65, (2) 323 (1872).

⁷Lewis and Chang, op. cit. p. 127-131.

⁸Sherwood, op. cit., p. 3.

through which change of condition may be neglected, dx . The number of molecules of each may be taken as proportional to the partial molal densities $\frac{\rho_A}{M_A}$ and $\frac{\rho_B}{M_B}$ where ρ_A and ρ_B represent the partial densities expressed as weight per unit volume and M_A and M_B are the respective molecular weights. The total frictional resistance to diffusion of A is given by the expression, $\alpha_{AB} \rho_A \rho_B (u_A - u_B) dx$, where α_{AB} is the coefficient of resistance to diffusion of component A through B. We can consider that the influence of any external forces in comparison with this frictional resistance, and that the acceleration of the molecules of gas A is small and negligible. Then this frictional force must be overcome by an equivalent drop in concentration of partial pressure p_A of the diffusing gas over the section dx considered. This may be written as

$$-dp_A = \alpha_{AB} \rho_A \rho_B (u_A - u_B) dx. \quad (1)$$

This is Maxwell's basic concept or fundamental equation of diffusion. The dp_A has the negative sign since there is a decrease in partial pressure of the gas A. The α_{AB} constant may also be written α_{BA} since it depends merely on which of the gases is considered and since the interdiffusion of the two gases is dependent equally on the nature of both gases it will be written as α .

We can define

$$N_A = \frac{u_A \rho_A}{M_A} \quad (2)$$

where N_A is a representation of the rate of diffusion expressed as moles per unit area and M_A is the molecular weight of gas A. Also

$$\rho_A = \frac{M_A p_A}{RT} \quad (3)$$

which assumes the perfect gas laws, where T is the absolute temperature, and R the gas constant. In like manner,

$$N_B = \frac{u_B \rho_B}{M_B} \quad (4)$$

and

$$\rho_B = \frac{M_B p_B}{RT} \quad (5)$$

Considering this development as applied to the case of equal molal diffusion of A and B in opposite directions for which $N_A = -N_B$ then (4) is the negative of (2) or

$$\frac{u_A \rho_A}{M_A} = - \frac{u_B \rho_B}{M_B} \quad (6)$$

For a total constant pressure $P = p_A + p_B$ combining the equality expressed by (6) we can write

$$\frac{u_A \rho_A}{M_A} = - \frac{u_B \rho_B}{M_B} = - \frac{RT dp_A}{\alpha P dx} = \frac{R^2 T^2}{\alpha M_A P} \frac{d p_A}{dx} \quad (7)$$

For a small element dx of unit cross section in the direction of diffusion the weight of gas A contained in the element is $\rho_A dx$ and the depletion rate of A from the element is

$$- \frac{\partial}{\partial t} (P_A) dx \quad (8)$$

where t represents time. The input equals the output plus the accumulation so we have for an input rate, $u_A P_A$ an output rate

$$u_A P_A + \frac{\partial}{\partial x} (u_A P_A) dx \quad (9)$$

which, equated to the depletion

$$- \frac{\partial}{\partial t} (P_A) dx = \frac{\partial}{\partial x} (u_A P_A) dx \quad (10)$$

gives the relationship

$$\frac{\partial P_A}{\partial t} + \frac{\partial}{\partial x} (u_A P_A) = 0 \quad (11)$$

called the equation of continuity.⁹ Combining Equations (7) and (11) we get

$$\frac{\partial P_A}{\partial t} = \frac{R^2 T^2}{\alpha P} \frac{\partial^2 P_A}{\partial x^2} \quad (12)$$

The diffusion constant or coefficient is defined by Maxwell as

$$D = \frac{R^2 T^2}{\alpha P} \quad (13)$$

where P is the total pressure defined in a foregoing paragraph. Assuming constant D and P , substitution of the group (Equation (13)) in (12) gives

⁹Sherwood, op. cit., p. 4 and 5.

$$\frac{\partial p_A}{\partial t} = D \frac{\partial^2 p_A}{\partial x^2} \quad (14)$$

which in terms of partial pressures and concentrations, can be expressed as

$$\frac{\partial p_A}{\partial t} = D \frac{\partial^2 p_A}{\partial x^2} \quad (15)$$

and

$$\frac{\partial c_A}{\partial t} = D \frac{\partial^2 c_A}{\partial x^2} \quad (16)$$

Equation (16) is frequently referred to as Fick's second law of diffusion. The diffusion coefficient here used designates the coefficients of the pair of gases considered and differs from the "self diffusion coefficient" of either of the individual gases.

The Diffusion Coefficient.--- The diffusion coefficient for a pair of gases as derived by O. E. Meyer from simple kinetic theory considerations is given by¹⁰

$$D_{AB} = \frac{1}{3} (C_B \bar{v}_A \lambda_A + C_A \bar{v}_B \lambda_B) \quad (17)$$

where C_A and C_B are the mol fractions of each component, \bar{v}_A and \bar{v}_B , the mean molecular speeds, and, λ_A and λ_B , the mean free paths.*

¹⁰Jeans, op. cit., p. 201.

*The subscript letters A and B designate the two molecular species and is added here to indicate that the relationship is an expression for the mutual diffusion coefficient and to distinguish it from that of the self diffusion coefficients D_{AA} and D_{BB} .

The predicted strong dependence of D_{AB} in equation (17) on concentration is not in accord with experimental facts. Early work on the diffusivity of gases (summarized by A. Lonius in 1909---his tabulation is also given by Loeb)¹¹ showed that the variation of the diffusion coefficient, D , with composition was small---up to 8 percent.

In a theoretical treatment of mutual diffusion by Stefan's momentum transfer method, Furry¹² gives a result which indicates no variation of the coefficient with concentration. His treatment consists, essentially, of a calculation of \dot{m}_{AB} , the momentum transferred per unit volume per unit time from molecules of type A to molecules of type B. Collisions of like molecules do not contribute to the transport. It is found that $\dot{m}_{AB} = f(n, T, \mu, S_{AB}) \Gamma_A$ where n is the total numerical density, μ is the reduced mass, S_{AB} , the collision cross section and Γ_A , the transport in number of molecules per unit area in unit time. Since

$$-\dot{m}_{AB} dx = dp_A = k T dc, \quad (18)$$

$$f(n, T, \mu, S) \Gamma_A = k T \frac{dc}{dx} \quad (19)$$

and

$$D_{AB} \approx \frac{k T}{f(n, T, \mu, S_{AB})} \quad (20)$$

¹¹L. R. Loeb, Kinetic Theory of Gases, (McGraw-Hill Book Co., 1927) p. 237.

¹²W. H. Furry, Am. J. of Physics, 16, 63 (1948).

The function f includes integrals involving the intermolecular interaction potentials. A more exact treatment is given by Chapman and Enskog¹³ involving the solution of the Boltzman differential equation. The first approximation is identical with the results obtained by the momentum transfer treatment of Stefan and the second approximation yields a small dependence on concentration. If it is postulated that molecules behave as point sources of attractive or repulsive fields, then the force law may be written as $F = \frac{K}{r^p}$ and U , the interaction potential, $U = \frac{K}{r^{p-1}}$. In order to evaluate the required integrals a knowledge of the force constants is required. Conversely, from experimental values of the diffusion coefficient, viscosity, thermal conductivity, and thermal diffusion ratio, these constants may be evaluated. The first approximation to the diffusion coefficient in a binary mixture $(D_{AB})_1$ for the model of rigid elastic spheres is¹⁴

$$(D_{AB})_1 = \frac{3}{8(n_A + n_B)\sigma_{AB}^2} \left\{ \frac{kT(m_A + m_B)}{2\pi m_A m_B} \right\}^{1/2} \quad (21)$$

where n_A and n_B , refer to the number of molecules per cc, m_A and m_B , refer to the molecular masses, $\sigma_{AB} = 1/2 (\sigma_A + \sigma_B)$ equals the collision cross section, k is Boltzman's constant, and T is the absolute temperature. For molecules treated as point sources repelling each other with a force $K_{AB}r^{-p}$ the corresponding expression is

¹³S. Chapman and T. G. Cowling, Mathematical Theory of Non-Uniform Gases, (Cambridge University Press, 1939) p. 245.

¹⁴W. Jost, Diffusion, (Academic Press, 1952), p. 421.

$$(D_{AB})_1 = \frac{3}{8n \bar{A}_A(\gamma) \Gamma(3 - \frac{2}{\gamma-1})} \left\{ \frac{kT(m_A + m_B)}{2\pi m_A m_B} \right\}^{1/2} \cdot \left\{ \frac{2kT}{K_{AB}} \right\}^{\frac{2}{\gamma-1}} \quad (22)$$

where $n = n_A + n_B$, and $\bar{A}_A(\gamma)$ is a numerical value depending on the force law. The term $\Gamma(3 - \frac{2}{\gamma-1})$ is referred to as the Gamma function and is of the dimension of a reciprocal length. Considering the molecules as rigid elastic spheres with a central field of force (Sutherland's Model),¹⁵ the expression is obtained

$$(D_{AB})_1 = \frac{3}{8n\sigma_{AB}^2} \left\{ \frac{kT(m_A + m_B)}{2\pi m_A m_B} \right\}^{1/2} \left\{ 1 - \frac{\bar{S}_{AB}}{T} \right\} \quad (23)$$

where \bar{S}_{AB} is Sutherland's constant related to the law for the attracting force, but is usually empirically determined from the temperature dependence of the diffusion coefficient and the viscosity.

The theory as given by Chapman and Enskog is accurate insofar as it permits exact solutions of the equation for transport phenomena in gases, based upon certain molecular models.¹⁶ However, the choice of these models is not entirely free. They must be of spherical symmetry, and, therefore, an exact treatment of polyatomic molecules and the considerations of an exchange of internal energy of the molecules with kinetic energy of translation is excluded. Within limits, the theory is quite general and the solutions are obtained as successive approximations to the correct values.

¹⁵Ibid., p. 420.

¹⁶Ibid.

Diffusion in Porous Media.— Diffusion of gases in porous media is, in essential respects, a close approximation to that in capillary systems.^{17,18} In general, the laws and theory applicable to transport in long capillaries apply.

Consider an isothermal capillary system at very low pressures when the mean free paths of the molecules are much larger than the average pore diameter. Diffusion under the influence of a concentration gradient will then take place as molecular diffusion and the Knudsen equation applies.¹⁹ Under these conditions, the molecules in passing through the capillary collide frequently with the walls but only rarely with one another. At high pressures, when the mean free path of the molecules is much smaller than the capillary diameter the gases are transferred by a mass diffusion or capillary transpiration. The molecules in passing through the capillary will collide frequently with the wall and with one another and Fick's law is applied to this case.

It is usually taken ^{for} granted that the diffusivity in a porous body is independent of its thickness. This is based on tradition and elementary considerations of atomistics. This postulate seems so well established that no one has conducted a rigorous experimental test of it.²⁰

¹⁷R. D. Present and A. J. de Bethune, Phys. Rev., 75, 7, 1050 (1949).

¹⁸F. A. Schwertz, Am. J. of Physics, 15, 31 (1947).

¹⁹M. Knudsen, Ann. d. Physik (4) 28, 75 (1908).

²⁰L. S. Darken, Atom Movements-Seminar, (American Society of Metals, Publ., 1951), p. 13.

CHAPTER III

STATEMENT AND GENERAL SOLUTION OF THE PROBLEM

The problem considered here is that of the one-dimensional counter-current diffusion of two gases taking place through a porous medium or plug. The porous plug separates two gas volumes, 1, and 2, and is given a preliminary treatment to justify some statement about the initial distribution of gas concentration (i.e., $C_0(x)$) in it. Diffusion is allowed to proceed for a definite time and the gas volumes are kept homogeneous by some means of stirring or mixing. The concentration in 1 and 2 change from their original values ${}_1C_0$ and ${}_2C_0$ to different values ${}_1C(t)$, ${}_2C(t)$ in time t , and from a knowledge of these values it is desired to determine the diffusion constant of one of the gases as it diffuses into the other.

Let the porous plug be bounded by planes $x = 0$ and $x = l$. Well-stirred gaseous solutions of volumes, g , and h , and ${}_2C_0$, ${}_1C_0$ are in contact with the two sides of the plug. The first extends from $x = 0$ to $x = -g$; the second solution, in contact with boundary $x = l$ extends to $x = l + h$. The initial distribution of concentration across the medium of "effective" volume, l , is $C_0(x)$. After a time t the concentrations in the two gas volumes will be denoted by ${}_2C(t)$ and ${}_1C(t)$ and the distribution in the medium by $C(x,t)$. Then the boundary conditions for which the equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (24)$$

is to be solved are

$$(i) \quad C = C_0(x) \text{ at } t = 0 \text{ for } 0 < x < \ell.$$

$$(ii) \quad C(0, t) = {}_2C(t); \quad C(\ell, t) = {}_1C(t) \text{ for } t > 0.$$

$$(iii) \quad C = {}_2C_0 \text{ at } t = 0 \text{ for } -g < x < 0, \text{ and}$$

$${}_1C_0 \text{ at } t = 0 \text{ for } \ell < x < \ell + h.$$

$$(iv) \quad \frac{\partial {}_2C}{\partial t} = \frac{D}{g} \left(\frac{\partial C}{\partial x} \right)_{x=0}; \quad \frac{\partial {}_1C}{\partial t} = -\frac{D}{h} \left(\frac{\partial C}{\partial x} \right)_{x=\ell}.$$

The equations (iv) express the proportionality of rate of increase of concentration in the gas volumes to rate of supply of concentration changing constituent at the respective boundaries.

Let the solution of (24) be

$$C = c_1 + c_2 \quad (25)$$

where c_1 and c_2 are solutions which satisfy Equation (24). The solution of (24) which vanishes at $x = 0$ and at $x = \ell$ and which satisfies (i) is given by the known formula

$$c_1 = \sum_{n=1}^{\infty} a_n e^{-\alpha_n^2 t} \sin \frac{n\pi x}{\ell} \quad (26)$$

where

$$a_n = \frac{2}{l} \int_0^l c_0(y) \sin \frac{n\pi y}{l} dy \quad (27)$$

and

$$\alpha_n = \frac{Dn^2\pi^2}{l^2} \quad (28)$$

By Duhamel's theorem¹ the solution of (24) which corresponds to zero initial concentration in the medium and the faces maintained, respectively, in contact with gases of concentrations $c_2(t)$ and $c_1(t)$ is

$$c_2 = \int_0^t \left\{ c_2(\tau) \frac{\partial}{\partial t} F_1(x, t-\tau) + c_1(\tau) \frac{\partial}{\partial \tau} F_2(x, t-\tau) \right\} d\tau, \quad (29)$$

or

$$c_2 = - \int_0^t \left\{ c_2(\tau) \frac{\partial}{\partial \tau} F_1(x, t-\tau) + c_1(\tau) \frac{\partial}{\partial \tau} F_2(x, t-\tau) \right\} d\tau \quad (30)$$

¹H. S. Carslaw and J. C. Jaeger, Conduction of Heat in Solids, (Oxford Press 1947), p. 82.

which may be written

$$c_2 = {}_2C_0 F_1(x, t) + {}_1C_0 F_2(x, t) + \int_0^t \left\{ {}_2C'(\tau) F_1(x, t-\tau) + {}_1C'(\tau) F_2(x, t-\tau) \right\} d\tau \quad (31)$$

where

$$F_1(x, t) = 1 - \frac{x}{l} - \frac{2}{\pi} \sum_{n=1}^{\infty} \left(\frac{1}{n}\right) e^{-\alpha_n t} \sin \frac{n\pi x}{l} \quad (32)$$

and

$$F_2(x, t) = \frac{x}{l} + \frac{2}{\pi} \sum_{n=1}^{\infty} n \left(\frac{(-1)^n}{n}\right) e^{-\alpha_n t} \sin \frac{n\pi x}{l} \quad (33)$$

After substitution of (32) and (33) in (31) the solution of (24) written as $C = c_1 + c_2$ satisfies (i) and (ii). After differentiating with respect to x , one may write²

$$-l \left(\frac{\partial C}{\partial x} \right) = {}_2C - {}_1C + 2 \sum b_n e^{-\alpha_n t} \cos \frac{n\pi x}{l} + 2 \sum \cos \frac{n\pi x}{l} \int_0^t e^{-\alpha_n(t-\tau)} ({}_2C' - (-1)^n {}_1C') d\tau \quad (34)$$

where

$$b_n = {}_2C_0 - (-1)^n {}_1C_0 - n \frac{\pi a_n}{2} \quad (35)$$

²C. Barnes, Physics 5, 4 (1934).

So Equations (iv) now give, respectively

$$-\frac{l \cdot g}{D} \left(\frac{\partial {}_2C}{\partial t} \right) = {}_2C - {}_1C + 2 \sum b_n e^{-\alpha_n t} + 2 \sum \int e^{-\alpha_n(t-\tau)} \quad (36)$$

$$({}_2C' - (-1)^n {}_1C') d\tau$$

and

$$\frac{l \cdot h}{D} \left(\frac{\partial {}_1C}{\partial t} \right) = {}_2C - {}_1C + 2 \sum (-1)^n b_n e^{-\alpha_n t} + 2 \sum \int e^{-\alpha_n(t-\tau)} \quad (37)$$

$$(-1)^n e \quad ({}_2C' - (-1)^n {}_1C') d\tau$$

Solution of the problem in the form

$${}_2C(t) = C_\infty - \sum \frac{A_i}{\beta_i} e^{-\beta_i t} \quad (38)$$

$${}_1C(t) = C - \sum \frac{B_i}{\beta_i} e^{-\beta_i t} \quad (39)$$

(where C_∞ denotes the final uniform concentration of the gaseous solution given by $C_\infty(g + l + h) = ({}_2C_0)g + \int_0^l C_0(x)dx + ({}_1C_0)h$ may be had by substituting³

$$\frac{\partial {}_2C}{\partial t} = \sum_i A_i e^{-\beta_i t} \quad (40)$$

³H. W. March and W. Weaver, Phys. Rev. 31, 1072 (1928).

$$\frac{\partial_1 c}{\partial t} = \sum_i B_i e^{-\beta_i t} \quad (41)$$

in (36) and (37) respectively. The equations (36) and (37) will be satisfied identically by substituting (40) and (41) if A_i , B_i , and β_i satisfy the equations

$$A_i \left[\left(\frac{l \cdot g}{D} \right) - \frac{1}{\beta_i} + 2 \sum_n \frac{1}{(\alpha_n - \beta_i)} \right] = B_i \left[-\frac{1}{\beta_i} + 2 \sum_n \frac{(-1)^n}{(\alpha_n - \beta_i)} \right] \quad (42)$$

$$B_i \left[\left(\frac{l \cdot h}{D} \right) - \frac{1}{\beta_i} + 2 \sum_n \frac{1}{(\alpha_n - \beta_i)} \right] = A_i \left[-\frac{1}{\beta_i} + 2 \sum_n \frac{(-1)^n}{(\alpha_n - \beta_i)} \right] \quad (43)$$

$$b_n = \sum_i \frac{(A_i - (-1)^n) B_i}{(\alpha_n - \beta_i)} \quad (44)$$

If equations (42), (43), (44) lead to unique values for the numbers A_i , B_i , β_i , equations (40) and (41) will yield the problem solution. Using the formula

$$\tan Z = \frac{2Z}{\left(\frac{\pi}{2}\right)^2 - Z^2} + \frac{2Z}{\left(\frac{3\pi}{2}\right)^2 - Z^2} + \frac{2Z}{\left(\frac{5\pi}{2}\right)^2 - Z^2} + \dots \quad (45)$$

and letting

$$z_i^2 = \frac{\beta_i \cdot l^2}{D} \quad (46)$$

the equations (42), (43) and (44) become

$$A_i \left(\frac{1}{\gamma_1} - \frac{\cot z_i}{z_i} \right) = -B_i \left(\frac{1}{z_i \sin z_i} \right) \quad (42')$$

$$B_i \left(\frac{1}{\gamma_2} - \frac{\cot z_i}{z_i} \right) = -A_i \left(\frac{1}{z_i \sin z_i} \right) \quad (43')$$

$$b_n' = \frac{D}{l^2} \left[z_0^2 - (-1)^n z_0 - \frac{n\pi}{l} \int_0^l c_0(y) \sin \frac{n\pi y}{l} dy \right] = \sum_i \left(\frac{A_i - (-1)^n B_i}{n^2 \pi^2 - z_i^2} \right) \quad (44')$$

where

$$\gamma_1 = \frac{l}{g} \quad \text{and} \quad \gamma_2 = \frac{l}{h} \quad (47)$$

Simultaneous elimination of A_i , B_i , from (42') and (43') gives

$$z^2 - (\gamma_1 + \gamma_2) z \cot z - \gamma_1 \gamma_2 = 0 \quad (48)$$

The roots of (48) give the numbers β_i . By finding the points of intersection of the graphs $y = z^2 - \gamma_1 \gamma_2$ and $y = (\gamma_1 + \gamma_2) z \cot z$, one can readily determine the z 's for which real positive values only

are taken. From the infinite set of linear equations (44') A_i may be had in terms of B_i , β_i , and D and (42') and (43') can be made to yield B_i in terms of A_i and β .

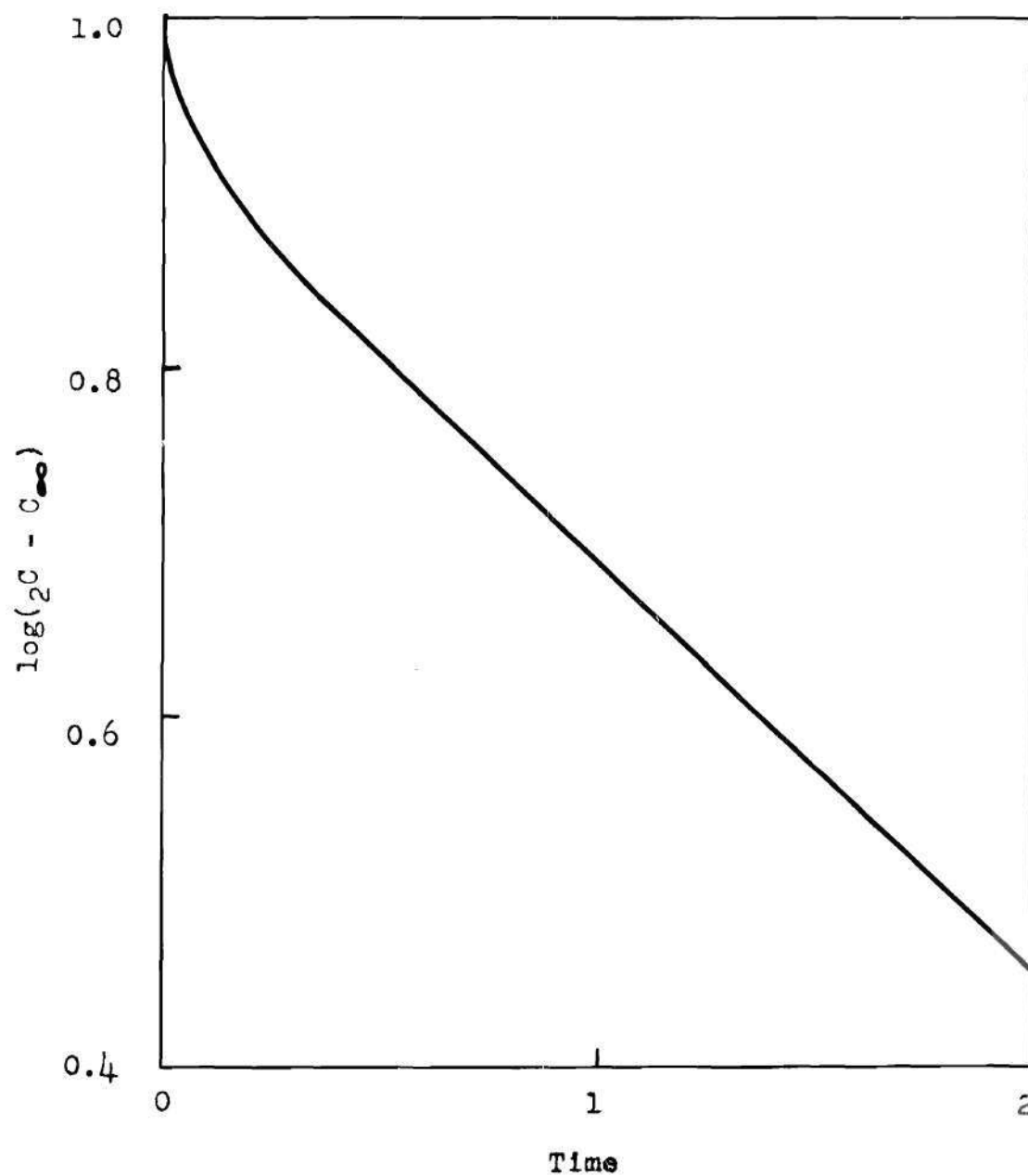
Considering the A 's, B 's, and β 's as known, (38) and (39) then represent the concentrations in the two gas volumes in terms of final uniform concentration C_∞ and \underline{t} . For time $t = 0$ they become

$${}_2C_0 = C_\infty - \sum \frac{A_i}{\beta_i} \quad (49)$$

$${}_1C_0 = C_\infty - \sum \frac{B_i}{\beta_i} \quad (50)$$

either of these permits a numerical evaluation of the A_i , B_i . In the ratios $\sum \frac{A_i}{\beta_i}$, $\sum \frac{B_i}{\beta_i}$ which appear before the exponential terms of (38) and (39), the D cancels, since it is a simple multiplier in A_i , B_i , and β_i . In all diffusion problems at large values of \underline{t} , all the exponential terms except the first become small so that if a plot of $\log({}_2C - C_\infty)$ against \underline{t} is made, a curve is obtained such as shown in Figure 1, in which the curve approaches asymptotically a straight line. The slope of this line is $-\beta_i$. In any case, at small values of \underline{t} it will not be necessary to take many terms of the exponential series, in solving for A_i and B_i .⁴

⁴R. M. Barrer, Diffusion in and Through Solids, (Cambridge University Press 1941), p. 26.



(Abcissae and Ordinate Units Arbitrary)

Figure 1. A Typical Diffusion Rate. $\log (2C - C_{\infty})$ vs Time

By means of (38) and (39) for ${}_2C$, and ${}_1C$, the concentration distribution in the plug is found from (26) and (29) to be

$$C(x,t) = {}_2C \left(1 - \frac{x}{l}\right) + {}_1C \frac{x}{l} - \frac{2}{\pi} \sum \frac{1}{n} \sin \frac{n\pi x}{l} \sum_i \frac{(A_i - (-1)^n B_i) e^{-\beta_i t}}{(\alpha_n - \beta_i)} \quad (51)$$

which satisfies (24) and conditions (i), (ii), (iii), and (iv). This considers that due account is taken of conditions involved in (42'), (43'), (44') and (38), (39). The γ terms associated with these equations are expressions of the ratios of the "effective" porous plug volume to that of respective end containers. The implied assumptions that D is independent of concentration and concentration gradient permit this development.

CHAPTER IV

EXPERIMENTAL EQUIPMENT AND PROCEDURE

Equipment.— The equipment and associated instrumentation used in the investigation of diffusion through porous media are shown in Figures 2 through 4. Figure 2 is an overall view of the constant temperature air bath, the control panel, and the various instruments and meters used. Figure 3 is a close-up photograph of the constant temperature air bath with top removed showing the numerous pieces of equipment contained in it. Figure 4 is a close-up view of the control panel showing the controls, switches, and meters which constitute this unit.

Figure 5 is a schematic diagram of the diffusion equipment which, as is evident, is a symmetrical arrangement. Pure gases are introduced to the system from cylinders at points A and B. Point A is associated with the left half of the system and point B the right half. Gases on entering the system passed through an electrically heated preheater which consisted of two twenty-foot coils of 1/4" copper tubing mounted with a double-pass arrangement in an insulated tank of water. The temperature in the preheater was controlled by a Fenwal thermo-regulator. The preheater was thus placed in the system just before the constant temperature bath and in which the gases were heated to approximately 2° F above the bath temperature. Fifteen-foot coils of 1/4" copper tubing

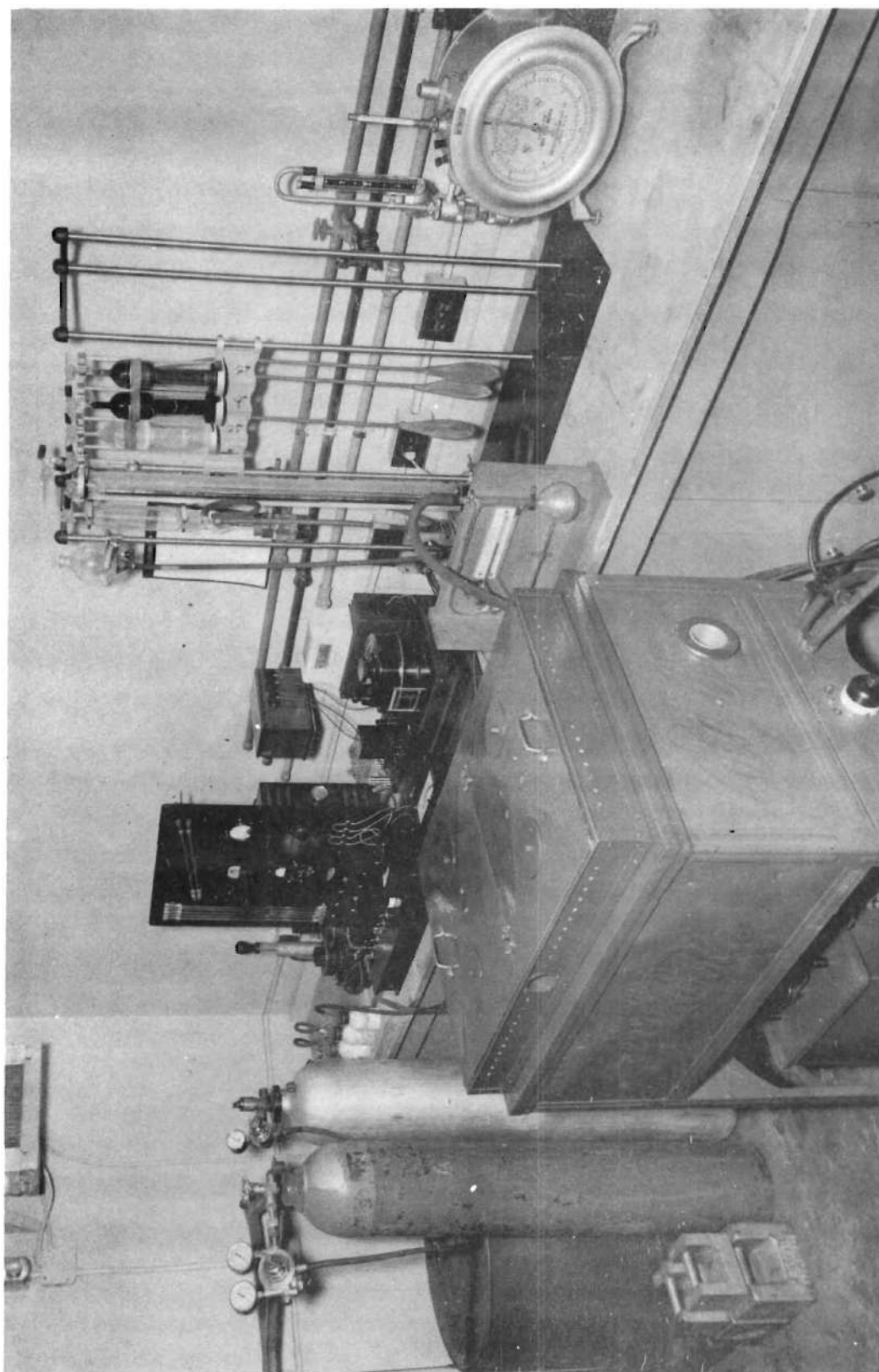


Figure 2. Overall View of Equipment

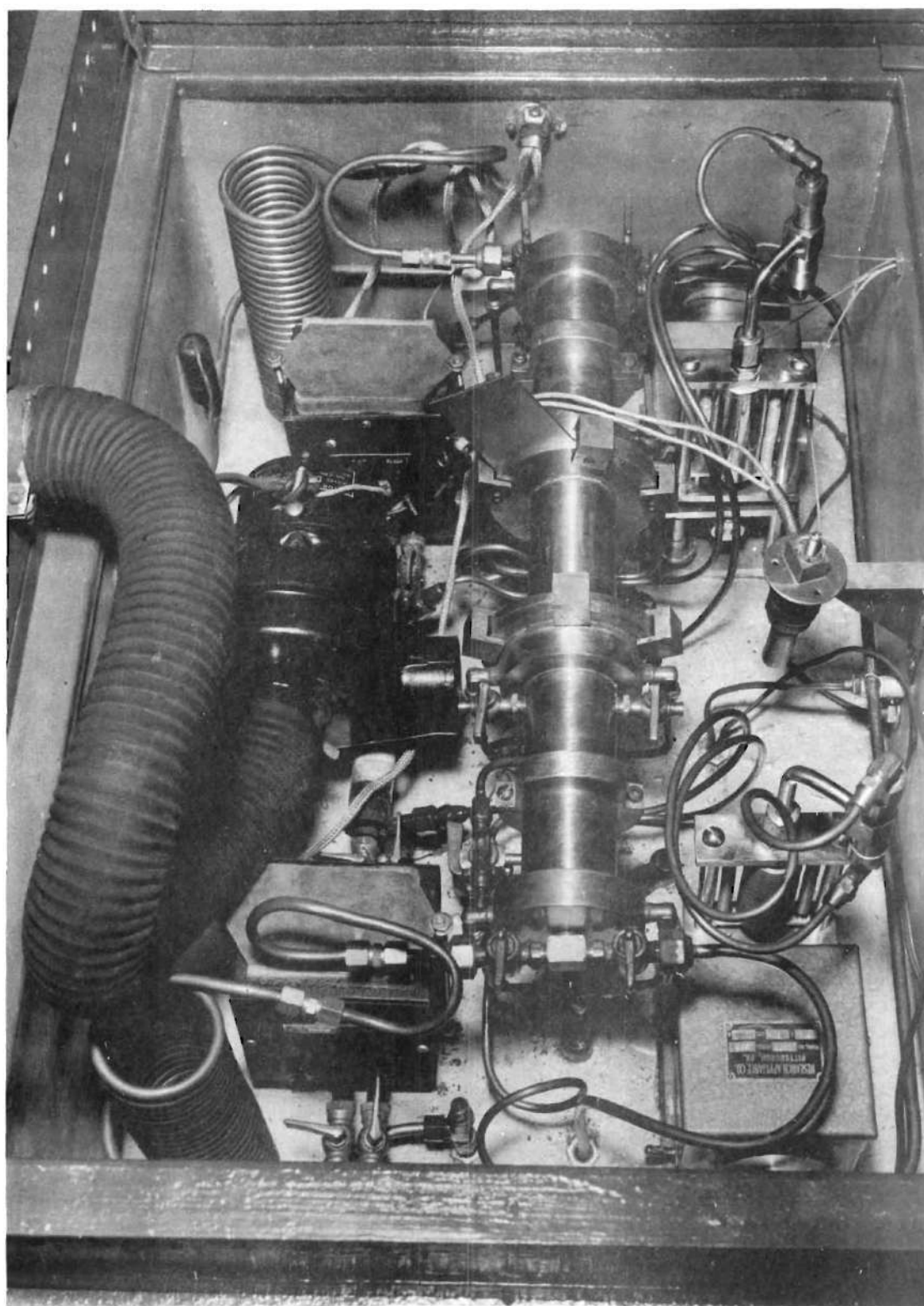


Figure 3. View of Equipment Arrangement in Constant Temperature Bath

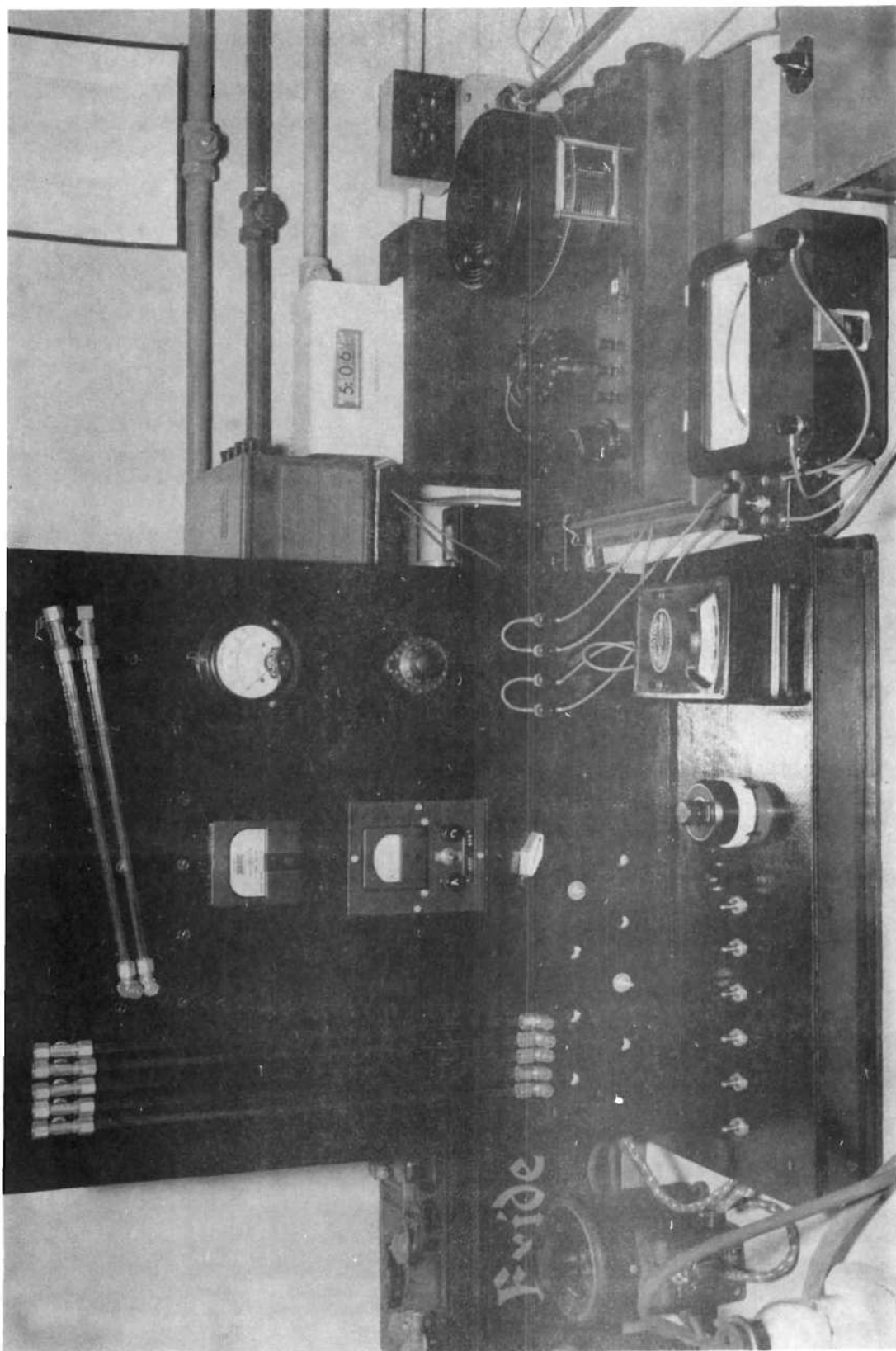


Figure 4. Control Panel and Associated Equipment

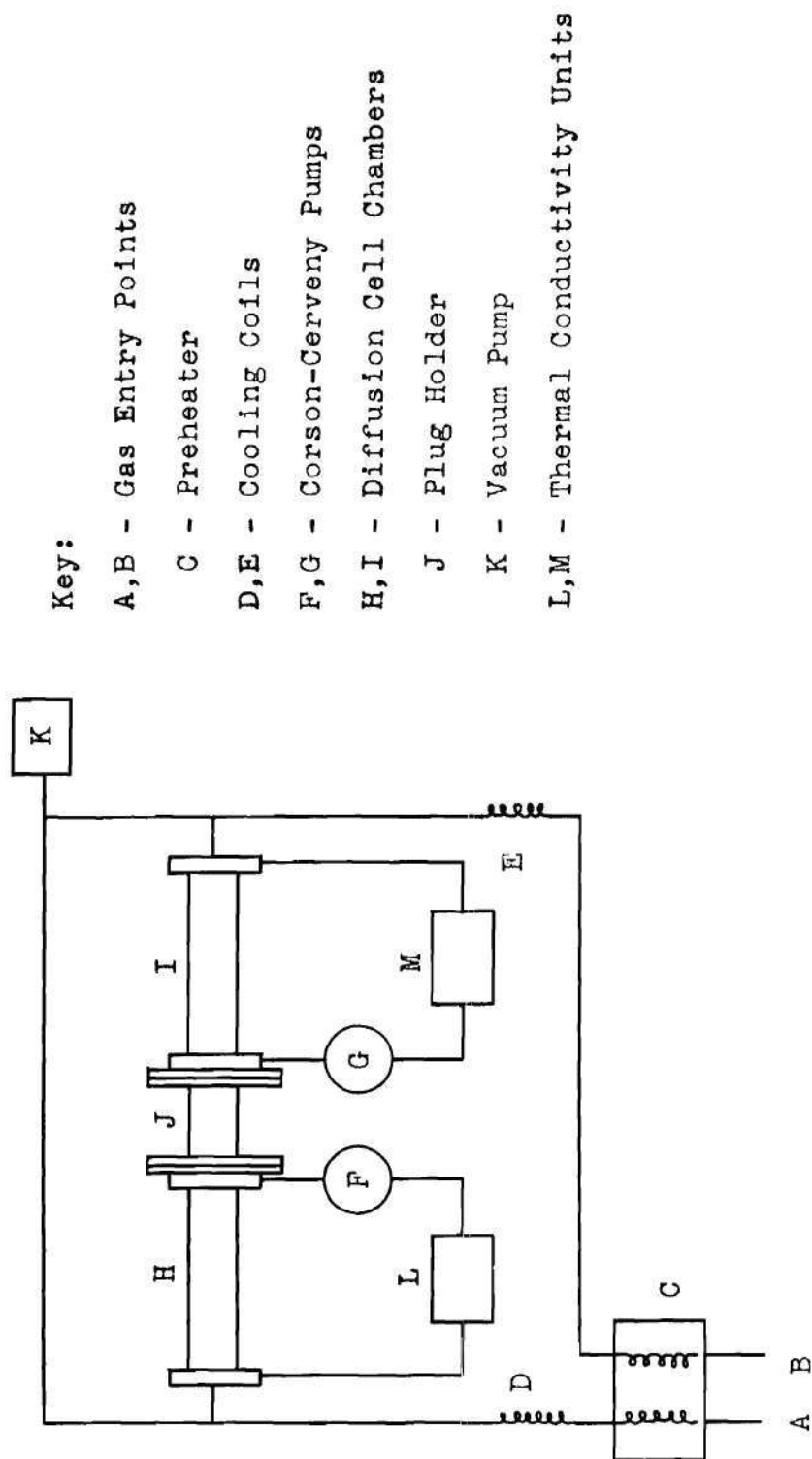
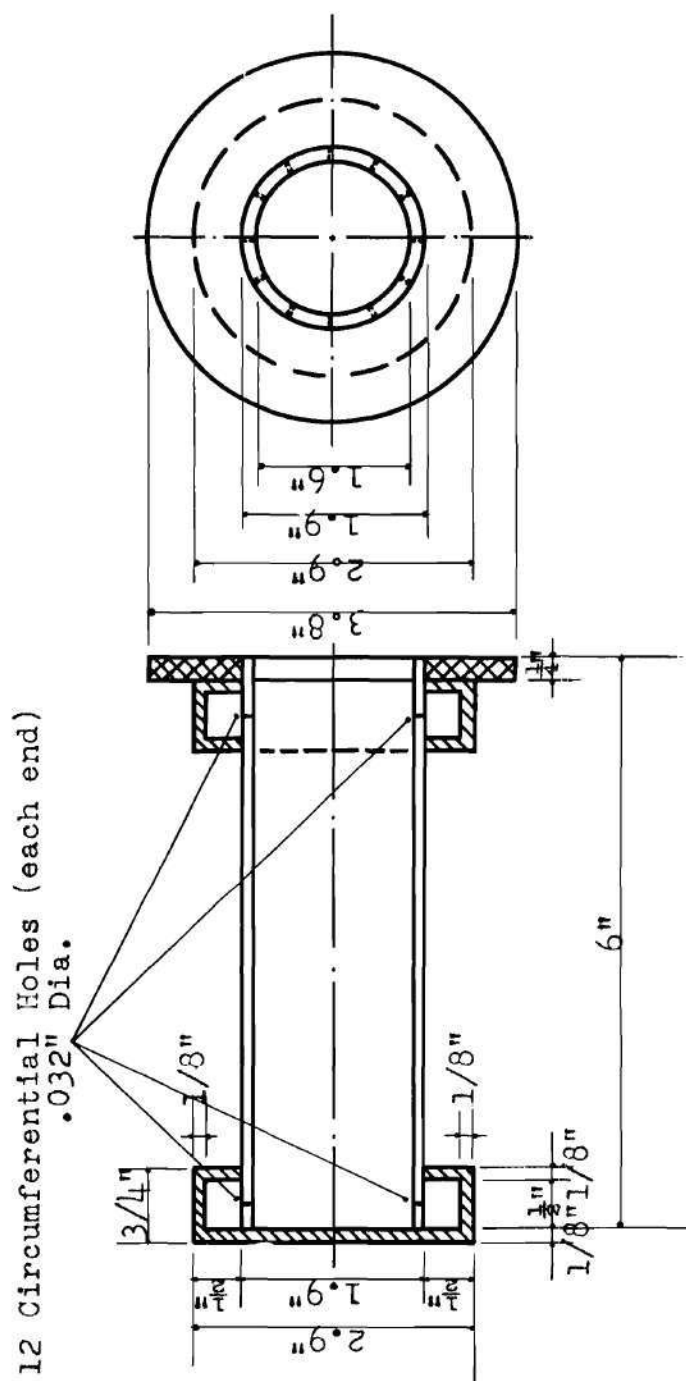


Figure 5. Schematic Diagram of Diffusion Equipment

were placed in the lines between the preheater and the diffusion cell proper within the bath and served to bring the gas temperature down to that of the bath.

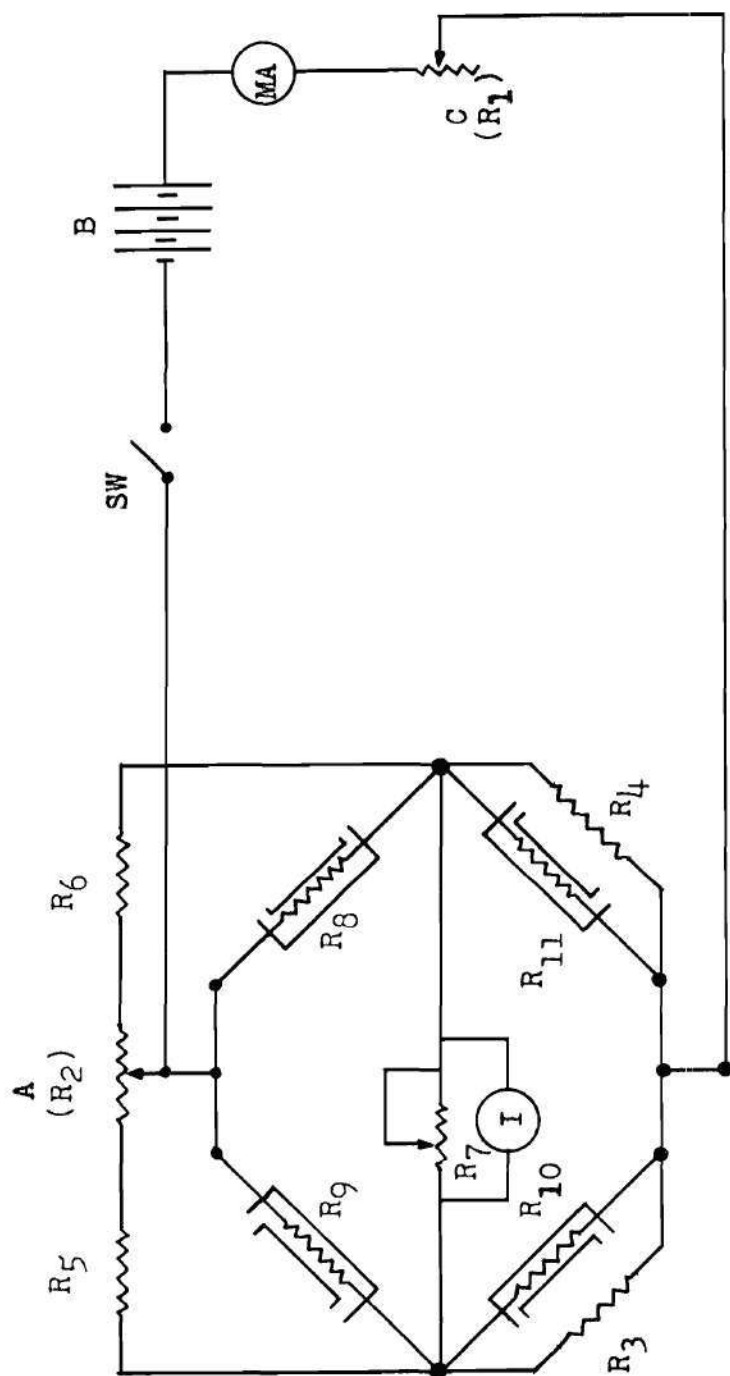
The construction of the diffusion cell is shown in Figure 6. As used in the experimental work, two cell sections were clamped together with the porous plug mounted in a flanged cylindrical holder separating them. This construction provided a definite cell geometry in that the volume on both sides of the porous plug enclosed between the cell half and porous medium were equal and always remained the same irrespective of plug length.

During the course of an experimental run, the gas in each half of the diffusion cell separated by the plug was analyzed by means of a thermal conductivity gas analyzer. This instrument measures changes in the thermal conductivity of a gas and thereby the changes in composition, as a function of the change in resistance of a heated platinum filament. The analyzer sensing system consists of two thermal conductivity cell units (Model 30-S, double pass with M/T filaments) which were purchased from the Gow-Mac Instrument Co. of Newark, New Jersey. These units, L and M, operated with a common current control potentiometer (Gow-Mac Model RCCT), not shown on sketch, permitted alternate readings of the gas compositions in each cell half. A small sampling stream of gas was circulated continuously through each of the conductivity cells by means of Corson-Cervený (No. 1000, Type C, 3/4" x 3") micro-bellows pumps, F, and G. In Figure 7, the electrical circuit is shown which was used to measure the relative change in the thermal conductivity of the gas



Scale: 1/2.

Figure 6. Sketch of Diffusion Cell Construction (Half)



Key:

R_1 - 20 Ohms, Ohmite Current Control, C

R_2 - 2 Ohms, Ohmite Zero Adjust., A

R_3 , R_4 - 820 Ohms, IRC, (10%)

R_5 , R_6 - 560 Ohms, IRC, (10%)

R_7 - 0-100 Ohms, Helipot, ($\pm 0.1\%$)

R_8 , R_9 , R_{10} , R_{11} , - 30 Ohms, Filaments,

T. C. Units

B - 6 Volt Storage Battery

I - Indicating Instrument (Potentiometer)

MA - Milliammeter

SW - on-off switch

Figure 7. Analyzer Schematic Electrical Circuit

passing through the conductivity cells. The circuit is that of a Wheatstone bridge and operates as an "unbalanced bridge", that is say, the analysis is based on constant current conditions and degree of bridge unbalance. Calibration details are given in the Appendix.

Evacuation of gases from the diffusion cell was achieved by means of vacuum pump (Cenco Hi-Vac), K. This served in both the plug "degassing" and leak testing operations.

The constant temperature bath shown in Figures 2 and 3 was constructed from an ice-type soft drink cooler with inside dimensions of 18" x 27" x 11". Heating of the bath was achieved by means of a 750 watt Calrod tubular heater mounted around the inside walls of the cooler with insulated studs, and a small 50 cfm furnace blower gave the necessary air circulation. A Fenwal thermo-regulator was used in conjunction with a relay which activated the heater circuit, thus providing temperature control of the bath. No provisions were made for cooling the bath; consequently all experimental operations were conducted at temperatures above room conditions. Data presented in this thesis were obtained at 104° F (40° C) for this reason. Temperature control of the bath under normal operations was within $\pm 0.2^\circ$ F. However, under other conditions of operation control of temperature approaching a figure of $\pm 0.1^\circ$ F has been attained.

The circuit components of the thermal conductivity analyzer not contained within the bath were mounted on the control panel shown in

Figure 4. These components were totally enclosed, except for the ends of control shafts and indicating dials, within a thermostatically controlled jacket. A 25-watt incandescent lamp activated by a Fenwal thermoregulator and a small circulating fan provided satisfactory temperature control of this space (on the back of the control panel). No observations ever proved the necessity of this provision but it was installed at the outset of the problem as a precaution.

Observation of temperatures at various points in the equipment were made during the experimental work by means of a type K-2 (Leeds and Northrup) potentiometer and a lamp and scale galvanometer used in conjunction with standardized iron-constantan thermocouples.

Associated with the diffusion equipment were a 10 cu ft telescoping gas holder and a Precision (Fisher Scientific Co.) Orsat type gas analyzer employed in the calibration of the thermal conductivity analyzer. These items are shown in Figure 2.

Material.— The porous plugs used in the diffusion runs were compressed (dry) from powdered potassium perchlorate. This media was chosen because of the fact that it possesses a wide compressibility range and porosity could be varied with negligible effect on particle size and shape. Thus, a predetermined porosity figure for any length of plug could be readily produced. As mentioned previously, the plug holders were flanged cylinders and were from 1-1/2" ID stainless steel pipe. Figure 8 is a photograph showing the various holders and accessories required. The powdered perchlorate was placed in a filling tube (while clamped to a

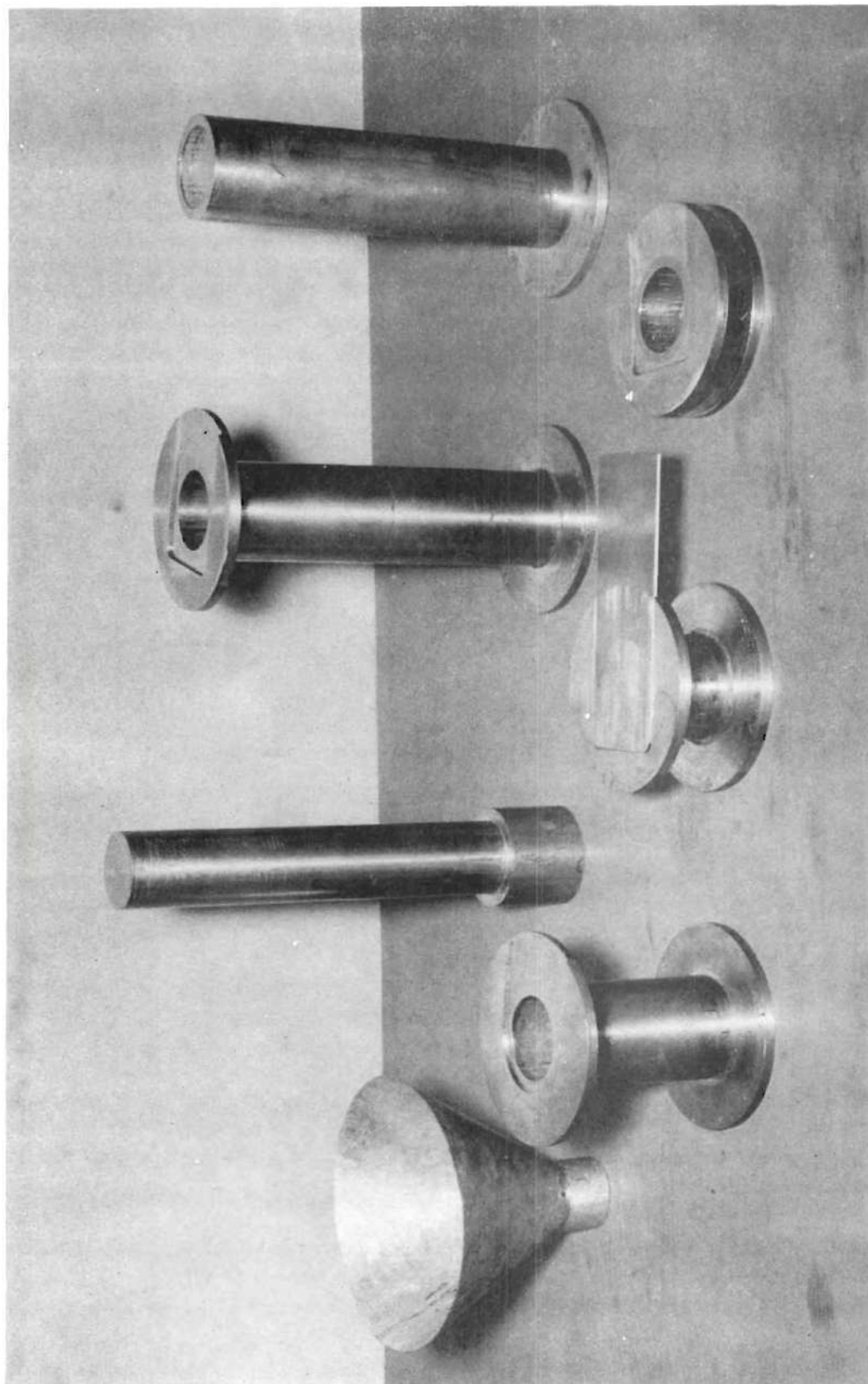


Figure 8. Plug Holders and Filling Equipment

holder) and pressed with a fitted plunger into the holder by means of a Riehle testing machine. Pressures required for this operation ranged from approximately 150 lbs for a porosity of 0.40 to 20,000 lbs for a porosity of 0.20. Pressing rate averaged 0.07 in/min.

The gases used were nitrogen and carbon dioxide. Water-pump nitrogen was obtained from the National Cylinder Gas Co. of Atlanta and was of 99.6 + percent purity. The carbon dioxide was obtained from the Liquid Carbonic Corp. of Atlanta and had specifications of 99.7 + percent CO_2 ($\approx 0.3\% \text{N}_2$). The carbon dioxide was used directly from the cylinders, but the nitrogen was passed through a drying train consisting of a series of bottles packed with P_2O_5 -coated 1/4" Raschig rings. This particular type of train proved highly satisfactory and permitted fairly high gas flow rate as well.

Procedure.-- Preliminary to the initiation of each diffusion run a systematic series of leak tests were conducted, which proved to be an absolute necessity for satisfactory operation. Runs were not attempted until leaks were minimized to a point that the diffusion cell could be evacuated to approximately 2 mm Hg.

A minimum of two runs were made with each plug of a given length and porosity. One run was made with the plug initially saturated with one of the gases and a subsequent run made with the plug saturated with the second gas. A thin sliding gate was fitted to one end of each plug holder and provided isolation of one of the cell chambers. This device permitted preliminary saturation of the plug with the gas as contained

in one of the chambers (dependent on the orientation of the gate) and prevented contamination of the gas in the other.

A typical diffusion run was made as follows: The diffusion cell was evacuated and the plug "degassed" for a period of time determined by the length of plug under study. Periods of approximately 5 minutes for a 1 inch plug and 20 minutes for an 8 inch plug were used and proved to be adequate. Following degassing, the vacuum was broken by admitting the gases to the respective cell chambers. This in turn saturated the plug determined by its gate's orientation. Normally, as a precaution, the unit was again degassed and gases admitted to the chambers for a second time for the purpose of further diluting any residual contaminating gases present in the plug. Flow rates of the gases into the chambers of the diffusion unit were not controlled except between rather wide limits, and were estimated by the low pressure gauges on the gas cylinders. This was not a critical step in operation whatsoever and the preheater capacity far exceeded the demand. Accordingly, the presence of "cold" gas in the unit was never observed. After the charging operation and the closing of all associated valving, the excess pressure in the chambers was vented to the atmosphere. A check of the gas compositions in each half of the diffusion cell was then made. Following this step the sliding gate was opened and observations of the gas compositions with time made by alternately taking reading in each half. This was continued until the diffusion had proceeded to approximately 90 per cent of equilibrium as estimated by the difference in the compositions in the two gas chambers. Data readings were normally made

every two minutes for each chamber (readings being staggered between each other) and continued as long as change of composition between two minute readings was significant, after which time wider intervals were taken. Because of the large number of readings required for each run a special "log sheet" was developed, a copy of which appears in the Appendix.

Roughly speaking, 1 inch runs averaged 30 minutes, depending on porosity, and 8 inch runs from 4 to 6 hours. All runs were made at atmospheric pressure.

CHAPTER V

DATA AND RESULTS

Application of the General Solution.— For the case involved in this study the volume ratios γ_1 and γ_2 are equal to γ and the subscript will be dropped.

Let the positive roots of equation (48) with $\gamma_1 = \gamma_2 = \gamma$ be z_i where $i = 0, 1, \dots$, arranged in order of magnitude; standard processes for finding the roots of such an equation give^{1, 2}

$$z_0 = (2\gamma)^{1/2} \left(1 - \frac{1}{12}\right) \gamma + \left(\frac{11}{1440}\right) \gamma^2 - \dots, \quad (52)$$

$$z_i = i\pi + \frac{2\gamma}{i\pi} - \frac{4\gamma^2}{i^3\pi^3} + \dots, \quad i = 1, 2, \dots. \quad (53)$$

We are disregarding here powers of γ greater than the second since the quantity involved is obviously very small for our purposes. When $\gamma_1 = \gamma_2$, (42') and (43') show that

$$A_i = (-1)^{i+1} B_i \quad (54)$$

¹Barnes, op. cit., p. 7.

²Barrer, op. cit., p. 26.

thus the linear equations for A_i become

$$b_n' = \sum_i A_i (1 + (-1)^{n+i}) / (n^2 \pi^2 - z_i^2)^2 \quad (55)$$

The A_i values depend on the initial concentration in the plug, $C_0(x)$. Let us consider that the initial treatment of the plug is such that it is saturated with the gas of container 1 and contains no amount of that constituent of container 2. Then ${}_1C_0 = 0 = C_0(x)$. For this case

$$b_n' = \frac{D_2 C_0}{l^2} \quad (56)$$

and equations (55) become³

$$d_n = \sum_i^{\infty} \alpha_{ni} A_i$$

with

$$d_n = \frac{D_2 C_0}{l^2} - \left(\frac{(1 + (-1)^n)}{(n^2 \pi^2 - z_0^2)} \right) A_0, \quad (57)$$

and

$$\alpha_{ni} = \left(\frac{(1 + (-1)^{n+i})}{(n^2 \pi^2 - z_i^2)} \right) \quad (58)$$

³C. Barnes, loc. cit.

The solution is, following Barnes⁴

$$A_i = \left(\frac{4\gamma}{i^2 \pi^2} \right) A_0 - 2\gamma \left(\frac{D_2 C_0}{l^2} \right) \left(\frac{1 - 4\gamma}{i^2 \pi^2} \right) \text{ for } i \text{ even,} \quad (59)$$

$$A_i = -2\gamma \left(\frac{D_2 C_0}{l^2} \right) \left(\frac{1 - 2\gamma}{i^2 \pi^2} \right) \text{ for } i \text{ odd.} \quad (60)$$

With roots (53) these values of the A_i give

$$\sum_1^{\infty} \frac{A_i}{z_i^2} = \left(\frac{\gamma}{360} \right) A_0 - \gamma \left(\frac{D_2 C_0}{l^2} \right) \left(\frac{1}{3} - \frac{49\gamma}{360} \right), \quad (61)$$

and from equations (49), (50), (53) and

$$C_{\infty} - 2C_0 = - \left(\frac{2C_0}{2} \right) \left(1 + \frac{\gamma}{2} - \frac{\gamma^2}{4} \right), \quad (62)$$

we get

$$\left(\frac{A_0}{2\gamma} \right) \left(1 + \frac{\gamma}{6} + \frac{\gamma^2}{90} \right) + \left(\frac{D_2 C_0}{2l^2} \right) \left(1 - \frac{\gamma}{6} + \frac{\gamma^2}{45} \right) = 0 \quad (63)$$

It follows

$$\frac{A_0}{\beta_i} = - \left(\frac{2C_0}{2} \right) \left(1 - \frac{\gamma}{6} + \frac{\gamma^2}{60} \right) \quad (64)$$

$$\frac{A_i}{\beta_i} = - \left(\frac{2C_0}{2} \right) \left(\frac{4\gamma}{i^2 \pi^2} \right) \left(\frac{1 - 6\gamma}{i^2 \pi^2} \right) \text{ for } i \text{ even or odd.} \quad (65)$$

⁴ibid.

from which can be obtained

$$\begin{aligned}
 {}_2C = {}_2C_0 \left[1 - \frac{\gamma}{2} + \frac{\gamma^2}{4} + \left(1 - \frac{\gamma}{6} + \frac{\gamma^2}{60} \right) e^{-\frac{2\gamma Dt}{l^2} \left(1 - \frac{\gamma}{6} + \frac{\gamma^2}{45} \right)} \right. \\
 \left. + \sum_{i=1}^{\infty} \frac{4\gamma}{i^2 \pi^2} \left(1 - \frac{6\gamma}{i^2 \pi^2} \right) e^{-\frac{Dt(i^2 \pi^2 + 4\gamma)}{l^2}} \right], \quad (66)
 \end{aligned}$$

$$\begin{aligned}
 {}_1C = {}_2C_0 \left[1 - \frac{\gamma}{2} + \frac{\gamma^2}{4} - \left(1 - \frac{\gamma}{6} + \frac{\gamma^2}{60} \right) e^{-\frac{2\gamma Dt}{l^2} \left(1 - \frac{\gamma}{6} + \frac{\gamma^2}{45} \right)} \right. \\
 \left. - \sum_{i=1}^{\infty} (-1)^i \frac{4\gamma}{i^2 \pi^2} \left(1 - \frac{6\gamma}{i^2 \pi^2} \right) e^{-\frac{Dt(i^2 \pi^2 + 4\gamma)}{l^2}} \right]. \quad (67)
 \end{aligned}$$

Experimental Results and Calculations.-- Experimental runs were conducted with porous plugs of lengths 1, 2, 4, and 8 inches with predetermined porosities ranging from 0.2 to 0.4. All data runs were made at 104° F and at the barometric pressure prevailing at the time of the individual runs. The variation of barometric pressure over the entire series of diffusion runs was from about 730 mm to 745 mm Hg. The gases used were carbon dioxide and nitrogen. Prior to the initiation of a diffusion run, the plug was treated to saturate it with one or the other of the gases in order to provide a known concentration distribution at the start. After a run in which the plug was initially treated with one of the gases, another run was made with an initial concentration of the second gas in the plug. This is the case for which the mathematical derivation is made above.

The data for the diffusion runs are shown in Figures 9 through 18 as plots of concentration versus time with ϵ (porosity) as parameter.

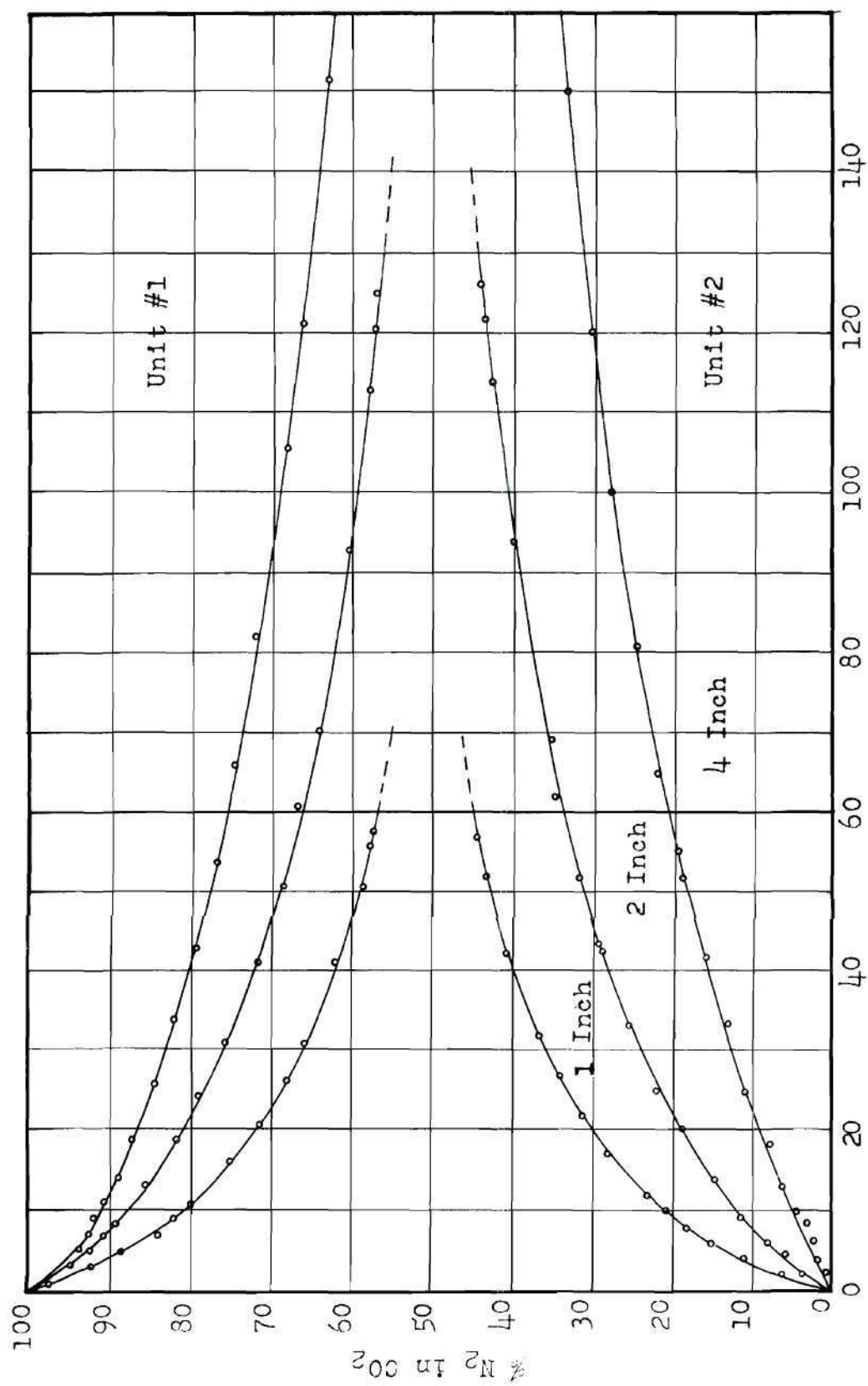


Figure 9. Diffusion Data. CO₂-Sat'd. Plugs: $\sigma = 0.20$

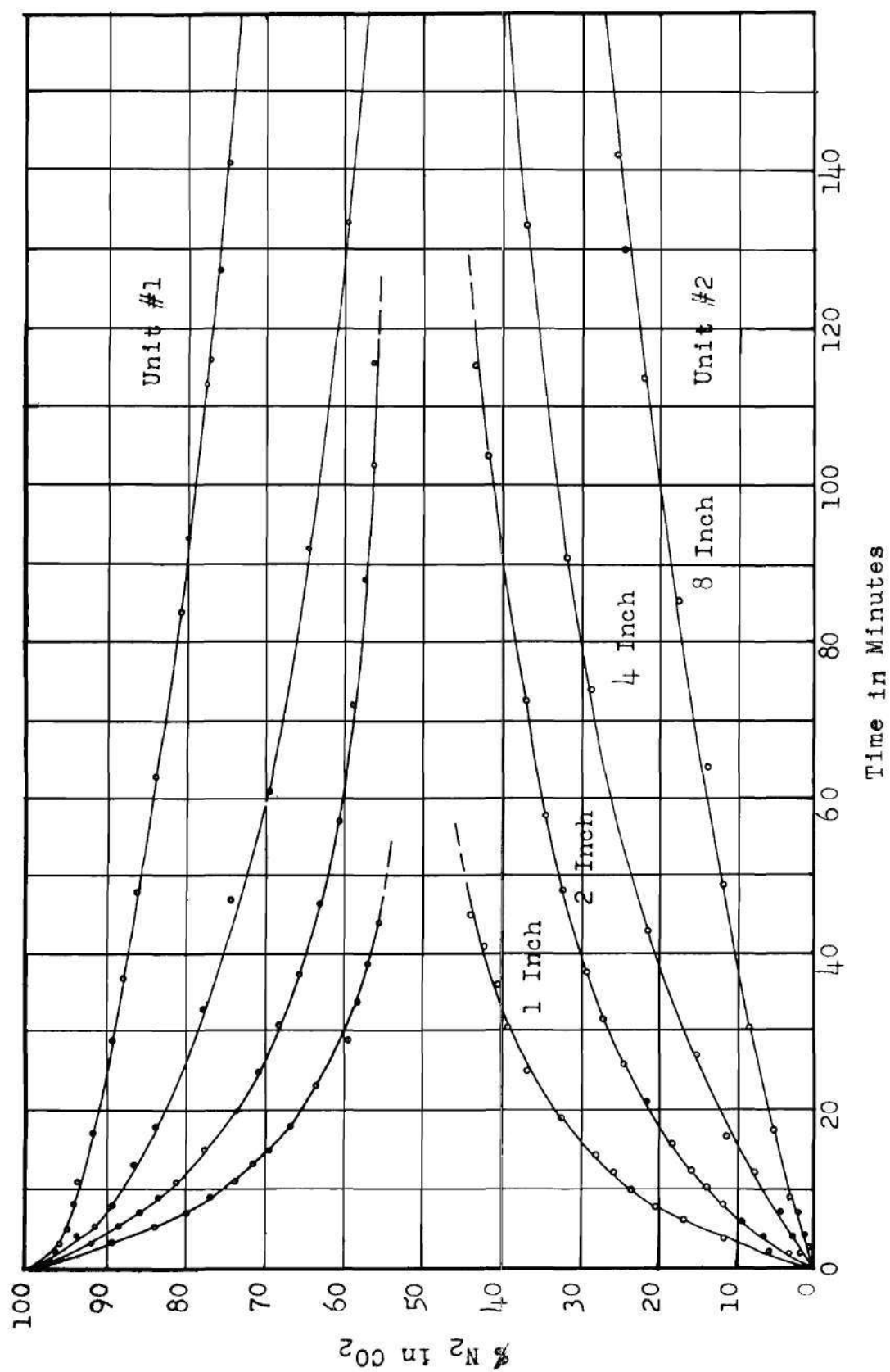


Figure 10. Diffusion Data. CC_2 -Sat'd. Plugs: $\epsilon = 0.25$

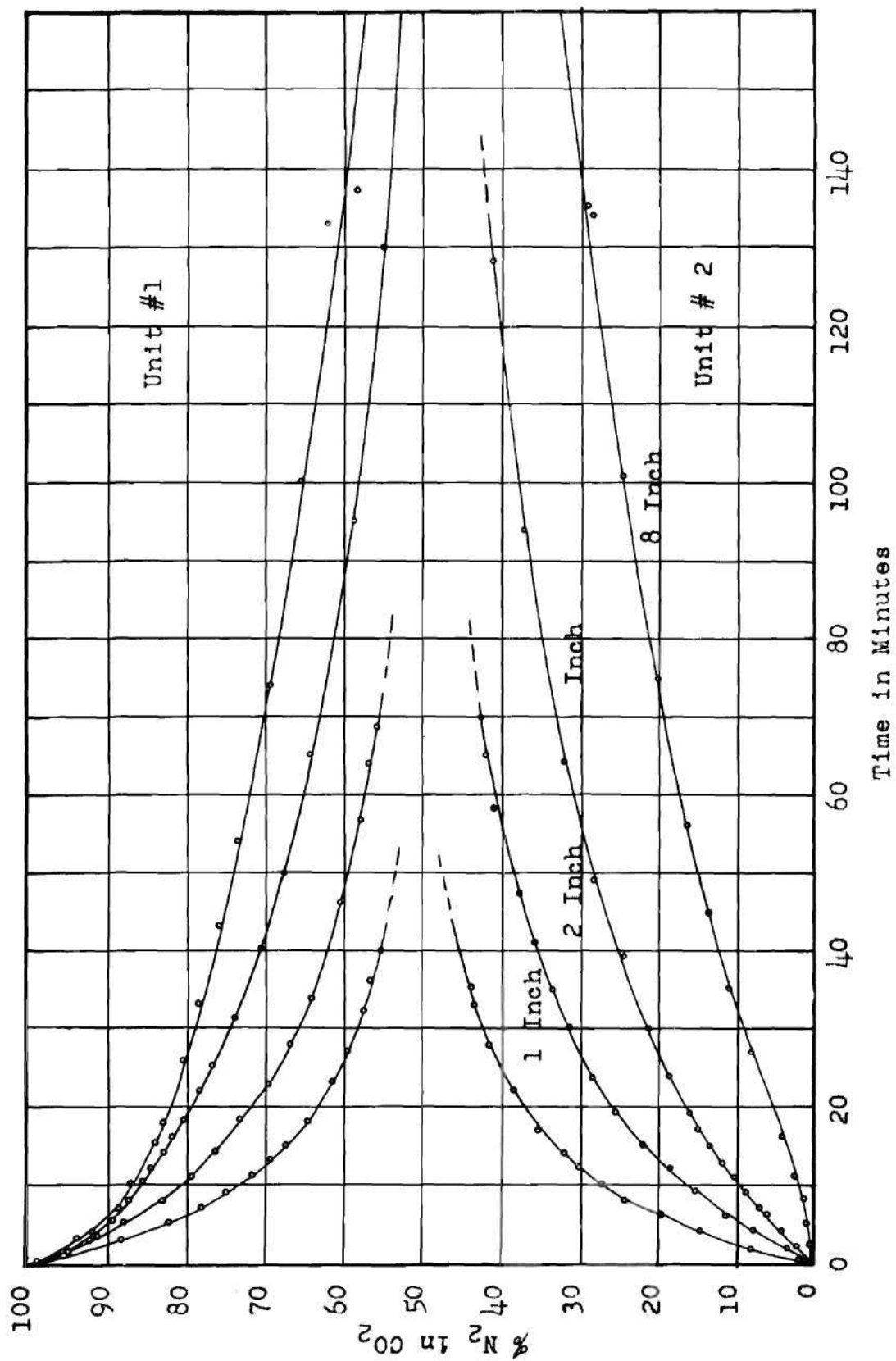


Figure 11. Diffusion Data. CO_2 -Sat'd. Plugs: $\epsilon = 0.30$

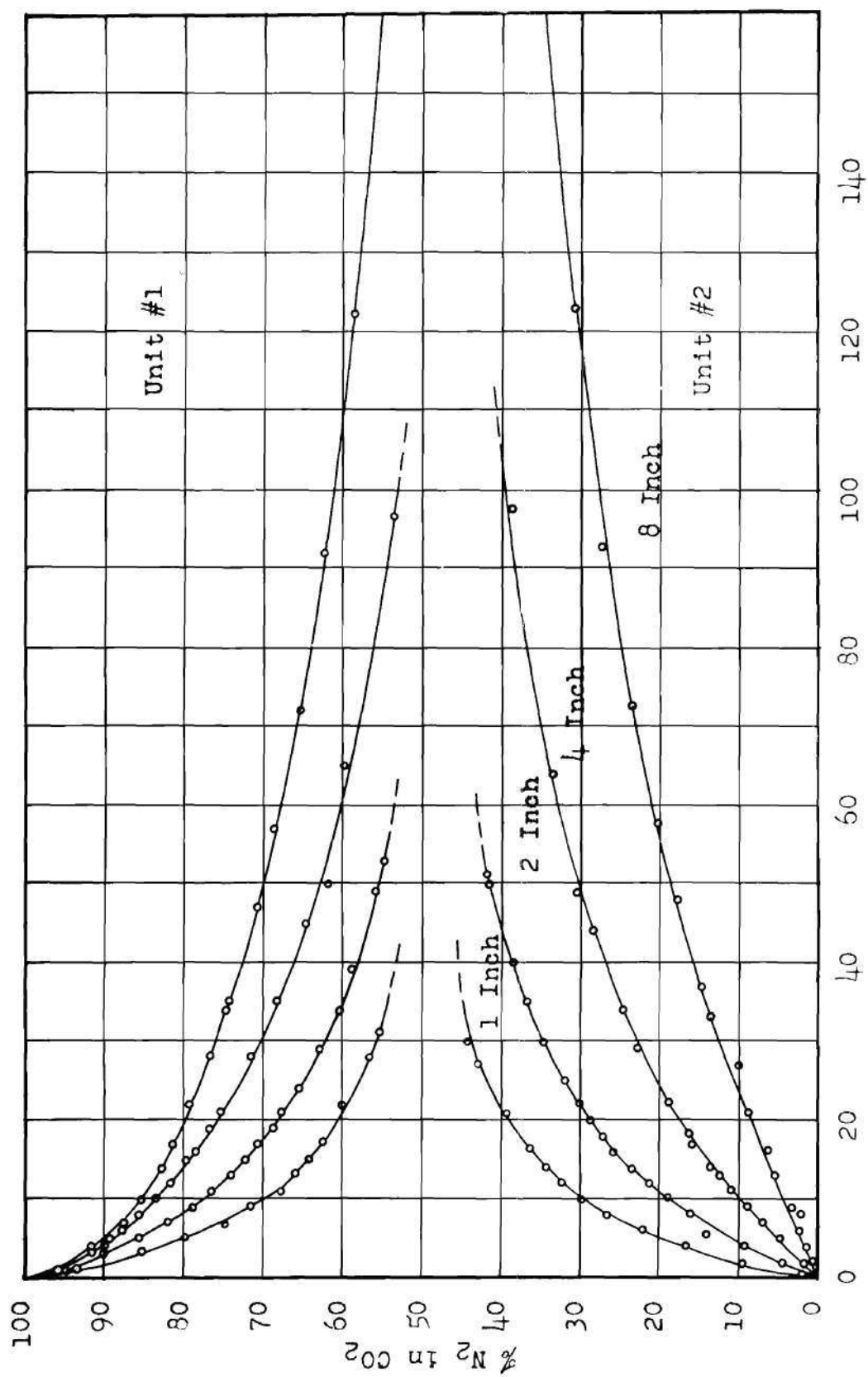


Figure 12. Diffusion Data. CO₂-Sat'd. Plugs: $\epsilon = 0.35$

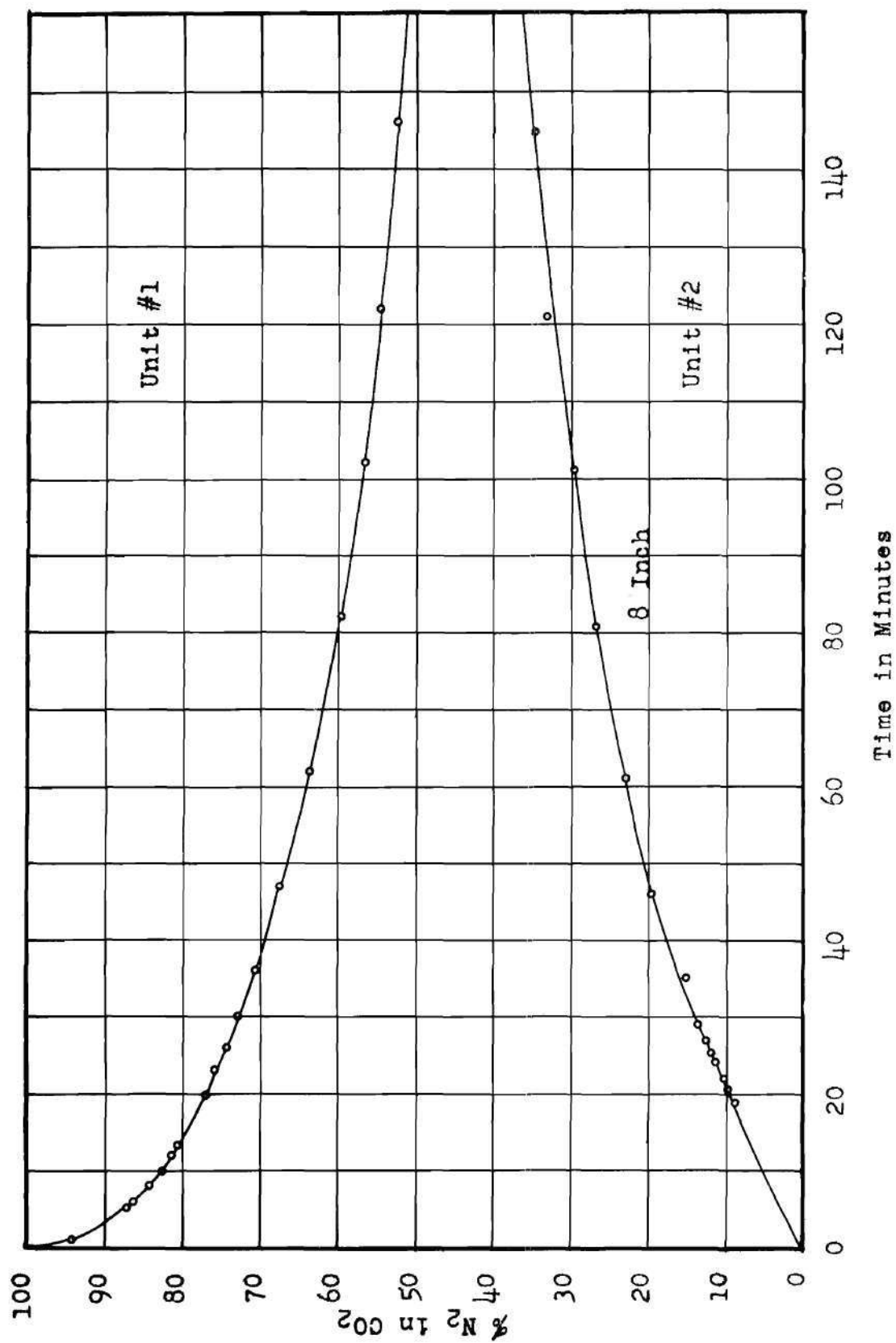


Figure 13. Diffusion Data. CO_2 -Sat'd. Plug: $\epsilon = 0.40$

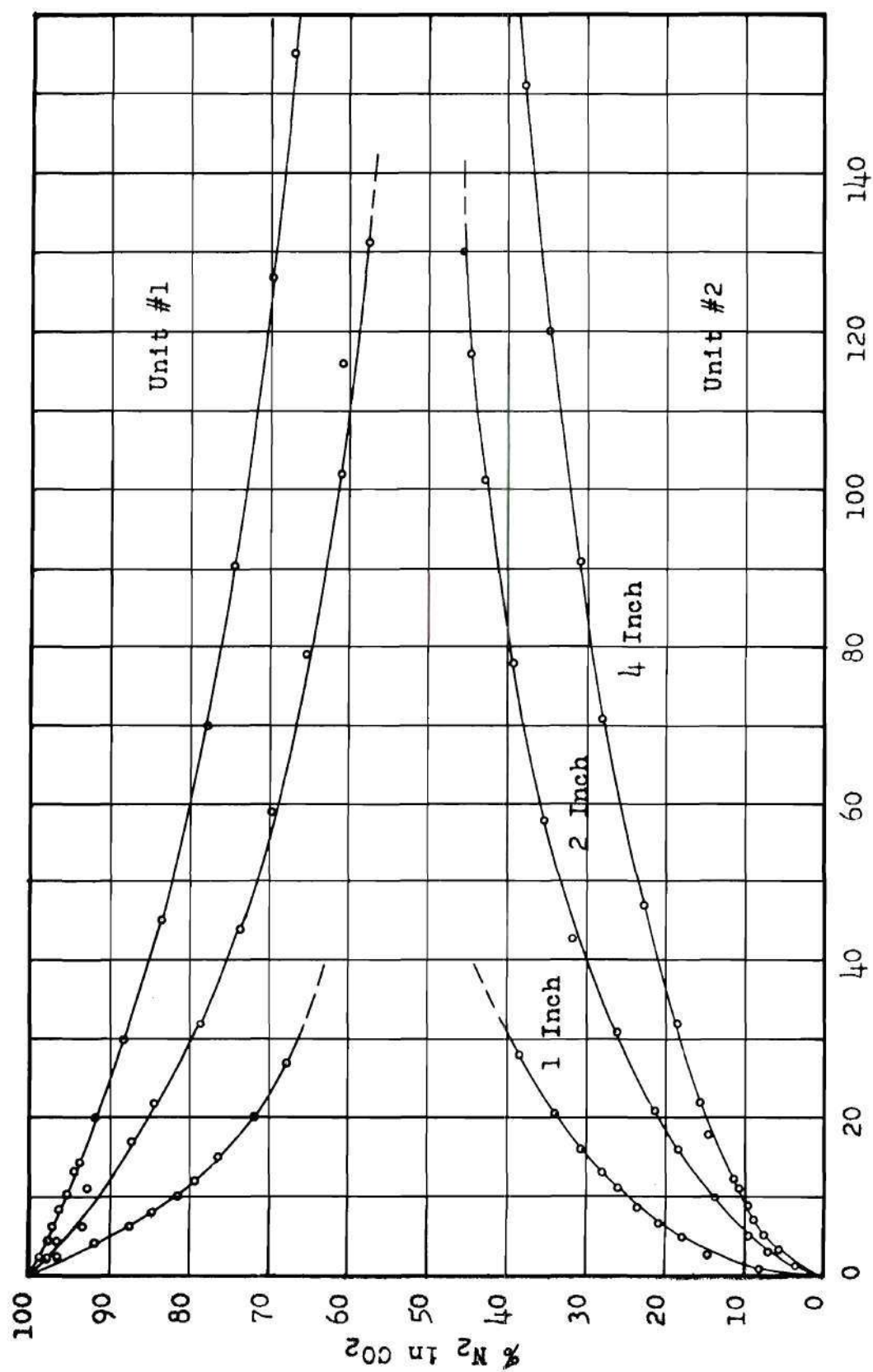


Figure 14. Diffusion Data. N_2 -Sat'd. Plugs: $\epsilon = 0.20$

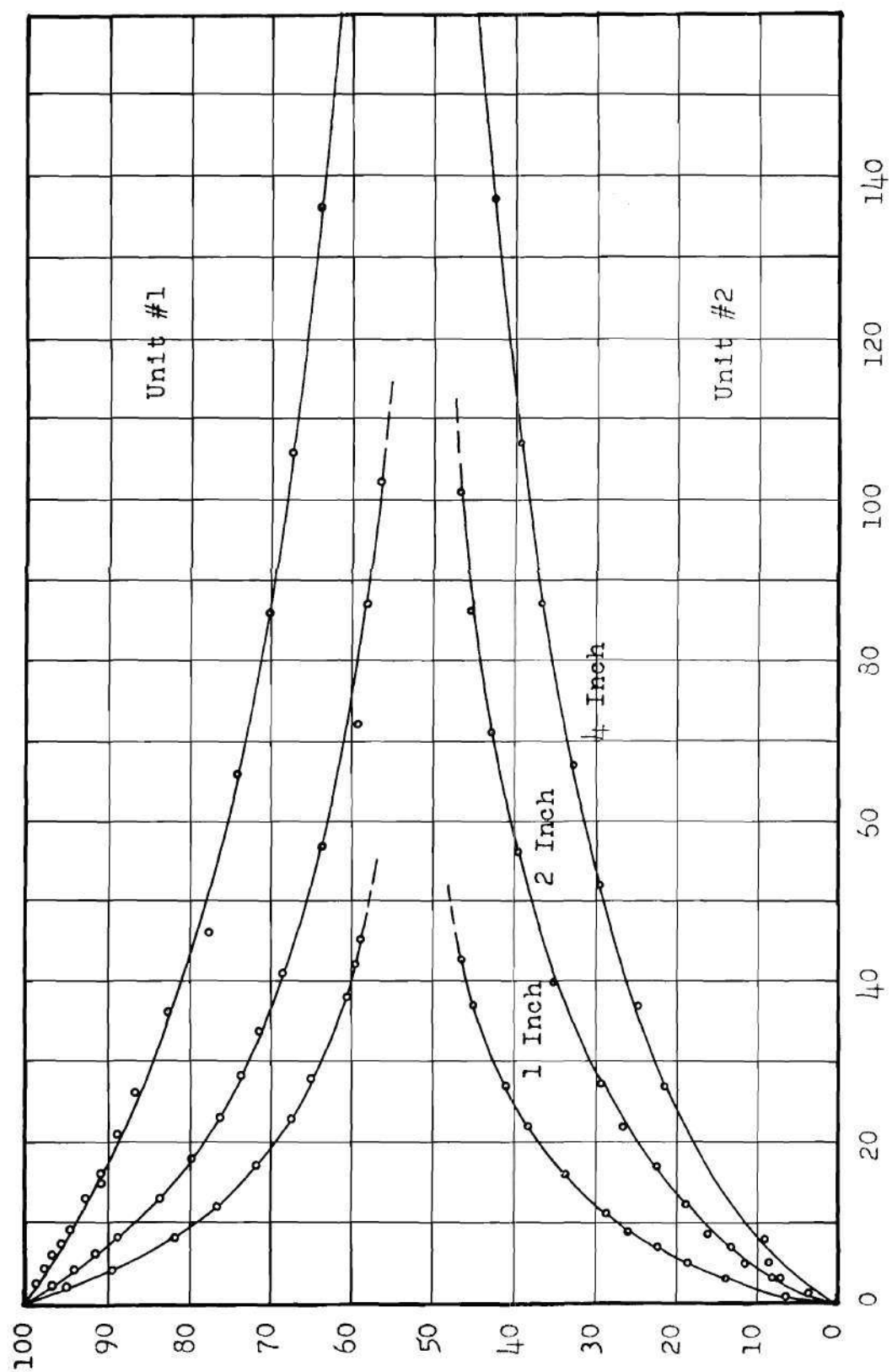


Figure 15. Diffusion Data. N_2 -Sat'd. Plugs: $\epsilon = 0.25$

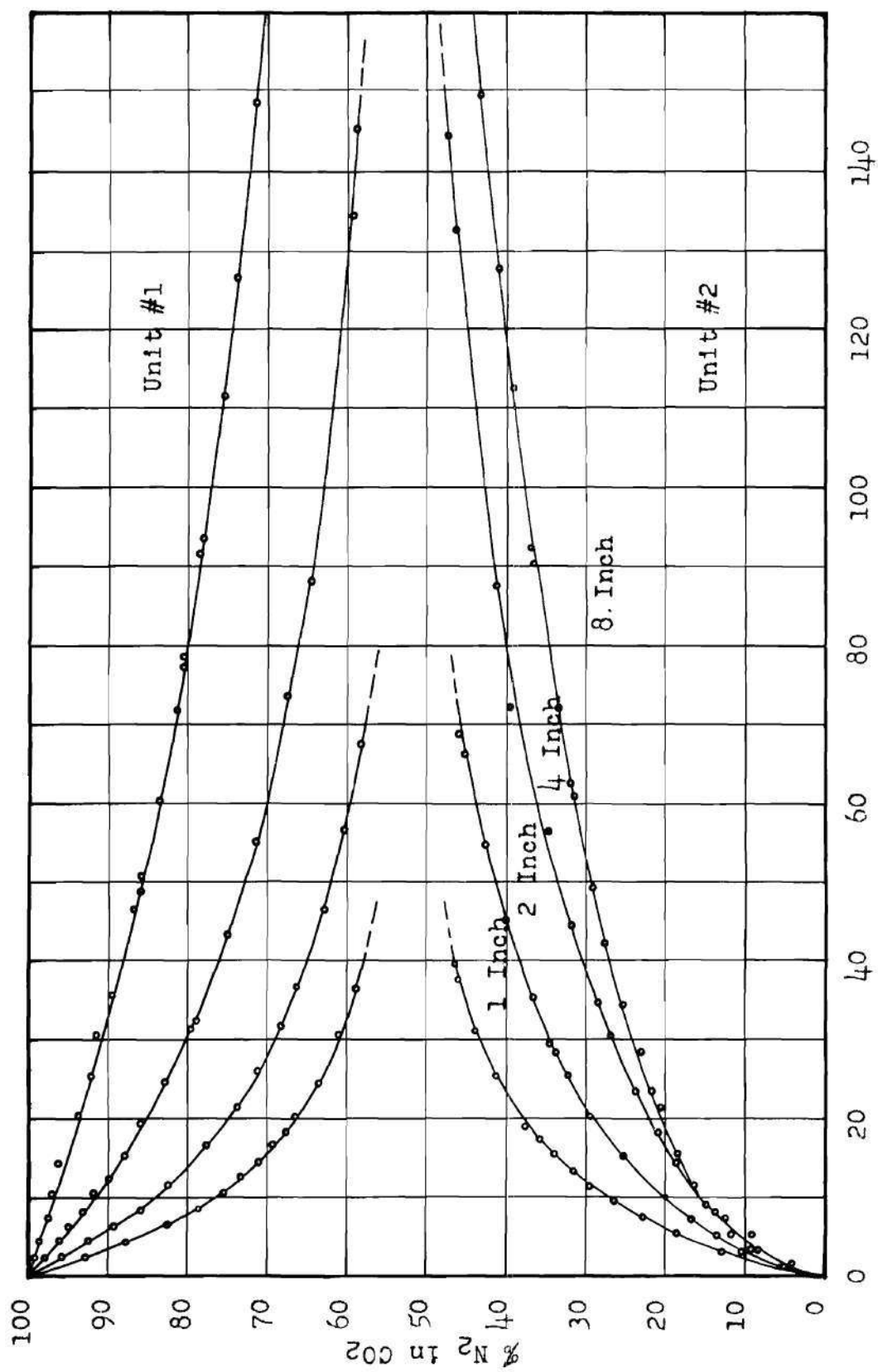


Figure 16. Diffusion Data. N_2 -Sat'd. Plugs: $\epsilon = 0.30$

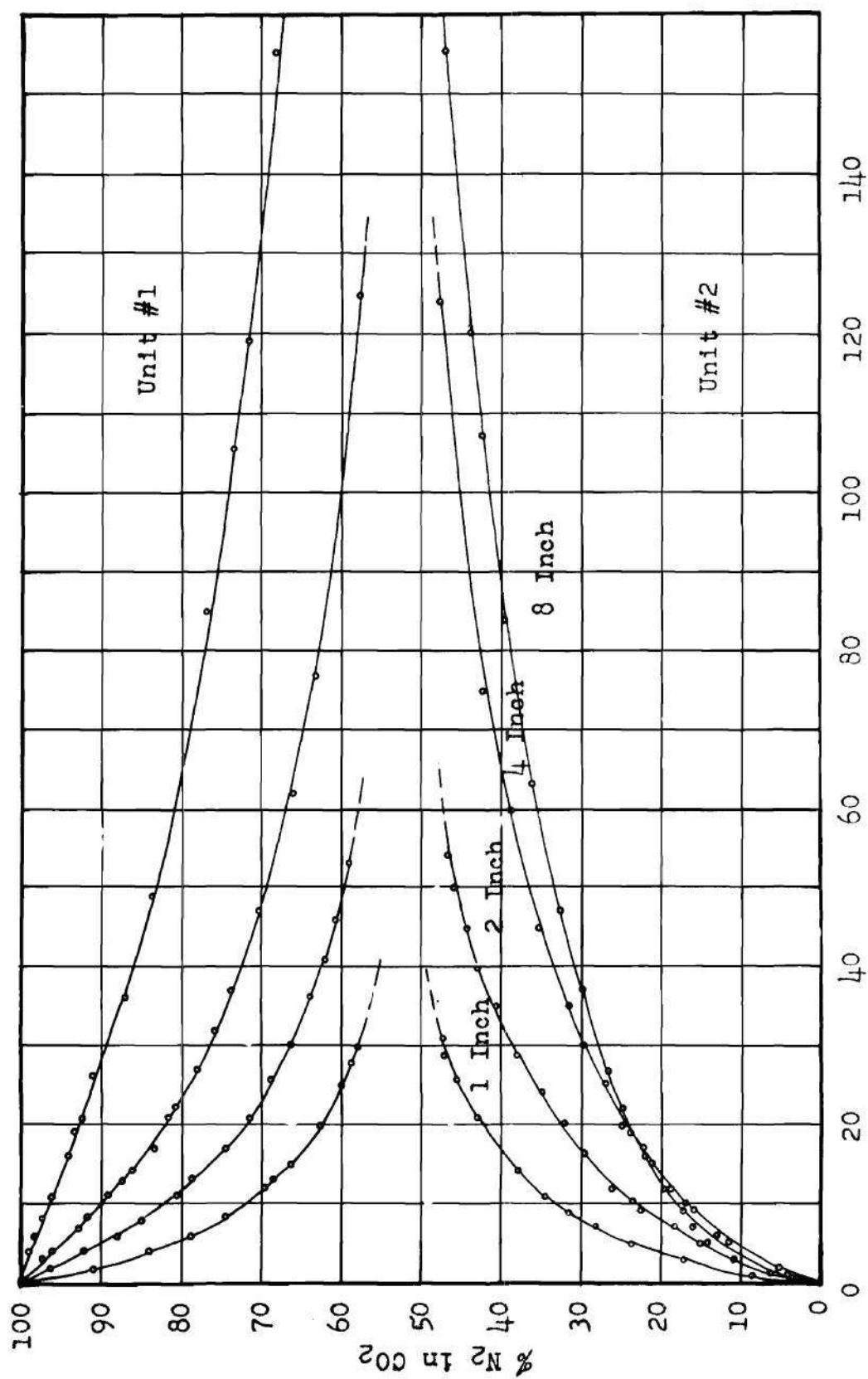


Figure 17. Diffusion Data. N_2 -Sat'd. Plugs: $\epsilon = 0.35$

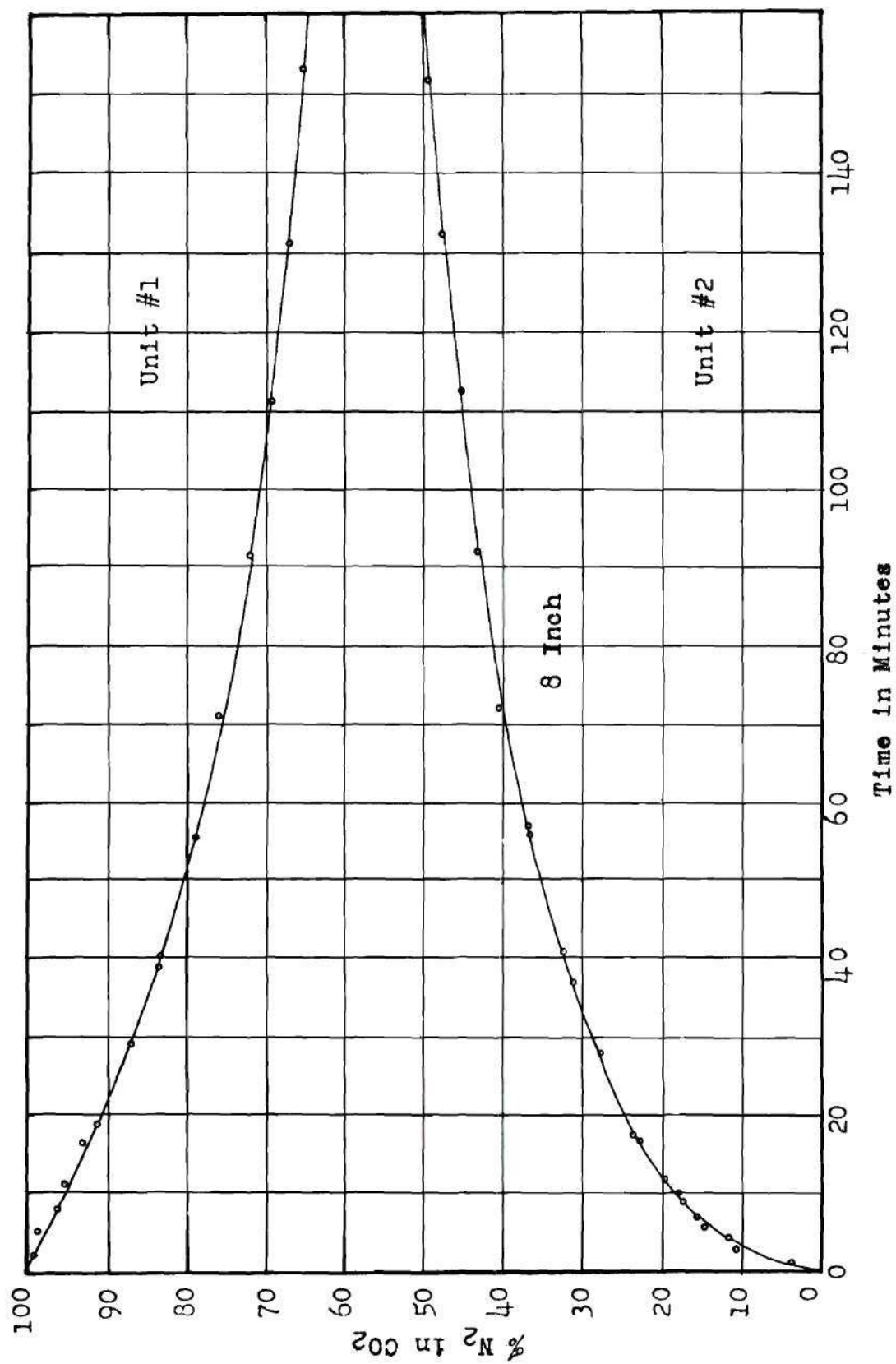


Figure 18. Diffusion Data. N_2 -Sat'd. Plug: $\epsilon = 0.40$

Figures 9 through 13 show the data for an initial plug saturation or treatment with CO_2 , and Figures 14 through 18, for the case of N_2 saturation. Complete run data is given in a section of the Appendix.

Calculations were made to determine the characteristic diffusion coefficient for each run using the equations derived above. To provide a basis for comparison of each run, calculations were made for the data values corresponding to 60 per cent of the equilibrium composition. To solve the appropriate equation for the diffusion coefficient, D , it was necessary to resort to a trial and error technique. Since the diffusion coefficient appears in the exponential index this proved to be the only method of handling this type of solution. If large values of t are used, as in this case, it is not necessary to expand the series beyond the summation.

The calculated diffusion coefficients for all runs are listed in Tables 1 and 2. Table 1 lists the values for runs made with plugs initially saturated with CO_2 and Table 2 for the case of N_2 saturation. A sample calculation using the trial and error method is given in the Appendix. Figures 19 and 20 are the corresponding correlations of diffusivity with porosity.

Table 1. Calculated Diffusion Coefficients- CO_2 Sat'd. Plugs

Plug Length in Inches	0.20	0.25	Porosity 0.30	0.35	0.40
1	.132	.137	.149	.156	-
2	.125	.118	.148	.158	-
4	.103	.128	.150	.156	-
8	-	.119	.139	.157	.164

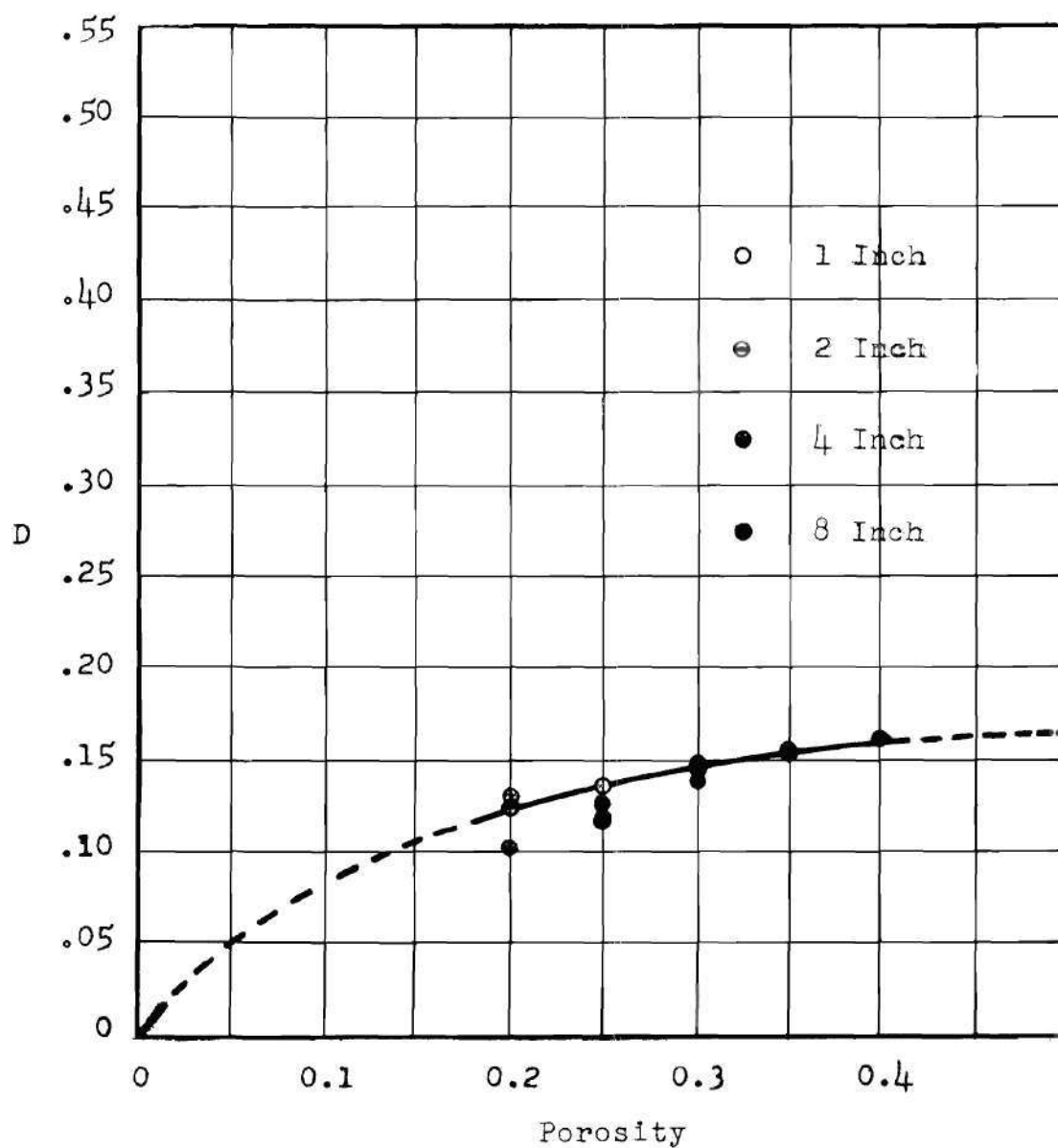


Figure 19. Diffusion Coefficient vs Porosity- CO_2 -Sat'd. Plugs

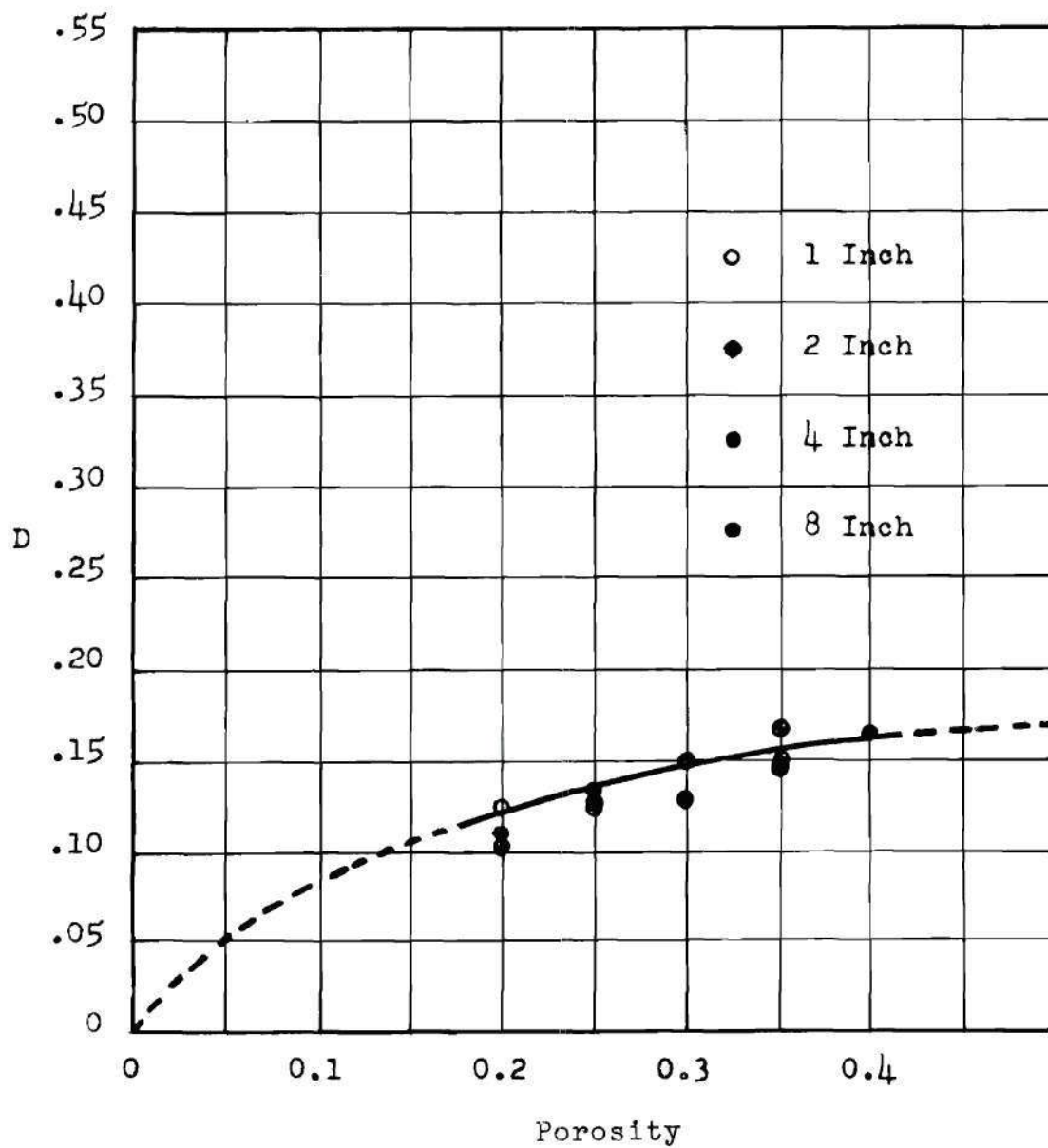


Figure 20. Diffusion Coefficient vs porosity- N_2 -Sat'd. Plugs

Table 2. Calculated Diffusion Coefficients- N_2 Sat'd. Plugs

Plug Length in Inches	0.20	0.25	Porosity 0.30	0.35	0.40
1	.125	.123	.129	.147	-
2	.110	.135	.150	.150	-
4	.103	.126	.150	.168	-
8	-	-	.130	.144	.166

Discussion of Results.--- Figures 19 and 20 show the effects of porosity variation on the diffusion coefficient through the range of values 0.2 to 0.4. The two plots are identical but are not precisely coincident. This is believed due to a slight observed difference in the volumes of the diffusion cell's two gas chambers. Measurements indicated a volume difference of approximately 6 to 8 cc's between the two. This difference did not cause an appreciable difference in the values of the γ terms used but does reflect itself slightly in the data.

The results show that the diffusivity value is independent of the geometric length or thickness of the medium. D values for all data plots (plugs 1 through 8 inches) show little departure from the established curves of Figure 19 and 20. However, at the low end of the porosity range an observed drift is seen in the points for the 4 and 8 inch plugs. This is believed due to a slight anisotropic effect of the plug-pressing operation. The assumption has been implied throughout the discussion that the perchlorate powder was randomly packed and no anisotropy existed in any

of the plug systems. This is an ideal state of affairs and in practice we cannot expect anything better than a good approximation to this ideal state. This effect of packing was pronounced only in the larger plugs at low porosity values and disappeared almost altogether at 0.30 and on to the upper limit. For these reasons, it was considered preferable to allow the 1 and 2 inch plugs to control the trend of the correlation curve through the low porosity region.

Extrapolation of the curves show that at some point above a porosity of 0.60 it is highly probable that the counter diffusion will take place as though the medium did not intervene. The value considered as the upper limit for D is that of the free diffusion coefficient as calculated by the Gilliland equation.⁵ The calculations for this are given in the Appendix.

Figure 21 is the correlation D/D_0 versus ϵ , where D_0 designates the free diffusion coefficient. The Buckingham⁶ relationship

$$\frac{D}{D_0} = \epsilon^2 \quad (68)$$

is included for comparison.

⁵Sherwood, op. cit., p.19.

⁶Buckingham, loc. cit.

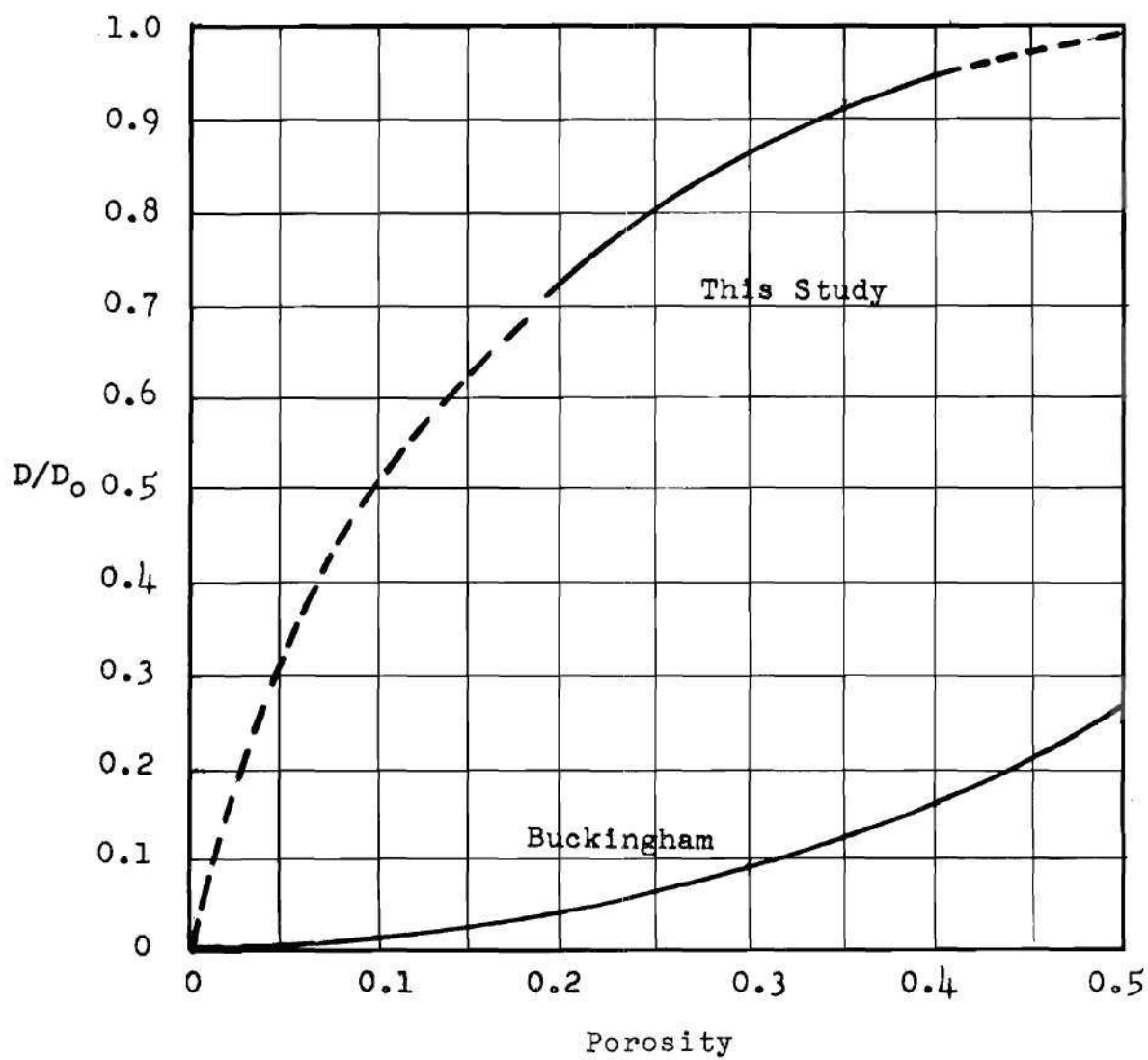


Figure 21. Diffusivity Ratio D/D_0 vs Porosity CO_2 -Sat'd. Plugs

CHAPTER VI

CONCLUSIONS

From the results of this study of diffusion in porous media the following conclusions may be drawn:

1. The diffusion coefficient for countercurrent diffusion through a porous medium is independent of medium thickness or geometric length of path.
2. The diffusion coefficient changes little with decreasing porosity until a porosity of approximately 0.5 is reached. In the range of porosity values 0.4 to 0.2 changes of slope of the correlation curve D vs ϵ begin to develop with an increasingly pronounced effect. This continues to the origin. Initially the slope is zero.
3. The mean values (average of all determinations for a given porosity) of the diffusion coefficient vs porosity for the countercurrent diffusion of CO_2 and N_2 as determined experimentally are:

Porosity:	0.20	0.25	0.30	0.35	0.40
D :	0.123	0.129	0.143	0.155	0.165

The calculated free diffusion coefficient is 0.169. This value corresponds to a porosity of 1.0.

APPENDIX

APPENDIX I

CALIBRATION OF EQUIPMENT

Preliminary to the calibration of the gas analyzer dry room air was placed in the reference chambers of the two thermal conductivity units. The associated shutoff cocks were then closed and these chambers allowed to remain undisturbed throughout the entire course of the experimental work.

The initial step in the calibration procedure is that of "zero" adjusting the unit with the sample chambers filled with the same gas as contained in the reference chambers. By means of the zero adjustment potentiometer, A (see Figure 7 for this item and subsequent circuit components), an adjustment was made such that a minimum deflection was observed on the indicating instrument, I, for a given setting of the control. Since this potentiometer serves both conductivity units the setting which results in "zero" deflection (indicating no unbalance of the bridge) for one unit will not necessarily produce zero for the second unit. For this reason, a minimum point is selected which results in a slight initial unbalance of the bridge, but to the same degree, for each unit. Both the instrument, I, and the bridge were linear for all possible degrees of unbalance and no difficulty was experienced from this initially unbalanced condition as discussed here. Adjustment of, A, was made only after setting of the standard potentiometer, R₇, and the current control, C, adjusted. The potentiometer,

R_7 , was set at 40 ohms (± 0.1 ohm) and control, C, was set such that the bridge current was always 140 ma (set to ± 0.25 ma). This value of current, read on meter, MA, was set each time a reading on, I, was taken. After the minimum for each unit was established, A was never disturbed during calibration and diffusion runs except when periodic checks (made by charging sample chambers again with air) indicated further adjustment was necessary.

The thermal conductivity cell units were calibrated simultaneously. Gases of known concentration were placed in the units' sample chambers and the indicated deflections on, I, recorded. As a check, second samples (duplicates of the first) were charged into the units and deflections observed and recorded. In the initial calibration of the cell units approximately twenty points were determined for the range of gas compositions used. In the case of the gases carbon dioxide and nitrogen, the calibration resulted in a straight-line relationship. This proved advantageous in subsequent calibrations since it was only necessary to obtain three or four points to establish an accurate calibration curve. Due to composition variations, subsequent calibration checks were necessary whenever new cylinders of nitrogen were put into use. The composition of the carbon dioxide did not change substantially from cylinder to cylinder to necessitate recalibration.

Figure 22 is a very small scale calibration curve as used in this work. From a large scale curve gas percentages ± 0.1 percent were read. However, this apparatus under other operating conditions is capable of $\pm .01$ percent accuracy.

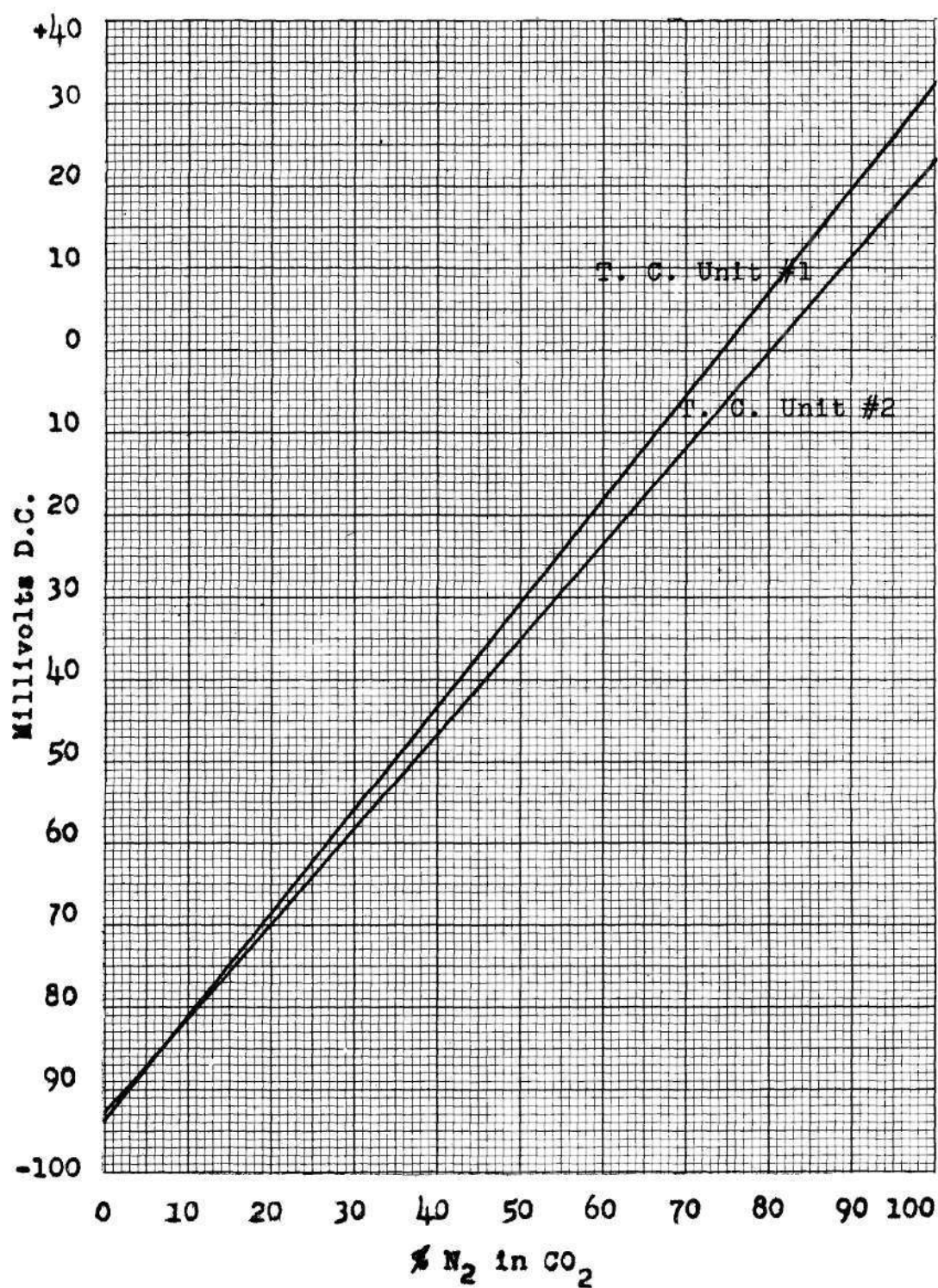


Figure 22. Calibration Curves. Thermal Conductivity Units

Throughout calibration runs the thermal conductivity units were maintained at $104^{\circ}\text{ F} \pm 0.1^{\circ}$ by the constant temperature bath. During experimental runs, which required longer periods of time and additional difficulties of control, the units were maintained, on the average, at $104^{\circ}\text{ F} \pm 0.2^{\circ}$. These instruments are somewhat dependent on temperature, but under conditions of operation encountered, a 1° F temperature change resulted in a negligible change in the gas analysis reading. A 5° F temperature change caused an error of less than 0.1 percent.

The effect of pressure on the operation of the conductivity units was small. When the sample chambers contained 100 percent carbon dioxide (the case when largest deflection was observed), a 70-75 mm Hg change in pressure produced approximately a 1.6 percent change in the analysis from the correct value. When the chambers contained 100 percent nitrogen, a 70-75 mm Hg pressure change produced only 0.2 percent error in the composition reading. Experimental runs were made at pressures within a few mm Hg of the pressure at which calibration curves were determined.

APPENDIX II

EXPERIMENTAL DATA

The data obtained in the experimental runs were recorded on "log sheets" and are transcribed in Tables 3-A through 3-D, and 4-A through 4-D. A sample "log sheet" is given in Figure 23 following the tabulations.

Listed in the tables are all significant data items, as well as, the calculated diffusion coefficient for each run. The numbers heading the columns refer to the thermal conductivity cell units. Unit #1 was associated with the N_2 side of the porous medium and #2 was associated with the CO_2 side. The time is recorded in minutes and the compositions in percentages of N_2 .

Table 3-A. Diffusion Data. 1 inch Plugs- CO_2 Sat'd.

Run: 1-9 ($\epsilon = 0.20$)				Run: 1-6 ($\epsilon = 0.25$)				Run: 1-3 ($\epsilon = 0.30$)				Run: 1-1 ($\epsilon = 0.35$)			
P: 733.5 mm				P: 731.1 mm				P: 732.8 mm				P: 735.8 mm			
D: 0.132				D: 0.137				D: 0.149				D: 0.156			
#1		#2		#1		#2		#1		#2		#1		#2	
t	%	t	%	t	%	t	%	t	%	t	%	t	%	t	%
0	99.4	0	1.3	0	99.4	0	1.3	0	99.4	0	1.5	0	99.4	0	1.5
1	97.0	2	6.4	1	96.8	2	5.7	1	95.2	2	7.8	1	93.5	2	9.3
3	92.0	4	10.7	3	89.1	4	11.7	3	88.0	4	14.2	3	85.2	4	16.8
5	88.1	6	14.5	5	83.9	6	16.4	5	81.9	6	19.6	5	79.3	6	21.9
7	84.8	8	18.0	7	79.9	8	20.0	7	77.7	8	23.6	7	74.5	8	26.3
9	81.9	10	20.7	9	76.5	10	23.4	9	74.3	10	27.0	9	71.3	10	29.5
11	79.4	12	22.9	11	73.7	12	25.7	11	71.3	12	29.6	11	67.4	12	32.1
16	74.4	17	27.5	13	71.4	14	28.0	13	69.0	14	31.9	13	66.0	14	34.1
21	70.6	22	30.7	15	69.6	16	29.8	15	67.2	17	34.3	15	64.0	16	36.0
26	67.6	27	33.6	18	66.9	19	32.4	18	64.3	22	38.1	17	62.3	21	39.6
31	65.1	32	36.2	23	63.4	25	36.2	23	61.1	28	41.0	22	60.0	27	42.5
41	61.3	42	40.2	29	59.4	31	38.9	27	59.2	33	43.1	28	56.2	30	43.8
51	58.6	52	43.1	34	58.4	36	40.3	32	57.3	35	43.9	31	55.2		
56	57.5	57	43.9	39	56.9	41	42.0	36	56.0						
58	57.0			44	55.4	45	43.4	40	55.0						

Table 3-B. Diffusion Data. 2 inch Plugs-CO₂ Sat'd.

Run: 2-9 ($\epsilon = 0.20$)				Run: 2-5 ($\epsilon = 0.25$)				Run: 2-3 ($\epsilon = 0.30$)				Run: 2-1 ($\epsilon = 0.25$)			
P: 746.0 mm				P: 733.2 mm				P: 734.4 mm				P: 735.1 mm			
D: 0.125				D: 0.118				D: 0.148				D: 0.158			
#1		#2		#1		#2		#1		#2		#1		#2	
t	%	t	%	t	%	t	%	t	%	t	%	t	%	t	%
0	99.4	0	1.4	0	99.4	0	0.0	0	100.0	0	0.0	0	100.0	0	0.0
1	96.8	2	3.5	1	96.0	2	3.2	1	95.6	2	3.4	1	94.8	2	4.2
3	94.3	4	5.9	3	91.5	4	6.8	3	91.1	4	7.7	3	89.5	4	9.2
5	92.2	6	8.0	5	88.4	6	9.5	5	87.5	6	11.1	5	85.4	6	13.5
7	90.4	9	11.1	7	85.6	8	11.8	8	82.8	9	15.1	7	81.7	8	16.0
8	89.2	14	14.5	9	83.2	10	13.4	11	79.2	12	18.5	9	78.9	10	18.6
13	85.4	20	18.8	11	80.9	12	15.5	14	76.1	15	21.8	11	76.2	12	21.0
19	81.2	25	21.5	15	77.3	16	18.6	18	73.0	19	25.1	13	74.0	14	23.5
24	78.5	33	25.1	20	73.5	21	21.6	23	69.3	24	27.9	15	72.0	16	25.1
31	75.2	42	28.6	25	70.7	26	24.4	28	66.6	30	30.9	17	70.2	18	26.9
41	71.3	43	28.9	31	68.0	32	26.8	34	63.9	35	33.1	19	68.6	20	28.5
51	68.2	52	31.4	37	65.7	38	29.1	40	61.5	41	35.3	21	67.3	22	29.8
61	66.5	62	34.2	47	62.5	48	32.0	46	60.1	47	37.1	24	65.4	25	31.6
70	63.6	69	35.2	57	60.4	58	34.0	57	57.8	58	40.5	29	62.7	30	34.5
93	60.0	94	39.5	72	58.2	73	36.9	64	56.4	65	41.8	34	60.4	35	36.5
113	57.5	114	42.2	88	56.9	89	39.3	69	55.0	70	42.0	39	58.8	40	38.4
121	56.7	122	43.0	103	56.1	104	41.6			71	42.2	49	55.9	50	41.3
125	56.4	126	43.4	116	55.9	116	43.0					53	54.9	51	41.5

Table 3-C. Diffusion Data. 4 inch Plugs-CO₂ Sat'd.

Run: 4-29 ($\epsilon = 0.20$)				Run: 4-28 ($\epsilon = 0.25$)				Run: 4-24 ($\epsilon = 0.30$)				Run: 4-23 ($\epsilon = 0.35$)			
P: 729.2 mm				P: 730.7 mm				P: 734.2 mm				P: 730.5 mm			
D: 0.103				D: 0.128				D: 0.150				D: 0.156			
#1		#2		#1		#2		#1		#2		#1		#2	
t	%	t	%	t	%	t	%	t	%	t	%	t	%	t	%
0	99.5	0	0.0	1	95.6	0	0.0	0	98.8	2	2.0	0	98.7	2	1.2
1	97.3	2	0.4	3	93.4	2	1.4	1	95.4	4	4.0	1	95.2	5	4.7
3	94.5	4	1.4	5	91.5	4	2.6	3	91.5	6	6.0	3	91.1	7	6.9
5	93.2	6	2.3	8	89.4	7	4.3	5	89.6	7	6.9	4	89.6	9	8.8
7	92.1	8	3.0	13	86.6	12	7.7	8	87.1	9	8.8	6	87.3	11	10.5
9	91.2	10	4.1	18	83.9	17	11.2	10	85.4	11	10.1	8	85.6	13	12.3
11	90.1	13	6.0	33	77.4	27	15.1	12	84.2	13	11.9	10	83.3	14	13.2
14	89.1	18	7.7	47	74.0	43	21.0	14	82.8	15	12.8	12	81.5	17	15.4
19	87.0	25	10.6	61	69.4	60	25.5	16	81.5	17	14.4	15	79.5	18	16.1

(Continued)

Table 3-C. Diffusion Data. 4 inch Plugs-CO₂ Sat'd.

(Continued)

Run: 4-29 ($\epsilon = 0.20$)				Run: 4-28 ($\epsilon = 0.25$)				Run: 4-24 ($\epsilon = 0.30$)				Run: 4-23 ($\epsilon = 0.35$)			
P: 729.2 mm				P: 730.7 mm				P: 734.2 mm				P: 730.5 mm			
D: 0.103				D: 0.128				D: 0.150				D: 0.156			
#1		#2		#1		#2		#1		#2		#1		#2	
t	%	t	%	t	%	t	%	t	%	t	%	t	%	t	%
26	84.6	33	12.8	92	64.0	91	31.5	18	80.2	19	15.7	16	78.5	22	18.9
34	81.8	42	15.5	134	59.0	131	36.8	22	78.2	23	18.0	19	76.4	29	22.3
43	79.3	52	18.2	166	56.4	165	39.4	25	76.5	24	18.5	21	75.2	34	24.2
54	76.7	55	19.0	197	54.5	196	41.3	31	73.8	30	20.7	28	71.4	44	27.9
66	74.2	65	21.0					40	70.3	39	24.6	35	68.3	49	30.5
82	71.4	81	24.1					50	67.3	49	27.8	45	64.6	64	33.0
106	67.1	100	27.3					65	63.6	64	31.4	50	61.8	98	39.1
121	65.8	120	29.7					95	58.5	94	36.7	65	59.7		
151	62.6	150	32.9					130	54.5	128	40.6	97	53.5		
181	60.2	180	35.5												
211	58.2	210	37.7												
214	58.0	240	39.3												
241	56.5	302	42.0												
301	54.1														

Table 3-D. Diffusion Data. 8 inch Plug-CO₂ Sat'd.

Run: 8-5 ($\epsilon = 0.25$)				Run: 8-3 ($\epsilon = 0.30$)				Run: 8-1 ($\epsilon = 0.35$)				Run: 8-6 ($\epsilon = 0.40$)			
P: 737.5 mm				P: 740.7 mm				P: 737.3 mm				P: 739.9 mm			
D: 0.119				D: 0.134				D: 0.157				D: 0.164			
#1		#2		#1		#2		#1		#2		#1		#2	
t	%	t	%	t	%	t	%	t	%	t	%	t	%	t	%
0	100	0	0.4												
1	96.7	2	0.8	0	100	0	0.0	0	100	0	0.3	0	100	0	0.0
3	95.7	4	1.6	1	94.6	2	0.0	1	95.6	2	0.3	1	94.1		
5	95.1	7	2.1	3	93.8	5	0.7	3	91.2	4	1.2	3	89.5	Check Ball Stuck	
8	94.2	9	3.0	4	91.2	8	1.6	5	88.9	6	2.1	5	87.1		
11	93.3	13	4.2	7	88.2	11	2.5	7	87.2	8	2.6	6	86.0	19	8.8
17	91.5	18	5.3	10	86.6	16	4.2	10	85.1	9	3.1	8	84.0	21	9.6
29	89.5	31	8.3	15	83.7	17	4.4	14	82.8	13	5.2	10	82.4	22	10.0
37	87.6	38	9.6	18	82.4	27	7.9	17	81.2	16	6.5	12	81.2	24	11.2
48	86.4	49	11.4	26	79.8	35	10.4	22	79.0	21	8.7	13	80.7	25	11.4
63	83.9	64	13.6	33	78.2	45	13.0	28	76.7	27	10.1	30	77.0	27	12.4
84	80.3	85	17.4	43	75.7	56	15.8	34	74.6	33	13.2	23	75.7	29	13.2

(Continued)

Table 3-D. Diffusion Data. 8 inch Plug-CO₂ Sat'd.

(Continued)

Run: 8-5 ($\epsilon=0.25$)				Run: 8-3 ($\epsilon=0.30$)				Run: 8-1 ($\epsilon=0.35$)				Run: 8-6 ($\epsilon=0.40$)			
P: 737.5 mm				P: 740.7 mm				P: 737.3 mm				P: 739.9 mm			
D: 0.119				D: 0.134				D: 0.157				D: 0.164			
#1		#2		#1		#2		#1		#2		#1		#2	
t	%	t	%	t	%	t	%	t	%	t	%	t	%	t	%
93	79.1	114	21.5	54	73.2	75	19.8	35	74.3	37	14.5	26	74.2	35	15.0
113	76.8	130	23.6	74	69.4	101	23.8	47	71.0	48	17.7	30	72.6	46	19.0
116	76.5	142	25.0	100	65.3	134	28.1	57	68.6	58	20.2	36	70.6	61	22.7
128	75.4	190	29.7	133	61.8	135	28.2	72	65.5	73	23.4	47	67.3	81	26.7
141	74.1	220	31.7	137	57.8	136	33.4	92	62.2	93	27.0	62	63.4	101	29.8
188	70.2	254	34.2	169	55.1	170	35.4	122	58.4	123	30.8	82	59.3	121	32.4
218	68.1	283	35.7	180	54.7	179	36.1	172	53.7	173	35.2	102	56.6	145	34.6
252	66.3	310	36.8	181	54.5	182	36.2	190	52.8	191	36.6	122	54.2	166	36.5
281	64.9	344	39.0									146	52.2		
309	64.2	377	40.3									166	50.7		
312	63.6	398	40.6												
343	62.2	429	41.9												
376	61.2	449	42.6												
377	60.5														
408	59.5														

Table 4-A. Diffusion Data. 1 inch Plugs-N₂ Sat'd.

Run: 1-10 ($\epsilon=0.20$)				Run: 1-8 ($\epsilon=0.25$)				Run: 1-LX ($\epsilon=0.30$)				Run: 1-2 ($\epsilon=0.35$)			
P: 733.5 mm				P: 731.2 mm				P: 737.8 mm				P: 733.7 mm			
D: 0.125				D: 0.123				D: 0.129				D: 0.147			
#1		#2		#1		#2		#1		#2		#1		#2	
t	%	t	%	t	%	t	%	t	%	t	%	t	%	t	%
0	99.4	0	1.3	0	99.4	0	1.3	0	99.6	0	0.6	0	100.0	0	1.4
2	96.5	1	7.8	2	94.4	1	6.5	2	92.8	1	4.9	2	90.5	1	8.4
4	91.9	3	14.4	4	89.0	3	13.6	4	87.2	3	12.8	4	83.5	3	17.0
6	87.3	5	17.4	6	85.0	5	18.2	6	82.0	5	18.4	6	78.4	5	23.4
8	84.1	7	20.3	8	81.6	7	22.0	8	78.6	7	22.8	8	74.2	7	27.7
10	81.2	9	23.0	10	78.6	9	25.4	10	75.4	9	26.3	10	71.6	9	31.3
12	79.0	11	25.6	12	76.2	11	28.6	12	73.3	11	29.2	12	69.2	11	34.2
15	75.9	13	27.7	17	71.3	16	33.2	14	70.8	13	31.4	13	68.0	14	37.6
20	71.9	16	30.6	23	67.1	22	38.0	16	69.1	15	33.5	15	66.0	16	39.2
27	67.6	21	33.7	28	64.3	27	40.4	18	67.4	17	35.5	20	62.3	21	42.9
		28	38.3	38	60.4	37	44.7	20	66.1	19	37.0	25	59.6	26	45.4
				42	59.6	43	46.4	24	63.4	25	40.6	28	58.5	29	46.4
				45	58.8	44	46.5	30	60.8	31	43.5	30	58.0	31	47.2
								36	58.9	37	45.5				
								38	58.4	39	46.2				

Table 4-B. Diffusion Data. 2 inch Plugs-N₂ Sat'd.

Run: 2-10($\epsilon=0.20$)				Run: 2-6($\epsilon=0.25$)				Run: 2-4($\epsilon=0.30$)				Run: 2-2($\epsilon=0.35$)			
P: 743.3 mm				P: 733.5 mm				P: 734.5 mm				P: 734.2 mm			
D: 0.110				D: 0.135				D: 0.150				D: 0.150			
#1		#2		#1		#2		#1		#2		#1		#2	
t	%	t	%	t	%	t	%	t	%	t	%	t	%	t	%
0	99.4	0	1.3	0	99.4	0	0.0	0	99.4	0	0.0	0	100.0	0	0.0
2	98.0	1	3.7	2	96.4	1	3.9	2	95.6	1	4.9	2	96.2	1	3.9
4	96.4	3	6.7	4	93.7	3	8.0	4	92.1	3	10.1	4	91.9	3	10.1
6	93.1	5	9.1	6	91.0	5	11.2	6	88.9	5	13.2	6	87.9	5	14.5
11	92.6	10	13.4	8	88.6	7	13.2	8	85.8	7	16.3	8	84.5	7	18.2
17	87.0	16	18.1	10	86.2	9	15.7	11	82.2	10	19.9	11	80.4	9	22.0
22	84.1	21	21.0	13	83.3	12	18.6	16	77.4	15	25.2	13	78.3	10	22.7
32	77.3	31	25.7	18	79.6	17	22.7	21	73.5	20	29.4	17	74.4	12	25.2
44	73.7	43	31.3	23	76.2	22	26.2	27	70.1	25	32.0	21	71.5	16	29.1
59	69.5	58	35.2	28	73.4	27	29.0	31	68.1	28	33.7	26	68.5	20	32.2
79	65.0	78	39.0	41	68.1	40	34.4	36	66.3	29	34.2	30	66.5	24	35.0
102	61.0	101	42.5	57	63.3	56	39.2	46	62.7	35	36.3	36	63.9	29	37.7
116	60.4	117	44.2	72	59.5	71	42.5	56	60.0	45	39.8	41	62.1	35	40.5
131	57.3	130	45.3	87	58.2	86	45.1	67	58.2	55	42.4	46	60.6	40	42.2
132	57.2			102	56.4	101	46.6			66	45.2	51	59.6	45	43.8
										68	45.5	53	59.1	50	45.4
														54	46.1

Table 4-C. Diffusion Data. 4 inch Plugs-N₂ Sat'd.

Run: 4-30($\epsilon=0.20$)				Run: 4-26($\epsilon=0.25$)				Run: 4-25($\epsilon=0.30$)				Run: 4-22($\epsilon=0.35$)			
P: 730.3 mm				P: 738.9 mm				P: 734.9 mm				P: 732.6 mm			
D: 0.103				D: 0.126				D: 0.150				D: 0.168			
#1		#2		#1		#2		#1		#2		#1		#2	
t	%	t	%	t	%	t	%	t	%	t	%	t	%	t	%
0	99.6	1	3.4	0	99.4	0	0.4	2	97.7	0	0.8	3	96.5	0	1.2
2	98.7	3	5.8	2	98.5	1	3.8	4	95.9	1	4.2	4	95.4	2	5.0
4	97.3	5	7.4	4	97.3	3	7.3	6	94.4	3	8.2	7	92.4	5	11.1
6	97.1	7	8.6	6	96.1	5	8.7	8	92.8	5	9.5	8	91.4	6	12.2
8	96.1	9	9.6	7	95.3	8	9.2	10	91.2	7	12.3	11	88.4	9	15.7
10	95.3	11	10.5	9	94.3			12	89.6	9	14.6	13	86.8	10	16.6
13	94.1	12	11.0	12	92.4	27	21.1	15	87.8	11	16.3	14	86.0	12	18.4
14	93.8	18	14.0	15	90.8	37	24.6	19	85.2	14	18.2	17	82.9	15	20.7
20	91.2			16	90.3	52	29.1	24	82.3	18	20.6	21	81.3	16	21.3
30	87.9	22	15.0	21	88.2	67	32.7	31	79.3	23	23.4	22	80.6	19	23.5
45	83.3	32	18.1	26	86.0	87	36.1	32	78.8	30	26.6	27	77.6	20	24.2

(Continued)

Table 4-C. Diffusion Data. 4 inch Plugs-N₂ Sat'd.
(Continued)

Run: 4-30 ($\epsilon = 0.20$)				Run: 4-26 ($\epsilon = 0.25$)				Run: 4-25 ($\epsilon = 0.30$)				Run: 4-22 ($\epsilon = 0.35$)			
P: 730.3 mm				P: 738.9 mm				P: 734.9 mm				P: 732.6 mm			
D: 0.103				D: 0.126				D: 0.150				D: 0.168			
#1		#2		#1		#2		#1		#2		#1		#2	
t	%	t	%	t	%	t	%	t	%	t	%	t	%	t	%
70	77.8	47	22.4	36	82.1	107	39.1	43	74.7	34	28.3	32	75.4	25	26.7
90	74.3	71	27.6	51	77.7	137	42.5	55	71.4	44	31.6	37	73.4	30	29.1
127	69.4	91	30.8	66	74.0	167	45.2	73	67.5	56	34.6	47	70.0	35	31.2
155	66.9	120	34.7	86	70.1			88	64.6	72	39.0	62	66.1	45	34.8
166	66.1	151	37.7	106	67.2			134	59.5	87	41.3	77	63.0	60	38.6
205	63.0	170	39.3	136	63.7			145	58.7	132	46.1	125	57.4	75	41.9
243	61.0	201	41.3	166	61.0					144	47.1			124	47.4
272	59.8	242	43.8												
300	58.9	274	45.3												
		299	46.0												

Table 4-D. Diffusion Data. 8 inch Plug-N₂ Sat'd.

Run: 8-4 ($\epsilon = 0.30$)				Run: 8-2 ($\epsilon = 0.35$)				Run: 8-7 ($\epsilon = 0.40$)			
P: 734.8 mm				P: 739.9 mm				P: 738.7 mm			
D: 0.130				D: 0.144				D: 0.168			
#1		#2		#1		#2		#1		#2	
t	%	t	%	t	%	t	%	t	%	t	%
0	99.6	0	0.5	0	99.6	0	0.4	0	100.0	0	0.0
2	99.5	1	5.1	2	99.4	1	6.2	2	100.0	1	3.9
4	98.4	3	9.4	4	98.6	3	10.9	5	98.4	3	10.4
6	97.6	5	11.6	6	98.0	5	13.6	8	96.6	4	11.9
7	97.2	8	14.0	8	97.4	7	15.6	11	95.2	6	14.4
10	96.9	11	16.0	11	96.2	9	17.0	16	93.0	7	15.4
14	95.6	15	18.4	16	94.0	12	19.0	19	91.2	9	17.2
20	93.6	21	20.7	19	93.4	17	21.5	29	87.2	10	17.7
25	91.9	23	21.5	21	92.4	22	24.2	39	83.4	12	19.7
30	91.2	28	22.9	26	90.4	27	26.2	40	83.1	17	22.6
31	90.8	34	25.2	36	87.0	37	29.4	55	79.1	18	23.2
35	89.2	42	27.3	49	83.1	47	32.5	71	75.8	28	27.6
46	86.3	49	28.9	50	82.7	63	35.9	91	72.5	38	31.2
48	85.7	61	31.2	64	79.9	84	39.3	111	69.6	41	32.4
50	85.6	62	31.5	85	76.2	107	42.2	131	67.7	56	36.6
60	83.5	72	33.4	106	72.9	120	43.8	153	65.6	57	36.8
71	81.5	90	36.4	119	71.7	156	47.0	171	64.4	72	40.0

(Continued)

APPENDIX III

MISCELLANEOUS CALCULATIONS

Sample Calculation.— The diffusion coefficient calculation for a sample diffusion run is given below:

Data: Run 1-3 (porosity 0.30)

Length: 1 inch (nominal) = 2.38 cm (corrected
for gate thickness)

C_{∞} (% N_2)	=	0.500
${}_1C_0$	=	0.994
${}_2C_0$	=	0.014
${}_2C(t)$	=	0.300
t (sec.)	=	750
V_1 (cm ³)	=	332
V_2	=	338
V	=	8.2
γ	=	0.0243

Calculations: Equation (67), Chapter V, is

$${}_2C = \frac{{}_1C_0}{2} \left[1 - \frac{\gamma}{2} + \frac{\gamma^2}{4} - \left(1 - \frac{\gamma}{6} + \frac{\gamma^2}{60} \right) e^{-\frac{2\gamma Dt}{l^2} \left(1 - \frac{\gamma}{6} + \frac{\gamma^2}{45} \right)} \right. \\ \left. - \sum_{i=1}^{\infty} (-1)^i \frac{4\gamma}{i^2 \pi^2} \left(1 - \frac{6\gamma}{i^2 \pi^2} \right) e^{-\frac{Dt}{l^2} (i^2 \pi^2 + 4\gamma)} \right]$$

Substitution in Equation (67) gives

$$\begin{aligned}
 .300 = .497 & \left[1 - .0122 + .000148 - (1 - .00405 + .000009) \right. \\
 & \exp \left\{ \frac{2(.0243)(D)(750)}{5.66} (1 - .00405 + .000013) \right\} \\
 & - \sum \frac{(-1)(4)(.0243)}{9.89} (1 - \frac{6(.0243)}{9.89}) \exp \left\{ \frac{-D(750)}{5.66} \right. \\
 & \left. \left. (9.89 + 4(.0243)) \right\} + \dots \right]
 \end{aligned}$$

The terms following the summation are negligible and are dropped. Assumption of values for D produces the value sought quite readily. For $D = 0.149$ the above simplifies to

$$.300 = .4979(.9879 - (.99595)\exp(-6.41)(.149))$$

$$.300 = .300. \quad (\text{Units of cm}^2/\text{sec})$$

It proved advantageous in these calculations to plot the values determined by successive trials for the porosity extremes. This enables one to better estimate the trial values of D and thus solving for D becomes much easier.

Calculation of Free Diffusion Coefficient.— From Sherwood¹ the Gilliland equation is

$$D = 0.0043 \frac{T^{3/2}}{P(V_A^{1/3} + V_B^{1/3})^2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \quad (69)$$

¹Sherwood, op. cit., p. 18.

where D = diffusion coefficient, cm^2/sec .

T = absolute temperature, degrees K.

M_A, M_B = molecular weights of the two gases,

P = total pressure, atm.

V_A, V_B = molecular volumes.

0.0043 = empirical constant

The values of V_A and V_B , respectively, are 31.2 and 29.6.

Substitution in the above Equation gives

$$D = \frac{0.0043 (273 + 40)^{3/2}}{.955 \{ (31.2)^{1/3} + (29.6)^{1/3} \}^2} \sqrt{\frac{1}{28} + \frac{1}{44}}$$

$$D = 0.169 \text{ (Units of } \text{cm}^2/\text{sec}).$$

APPENDIX IV

NOMENCLATURE

A	subscript, refers to gas A
A_i	a characteristic constant in the general solution
B	subscript, refers to gas B
B_i	a characteristic constant in the general solution
C	concentration expressed as mol fraction
C_A	concentration, mol fraction of gas A
C_B	concentration, mol fraction of gas B
$C(x,t)$	concentration in porous medium at distance x , and time t
C_0	concentration in porous medium at time $t = 0$
C_∞	final uniform concentration in system
${}_1C_0$	concentration in gas volume 1 at time $t = 0$
${}_2C_0$	concentration in gas volume 2 at time $t = 0$
${}_1C(t)$	concentration in gas volume 1 at time $t = t$
${}_2C(t)$	concentration in gas volume 2 at time $t = t$
D	diffusion coefficient in porous medium
D_{AB}	mutual diffusion coefficient for system of gases A and B
D_0	free diffusion coefficient
F_1	a Duhamel's theorem function
F_2	a Duhamel's theorem function

M_A	molecular weight of gas A
M_B	molecular weight of gas B
N_A	diffusion rate, gas A, moles per unit area
N_B	diffusion rate, gas B, moles per unit area
P	total pressure
R	gas constant
S_{AB}	collision cross section
\dot{S}_{AB}	Sutherland's constant
T	absolute temperature
a_n	a Fourier coefficient
b_n	a characteristic coefficient (includes Fourier coefficient)
c_1	a solution of the differential diffusion equation
c_2	a solution of the differential diffusion equation
d_n	a quantity in the applied solution
g	length and volume, gas container in general solution
h	length and volume, gas container in general solution
i	designates term of a series
k	Boltzman gas constant per molecule
l	length and effective volume, porous medium
m_A	molecular mass gas A
m_B	molecular mass gas B
n	designates term of a series
n	number of molecules per unit volume

n_A	number of molecules gas A per unit volume
n_B	number of molecules gas B per unit volume
p	partial pressure
p_A	partial pressure constituent A
p_B	partial pressure constituent B
t	time
u_A	velocity of gas A
u_B	velocity of gas B
x	distance or length
\bar{v}_A	mean molecular speed of gas A
\bar{v}_B	mean molecular speed of gas B
z	root of the general relation

 \dot{m}

momentum per unit volume per unit time

 Γ

transport in molecules per unit area

 Γ_A

transport of molecules A per unit area

 $\alpha, \alpha_{AB}, \alpha_{BA}$

coefficient of diffusional resistance

 α_n

an exponential index

 β_i

a characteristic constant

 $\gamma, \gamma_1, \gamma_2$

volume ratio

 ϵ

porosity

 λ

mean free path

 μ

reduced mass

ν	an integer
ρ	density
σ	collision cross section
τ	time

BIBLIOGRAPHY

BIBLIOGRAPHY

(Literature Cited)

- Benedict, M., Chemical Engineering Progress, 43, no. 2, 41 (1947).
- Lewis, W. K., and Chang, K. C., Transactions of the American Institute of Chemical Engineers, 21, 127 (1928).
- Sherwood, T. K., Absorption and Extraction, 1st ed., McGraw-Hill Book Co., New York, (1937).
- Toler, K., The Atlanta Journal-Constitution, 71, no. 8, 4-F (1953).
- Lavacot, F. J., Sc.D. Thesis, Washington University, (1951).
- Buckingham, E., Bulletin U. S. Department of Agriculture, no. 25, (1904).
- Penman, H. L., Journal of Agricultural Science, 30, 437 (1940).
- Jeans, J., Introduction to the Kinetic Theory of Gases, Cambridge University Press, Cambridge, (1940).
- Fick, A., Philosophical Magazine, Ser. 4, 10, 30 (1855).
- Stefan, J., Sitzungsberichte der Wiener Akademie der Wissenschaften, 63, no. 2, 63 (1871).
- Stefan, J., Sitzungsberichte der Wiener Akademie der Wissenschaften, 65, no. 2, 323 (1872).
- Loeb, L. R., Kinetic Theory of Gases, McGraw-Hill Book Co., New York, (1927).
- Furry, W. H., American Journal of Physics, 16, 63 (1948).
- Chapman, S., and Cowling, T. G., Mathematical Theory of Non-Uniform Gases, Cambridge University Press, Cambridge, (1939).
- Jost, W., Diffusion, Academic Press, New York, (1952).
- Present, R. D., and de Bethune, A. J., Physical Review, Ser. 2, 75, 1050 (1949).
- Schwartz, F. A., American Journal of Physics, 15, 31 (1947).

- Knudsen, M., Annalen der Physik, Ser. 4, 28, 75 (1908).
- Darken, L. S., Atom Movements-Seminar, American Society for Metals, Cleveland, (1951).
- Carslaw, H. S., and Jaeger, J. C., Conduction of Heat in Solids, Oxford University Press, Oxford, (1947).
- Barnes, C., Physics, 5, 4 (1934).
- March, H. W., and Weaver, W., Physical Review, 31, 1072 (1928).
- Barrer, R. M., Diffusion in and Through Solids, Cambridge University Press, Cambridge, (1941).

(Other References)

- DallaValle, J. M., Micromeritics, 2nd ed., Pitman Publishing Corp., New York, (1948).
- Daynes, H. A., Gas Analysis by Measurement of Thermal Conductivity, Cambridge University Press, Cambridge, (1933).
- Dushman, S., Vacuum Technique, John Wiley and Sons, New York, (1949).
- Dye, R. F., M.S. Thesis, Georgia Institute of Technology, (1950).
- Newman, F. H., and Searle, V. H. L., The General Properties of Matter, Longmans, Green and Co., London, (1948).
- Peirce, B. O., A Short Table of Integrals, 3rd ed., Ginn and Co., New York, (1929).
- Schwartz, F. A., Journal American Ceramic Society, 32, no. 12, 390 (1949).
- Whittaker, E. T., Proceedings of the Royal Society (London), 94A, 367 (1917).

VITA

Robert Fulton Dye was born at Gloster, Amite County, Mississippi, and received his elementary and high school education in the Gloster Public schools. He entered the Mississippi State College in September 1939 and received a B.S. in Chemical Engineering in January 1943. In February 1943 he entered the United States Army, attended Officer Candidate School at Camp Davis, North Carolina, and was commissioned Second Lieutenant, Coast Artillery Corps in May 1943. After receiving his commission, he attended Harvard University where he pursued a specialized course of study in electronics and radio engineering in the Graduate School of Engineering under the direction of Craft Laboratory of Physics. Subsequently, he attended Massachusetts Institute of Technology and followed a more advanced course in the same field, which was completed in 1944. He served overseas in the Central Pacific Theater from 1944-1946, and was released from active duty in 1946 with the rank of Captain. After being employed as a chemical engineer with Monsanto Chemical Company, Anniston, Alabama, and Columbia, Tennessee, from 1946-1949, he attended Georgia Institute of Technology from September 1949 to date. In September 1950 he obtained the M.S. degree in Chemical Engineering from this institution. His thesis was entitled: "Investigation of the Commercial Feasibility of Separation of Azeotropic Mixtures of n-Butyl Alcohol and Water by Gaseous Diffusion." He was appointed an assistant in Chemical Engineering at Georgia Tech from September 1950 to June 1951,

and from September 1952 to March 1953, and was recipient of the Shell Oil Company Fellowship from September 1951 to July 1952.

Mr. Dye is a member of the American Chemical Society, the American Institute of Chemical Engineers, and Phi Lambda Upsilon.